Organic Coatings

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Organic Coatings

Science and Technology

Third Edition

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Preface

Significant advances have been made since the publication of the second edition of *Organic Coatings: Science and Technology*. The third edition has been completely updated. Our purpose remains the same, which is to provide a reference and textbook that interrelates coatings technology with current scientific understanding.

Entire books could be written about the subject of each chapter, and many have been. To be as comprehensive as possible in the limited space available, we have had to limit coverage of each topic and have selected references for readers seeking more detailed information. We have striven to enhance the usefulness of this edition both as a classroom textbook on coatings science, as well as a reference book, by improving the presentation of each topic. The reader will benefit from having taken college level chemistry courses through organic chemistry, but no coursework in polymer science is assumed.

Many of the chapters include brief descriptions of coatings compositions and applications, supported by references, which could be omitted or used for outside assignments, such as term papers, particularly in an advanced course. These descriptions tend to be placed in the later sections of each chapter and tend to be more prevalent in the application chapters. These compositions and applications particularly enhance the value of the volume as a reference book and self-teaching text. We understand that the second edition was used widely for this purpose. We have also defined the jargon of coatings to help newcomers to the field understand its specialized language. Although the book is written specifically about coatings, many of the principles involved apply to the related fields of printing inks, adhesives, and parts of the plastics industry.

Coatings technology evolved empirically, by trial and error. The last few decades have seen a marked increase in scientific understanding of the applicable principles, but the complexities of the field are such that the formulator's art is still essential in developing and using coatings. The need to reduce air pollution while maintaining and, preferably, improving coating performance requires radically new formulations on a short time scale. Our conviction is that increased understanding of the underlying science can help formulators work more effectively and that an appreciation of a formulator's craft is essential for scientists working in the field.

We do not claim to provide a complete literature review on each topic, but believe that many of the key references are cited. Readers are cautioned that the quality of the literature in the coatings field is uneven. Many published papers and monographs are excellent, but some are not; unfortunately, some authors did not fully understand the complexity of the field.

Many of the chapters in this edition were reviewed by people with extensive working experience with the particular topic. These reviewers were: David Bittner, Randall Brady, Adelbert Braig, John Bright, David Cocuzzi, Nico Enthoven, Ray Fernando, Werner Funke, Loren Hill, George Pilcher, Bradley Richards, Christian Schaller, John G. Stauffer, and Peter Wolfgang. Special thanks to Clifford Schoff, who reviewed three chapters and a section of another. We acknowledge the contributions of students and staff from the Wicks and Thames/Rawlins Research Groups at the University of Southern Mississippi. Special appreciation is expressed for the assistance of Helen Rassier, Stacy Trey, and Todd Williams of the Wicks Research Group.

Symbols and Units

A	Arrhenius preexponential term
C	concentration, weight per unit volume of solution
°C	degrees Celsius
c	concentration, moles per liter
E	modulus; relative evaporation rate
E'	storage modulus (elastic modulus)
E''	loss modulus
E_a	thermal coefficient of reaction rate (Arrhenius activation energy)
F	functionality of a monomer
$\bar{F}$	average functionality of a monomer mixture
f	functionality of a polymer (resin)
$\bar{f}_n$	number average functionality of a polymer (resin)
G	free energy; Small's molar association constant; force applied in a tensile test
G_c	force to crack in a tensile test
g	gram
g	gravitational constant
H	enthalpy
h	film thickness
i	angle of incidence
K	Kelvin temperature
K	absorption coefficient

Note that all acronyms are listed in the index.

K_E	Einstein (shape) constant
k	rate constant
kg	kilogram
L	liter
M	molecular weight
$\bar{M}_c$	average molecular weight between cross-links
$\bar{M}_n$	number average molecular weight
$\bar{M}_w$	weight average molecular weight
mL	milliliter
mP·s	millipascal second = 1 centipoise
N	newton
N	number of moles; refractive index
P	vapor pressure, degree of polymerization
$\bar{P}_n$	number average degree of polymerization
$\bar{P}_w$	weight average degree of polymerization
p	extent of reaction
p_g	extent of reaction at gelation onset
Pa	pascal
Pa·s	pascal second = 10 poise
PDI	polydispersity index = $\bar{M}_w/\bar{M}_n$
R	gas constant
r	angle of reflection or angle of refraction
S	entropy; scattering coefficient
s	second
T	temperature; time
T_b	brittle–ductile transition temperature
T_g	glass transition temperature
T_m	melting point
$\tan \delta$	tan delta, loss tangent, E''/E'
V	molar volume
V_i	volume fraction of internal phase
w	weight fraction
X	film thickness
x	mole fraction
x	optical path length
γ	surface tension
$\dot{\gamma}$	shear rate
δ	solubility parameter; phase shift in viscoelastic deformation
ε	molar absorbance; strain
η	absolute shear viscosity
η_e	external phase viscosity; extensional viscosity
η_r	relative viscosity = η/η_s
η_s	viscosity of solvent
$[\eta]$	intrinsic viscosity
$[\eta]_w$	weight intrinsic viscosity
$[\eta]_\theta$	intrinsic viscosity under theta conditions

θ	contact angle
λ	wavelength
ν	kinematic viscosity; Poisson's constant
ν_e	mole of elastically effective network chains per cubic centimeter
ρ	density
σ	shear stress
σ_0	yield value
ϕ	packing factor
χ	activity coefficient

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What Are Coatings?

Look around you; coatings are everywhere. If you are indoors, there are coatings on the walls, refrigerator, cabinets, and furniture; less obviously, coatings are on the wires of electrical motors, printed circuits, inside television sets, and compact disks. If you are outdoors, coatings are on your house and car, as well as inside your car, under the hood, and on components of the automotive stereo and computer systems. Whether you drink beer or soft drinks, there are coatings on the inside and outside of the cans. The functional and decorative requirements of coatings span a broad spectrum. A diverse science and technology support the development, production, and use of coatings.

People entering coatings science should realize that although it is an old field, it is not a mature one; it offers exciting challenges and career opportunities. They will have opportunities to improve scientific understanding and to contribute to the major thrusts of coatings development: reducing emissions that cause air pollution, reducing energy requirements, and protecting metals against corrosion.

1.1. DEFINITIONS AND SCOPE

Coatings may be described by their appearance (e.g., clear, pigmented, metallic, or glossy) and by their function (e.g., corrosion protective, abrasion protective, skid resistant, decorative, or photosensitive). Coatings may be distinguished as organic or inorganic, although there is overlap. For example, many coatings consist of inorganic pigment particles dispersed in an organic matrix (the binder).

A confusing situation results from multiple meanings of the term *coating*. It is used to describe the material (usually, a liquid) that is applied to a substrate, the resulting "dry"

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film, and the process of application. Usually, the intended meaning of the word *coating* can be inferred from the context.

We limit our discussion to coatings with organic binders that are applied purposefully to a substrate. Many types of coatings are not included. Porcelain enamels on kitchen ranges are coatings, but they do not have organic chemical binders. Electroplated copper, nickel, and zinc coatings are excluded for the same reason. We further restrict our discussion of organic coatings to those materials that can be traced historically back to *paints*. What is the difference between a coating and a paint? Not much—the terms are often used interchangeably. However, it is fairly common practice to use *coatings* as the broader term and to restrict *paints* to the familiar architectural and household coatings and sometimes to maintenance coatings for bridges and tanks. We follow this practice. Some prefer to call sophisticated materials that are used to coat automobiles and computer components *coatings*, perhaps sensing that *paint* sounds too low brow. Still another common term that is essentially a synonym for *coating* and *paint* is *finish*.

In limiting the scope of this book to organic coatings that can be related to historic paints, we exclude many materials that could be called coatings. Printing inks, polymers applied during production of paper and fabrics, coatings on photographic films, decals and other laminates, and cosmetics are but a few examples. However, many of the basic principles that are covered in this book are applicable to such materials. Restrictions of scope are necessary if the book is to be kept to a reasonable length, but our restrictions are not entirely arbitrary. The way in which we are defining coatings is based on common usage of the term in worldwide business. It is close to the definition of organic coatings for statistical analyses of industrial output used by Bureau of Census of the U.S. Department of Commerce. The Census Bureau defines four broad categories: (1) architectural coatings, (2) product coatings used by original equipment manufacturers (OEM coatings), (3) special purpose coatings, and (4) miscellaneous. 2002 U.S. Census data reported that there were 1139 companies that manufactured paints and coatings [1].

The worldwide coatings market in 2003 was estimated at about \$70 billion [2]. The markets in North America, Europe, and Asia are roughly equal in size, with Asia growing fastest. The value of coating shipments in the United States in 2002 according to the *Current Industrial Reports—Paint and Coating Manufacturing* are shown in Table 1.1.

Architectural coatings include paints and *varnishes* (transparent paints) used to decorate and protect buildings, outside and inside. They also include other paints and varnishes sold for use in the home and by small businesses for application to such things as cabinets and household furniture (not those sold to furniture factories). They are often called *trade sales paints*. They are sold directly to painting contractors and do-it-yourself users through paint stores and other retail outlets. In 2003 in the United States, architectural

TABLE 1.1. U.S. Coatings Shipments, 2002

Coatings	Dollars × 10^9
Architectural	7.211
Product (OEM)	5.556
Special purpose	3.153
Miscellaneous	1.181
	17.101

Source: Ref. [1].

coatings accounted for about 58% of the total volume of coatings; however, the unit value of these coatings was lower than for the other categories, so they made up about 47% of the total value. This market is the least cyclical of the three categories. Although the annual amount of new construction drops during recessions, the resulting decrease in paint requirements tends to be offset by increased repainting of older housing, furniture, and so on, during at least mild recessions. Latex-based coatings make up about 77% of architectural coatings [2].

Product coatings, also commonly called *industrial coatings* or *industrial finishes*, are applied in factories on products such as automobiles, appliances, magnet wire, aircraft, furniture, metal cans, chewing gum wrappers—the list is almost endless. This market is often called the *OEM market*, that is, the original equipment manufacturer market. In 2003 in the United States, product coatings were about 29% of the volume and 33% of the value of all coatings. The U.S. shipments in 2003 were $8.6 billion of the world market, estimated at $24 billion [2]. The volume of product coatings depends directly on the level of manufacturing activity. This category of the business is cyclical, varying with OEM cycles. In most cases, product coatings are custom designed for a particular customer's manufacturing conditions and performance requirements. The number of different types of products in this category is much larger than in the others; research and development requirements are also higher.

Special purpose coatings include industrial coatings applied outside a factory, along with a few miscellaneous coatings, such as coatings packed in aerosol containers. It includes *refinish coatings* for cars and trucks that are applied outside the OEM factory (usually in body repair shops), *marine coatings* for ships (they are too big to fit into a factory), and striping on highways and parking lots. It also includes *maintenance paints* for steel bridges, storage tanks, chemical factories, and so on. In 2003 in the United States, special purpose coatings constituted about 13% of the total volume and 20% of the total value of all coatings.

The Census Bureau defines *miscellaneous paint and coating products* as paint removers, thinners, pigment dispersions, glazing compounds, and so on.

Coatings are used for one or more of three reasons: (1) for decoration, (2) for protection, and/or (3) for some functional purpose. The low gloss paint on the ceiling of a room fills a decorative need, but it also has a function: It reflects and diffuses light to help provide even illumination. The coating on the outside of an automobile adds beauty to a car and also helps protect it from rusting. The coating on the inside of a beverage can has little or no decorative value, but it protects the beverage from the can. (Contact with metal affects flavor.) In some cases, the interior coating protects the can from the beverage. (Some soft drinks are so acidic that they can dissolve the metal.) Other coatings reduce the growth of algae and barnacles on ship bottoms, protect optical fibers for telecommunications against abrasion, retard corrosion of bridges, serve as the recording medium on compact disks, and so on. Although the public most commonly thinks of house paint when talking about coatings, all types of coatings are important throughout the economy, and they make essential contributions to most high-tech fields. For example, computer technology depends on microlithographic coatings to construct microprocessors.

Traditionally, coatings have changed relatively slowly in an evolutionary response to new performance requirements, new raw materials, and competitive pressures. An important reason for the relatively slow rate of change is the difficulty of predicting product performance on the basis of laboratory tests. It is less risky to make relatively small changes in composition and check actual field performance before making further changes. Starting in the 1930s, the pace of technical change increased as new synthetic polymers were introduced. Since 1965 a major driving force for change has been the need to reduce *VOC* (*volatile organic compound*) emissions because of their detrimental effect on air quality. Coatings have been second only to the gasoline–automobile complex as a source of VOC pollutants responsible for excess ozone in the air of many cities on many days of the year. This situation has resulted in increasingly stringent regulatory controls on such emissions. The drive to reduce VOC emissions has also been fueled by the rising cost of organic solvents. Other important factors have also accelerated the rate of change in coatings. Increasing concern about toxic hazards has led to the need to change many raw materials that were traditionally used in coatings. Furthermore, manufacturers often want their coatings modified so that they can be used at faster production rates, baked at lower temperatures, or changed in color. Product performance requirements have tended to increase; most notable is the need for increased effectiveness of corrosion protection by coatings.

1.2. COMPOSITION OF COATINGS

Organic coatings are complex mixtures of chemical substances that can be grouped into four broad categories: (1) *binders*, (2) *volatile components*, (3) *pigments*, and (4) *additives*. *Binders* are the materials that form the continuous film that adheres to the *substrate* (the surface being coated), that bind together the other substances in the coating to form a film, and that present an adequately hard outer surface. The binders of coatings within the scope of this book are organic polymers. In some cases, these polymers are prepared and incorporated into the coating before application; in other cases, final polymerization takes place after the coating has been applied. Binder polymers and their precursors are often called *resins*. The binder governs, to a large extent, the properties of the coating film. The major resin types used in coatings are given in Table 1.2.

Volatile components are included in a large majority of all coatings. They play a major role in the process of applying coatings; they are liquids that make the coating fluid enough for application, and they evaporate during and after application. Until about

TABLE 1.2. U.S. Resin Sales by Type, 2004

Resin Type	Pounds × 10^6	Dollars × 10^6	Growth Rate (%)
Acrylics	925	1350	3
Alkyds	445	356	0 to −1
Amino resins	335	94	1 to 2
Cellulosics	31	59	−1
Epoxies	380	475	2
Polyesters	275	261	4
Urethanes	249	600	3
Poly(vinyl aetates)	640	992	1 to 2
Poly(vinyl chlorides)	240	156	0
Miscellaneous	200	400	av. 2
	3495	4743	av. 2

Source: Ref. [3].

1945, almost all of the volatile components were low molecular weight organic solvents that dissolved the binder components. However, the term *solvent* has become potentially misleading because since 1945, many coatings have been developed for which the binder components are not fully soluble in the volatile components. Because of the need to reduce VOC emissions, a major continuing drive in the coatings field is to reduce the use of solvents by making the coatings more highly concentrated (higher-solids coatings), by using water as a major part of the volatile components (waterborne coatings), and by eliminating solvents altogether. *Vehicle* is a commonly encountered term. It usually means a combination of the binder and the volatile components of a coating. Today, most coatings, including waterborne coatings, contain at least some volatile organic solvents. Exceptions are powder coatings, certain solventless liquid coatings, radiation-curable coatings, and a small but growing segment of architectural coatings.

Pigments are finely divided insoluble solid particles that are dispersed in the vehicle and remain suspended in the binder after film formation. Generally, the primary purpose of pigments is to provide color and opacity to the coating film. However, they also have substantial effects on application characteristics and on film properties. Although most coatings contain pigments, there are important types of coatings that contain little or no pigment, commonly called *clear coats*, or just *clears*. Clear coats for automobiles and transparent varnishes are examples.

Additives are materials that are included in small quantities to modify some property of a coating. Examples are catalysts for polymerization reactions, stabilizers, and flow modifiers.

Most coatings are complex mixtures. Many contain several substances from each of the four categories, and each substance is usually a chemical mixture. The number of possible combinations is limitless. The number of different applications is also limitless.

Formulation of paints started millennia ago as an empirical art or craft. Successive generations of formulators built on the experience of their predecessors and formulated coatings with increasingly better performance characteristics. Gradually, formulators began trying to understand the underlying scientific principles that control the performance of coatings. Most coating systems are so complex that our understanding of them today is still limited. Real progress has been made, but the formulator's art is still a critical element in developing high performance coatings. Because demands on suppliers of coatings to develop new and better coatings are increasing at an accelerating pace, time is now too limited to permit traditional trial and error formulation. Understanding the basic scientific principles can help a formulator design better coatings more quickly. In the chapters ahead, we present, to as great an extent possible, the current understanding of the scientific principles involved in coating science. Important considerations when working on a formulating problem, including experimental design and combinatorial or high throughput methods, are provided in Chapter 34.

We also identify areas in which our basic understanding remains inadequate and discuss approaches to more efficient and effective formulation despite inadequate understanding. In some cases, in which no hypotheses have been published to explain certain phenomena, we offer speculations. Such speculations are based on our understanding of related phenomena and on our cumulative experience acquired over decades in the field, but they are dangerous because they may be wrong. We recognize the risk that, with time, speculation tends to become accepted as fact and may even be cited as evidence or adopted as an experimentally supported hypothesis. It is our intent, rather, that such speculations promote the advancement of coatings science and technology by stimulating discussion that leads to experimentation designed to disprove or support the speculative proposal. We believe that the latter purpose outweighs the former risk, and we endeavor to identify the speculative proposals as such.

Cost is an essential consideration in formulation. Novice formulators are inclined to think that the best coating is the one that will last the longest time without any change in properties, but such a coating may be very expensive and unable to compete with a less expensive coating whose performance is adequate for the particular application. Furthermore, it is seldom possible to maximize all of the performance characteristics of a coating in one formulation. Some of the desirable properties are antagonistic with others; formulators must balance many performance variables while keeping costs as low as possible.

The formulator's product is a formula. A coatings company's formulas are among its most important assets. They are followed by the manufacturing department to produce the ultimate products. A formula includes a list of ingredients and amounts by weight and by volume, with the amounts often totaling 100 or 1000 gallons to facilitate scaling to different-sized equipment. It also includes specific manufacturing directions, warnings of safety hazards, information about individual ingredients, quality control tests, specifications, and cautions against potential manufacturing pitfalls, (e.g., "Do not heat above 50°C"). In addition, there should be a unique code number, a date, the name of the formulator, approval by a supervisor, a statement of why the formula was developed (if it is new) or changed (if it is a modification of an older formula). Typically, responsibility for a new formula is turned over to the manufacturing department after one to three successful production batches. The manufacturing department should not change formulas but should request changes from the technical department if changes are desired. It is important for companies to manage their formulas well, protecting their confidentiality while keeping them in good order. It should be anticipated that the formulas will play a central role in expansions, licensing, acquisitions, and certain legal actions, such as product liability suits.

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2

Polymerization and Film Formation

This chapter is designed to introduce the basic concepts of polymer chemistry and film formation.

2.1. POLYMERS

A polymer is a substance composed of macromolecules. Some authors reserve the term *polymer* to describe a substance and use the term *macromolecule* for the molecules making up the substance. This use distinguishes between the material and the molecules, but is not common in the coatings field. We use the term *polymer* for both meanings; depending on the context, the term refers to either the molecules or the substance. The structure of polymers is a multiple repetition of units (mers) derived from molecules of low relative molecular weight (MW) (monomers). (The more rigorous designation of MW is *molar mass*, but we use MW because it is much more commonly used in the coatings field.)

There is disagreement about how high the MW has to be for a material to qualify as a polymer. Some people refer to materials with MWs as low as 1000 as polymers; others insist that only materials with MWs over 10,000 (or even 50,000) qualify. The term *oligomer*, meaning "a few mers," is often used for materials having MWs of a few hundred to a few thousand. This additional term does not help the definition problem much because there is no clear-cut boundary between an oligomer and a polymer, but the term can be useful because it provides a name with which most can agree for materials containing 2 to about 20 mers.

Polymers occur widely in nature; familiar examples of biopolymers, which are produced by living organisms, are proteins, starch, cellulose, and silk. In the coatings field,

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we are concerned mainly with synthetic polymers, although some chemically modified biopolymers are also used.

Synthetic polymers and oligomers are prepared by *polymerization*, a sequence of chemical reactions in which small molecules are joined by covalent bonds. A polymer made from a single monomer is called a *homopolymer*. If it is made from a combination of monomers, it is often but not always called a *copolymer*. An example of a homopolymer is provided by the polymerization of vinyl chloride:

$CH_2{=}CHCl$	$X{-}(CH_2CHCl)_n{-}Y$
Vinyl chloride monomer	Poly(vinyl chloride)

In this example, the —(CH_2CHCl)— repeating unit is the mer, and n represents the number of mers joined together in the molecule. X and Y represent terminal groups on the ends of the chain of mers.

Polymers can be made in three important classes. When the mers are linked in chains, the polymers are called *linear polymers*, a term that is potentially misleading because the large molecules seldom form a straight line—they twist and coil. In linear copolymers, the various monomers may be distributed more or less at random throughout the chain (*random copolymers*), they may tend to alternate (*alternating copolymers*), or they may be grouped together (*block copolymers*). If there are forks in the chains, the polymers are called *branched polymers*. A polymer chain of one type of monomer having polymer branches of another type of monomer is called a *graft copolymer*. The third class, of particular importance in coatings, results from the bonding of chains with each other at several sites to form *cross-linked*, or *network*, *polymers*. These polymers are branched polymers where the branches are covalently bound to other molecules, so the mass of polymer consists mainly of a single interconnected molecule. A fourth class, *dendritic polymers*, may become important in coatings applications in the future.

Reactions that join polymer or oligomer molecules are called *cross-linking reactions*. Polymers and oligomers that can undergo such reactions are frequently called *thermosetting polymers*. Some confusion can result because the term *thermosetting* is applied not only to polymers that cross-link when heated, but also to those that can cross-link at ambient temperature. A polymer that does not undergo cross-linking reactions is called a *thermoplastic polymer*, because it becomes plastic (softens) when heated.

Polymers can also be formed from mers that contain multiple H-bonding sites, in which case the mers are joined together by hydrogen bonds rather than by covalent bonds. Such polymers are called *supramolecular polymers*, which are of particular interest when the hydrogen-bonding sites are four-centered, owing to greatly enhanced strength relative to three-centered hydrogen-bonds [1]. Coatings compositions in which multicenter hydrogen bonds complement covalent cross-links may be of potential interest for enhancing coatings properties, owing to thermal reversibility of the hydrogen bonds, as observed for polyurethanes (Chapter 12). Multicenter hydrogen-bond compositions have been disclosed for various applications related to coatings, including adhesives and molding compounds [2].

Another term commonly, but loosely, used in the coatings field is *resin*. This term overlaps the meanings of *polymer* and *oligomer*. Originally, the term referred to hard, brittle materials derived from tree exudates, such as rosin, dammar, and elemi.

A variety of these naturally occurring resins were used since prehistoric times to make coatings. In the nineteenth and early twentieth centuries, such resins were dissolved in drying oils to make *varnishes* (Section 14.3.2). The first entirely synthetic polymers used in coatings were phenol–formaldehyde polymers (Section 13.6), which replaced naturally occurring resins in many applications. Hence, it was natural to call them *phenol–formaldehyde resins* or *phenolic resins*. As more synthetic products were developed to replace naturally occurring resins, these products were also called resins.

When words do not have precise meanings, it is important to understand the context in which they are placed. Commonly, it is assumed, without much thought, that information that has been learned about high MW polymers is also applicable to low MW polymers or oligomers, because all are often called polymers. Many characteristics, however, depend on MW. Although much of the information available from studies of high-MW polymers can be useful in the coatings field, it must be used with caution, because the resins used in making coatings are commonly low MW polymers or oligomers, even though they are frequently called polymers. In the next set of subsections, we describe some of the key characteristics of synthetic polymers and oligomers.

2.1.1. Molecular Weight

For most pure organic compounds, the concept of molecular weight is straightforward—each compound has a MW. For synthetic polymers, however, the situation is more complex. All methods of synthesis lead to mixtures of molecules with different numbers of mers and, therefore, with different MWs. Even relatively simple thermoplastic homopolymers, such as polystyrene or poly(vinyl chloride), contain molecules with hundreds of different, although similar, structures. With copolymers, the number of different molecules present is much larger. There is a distribution of MWs in a synthetic polymer; accordingly, MWs can be defined only by a statistical calculation. In the simplest cases, the distribution of the number of molecules of each MW resembles a skewed Gaussian distribution, but in other cases, the distribution may be quite complex. Although many types of average MW can be calculated, the two most widely used are number and weight average MWs.

1. *Number average MW.* $\bar{M}_\mathrm{n}$ is the MW average based on summing the products of the numbers of molecules and their MWs and dividing by the sum of the number of molecules in the sample. Mathematically, it is expressed by the following equation, where M_1, M_2, and M_i are the MWs of the first, second, and *i*th species, respectively, and the N values are the numbers of molecules of each species present:

$$\bar{M}_\mathrm{n} = \frac{\sum N_1M_1 + N_2M_2 + \cdots}{\sum N_1 + N_2 + \cdots} = \frac{\sum_\mathrm{i} N_\mathrm{i}M_\mathrm{i}}{\sum_\mathrm{i} N_\mathrm{i}}$$

$$\bar{P}_\mathrm{n} = \frac{\sum_\mathrm{i} N_\mathrm{i}P_\mathrm{i}}{\sum_\mathrm{i} N_\mathrm{i}}$$

A similar equation is often used to represent the *number average degree of polymerization* $\bar{P}_\mathrm{n}$, where P is the number of mers in a molecule and P_i is the number of mers in the *i*th polymer. For homopolymers, $\bar{M}_\mathrm{n} = \bar{P}_\mathrm{n}$ times the MW of each mer; for copolymers, a weighted average MW of the mers is used. The differing weights of end groups can be neglected in calculating $\bar{M}_n/\bar{M}_w$ of high polymers, but not of oligomers, for which the effect can be appreciable.

2. *Weight average MW.* $\bar{M}_w$ is defined by the following equation, in which w_1, w_2, and w_i are the weights of molecules of species 1, 2, and *i*th: Since $w_1 = N_1M_1$, $\bar{M}_w$ can also be calculated from the numbers of molecules of the various species, as shown in the equation. *Weight average degree of polymerization* $\bar{P}_w$ is defined by analogous equations:

$$\bar{M}_w = \frac{w_1M_1 + w_2M_2 + \cdots}{w_1 + w_2 + \cdots} = \frac{\sum_i w_iM_i}{\sum_i w_i} = \frac{\sum_i N_iM_i^2}{\sum_i N_iM_i}$$

Figure 2.1 shows an idealized plot of the weight fraction of molecules of each MW as a function of degree of polymerization for oligomers made from the same monomer by three different processes [3]. In relatively simple distributions of MWs, such as those shown in Figure 2.2, the value of $\bar{P}_n$ is at, or near, the peak of the weight fraction ditribution curve. Because $\bar{M}_w$ and $\bar{P}_w$ give extra weight to higher MW molecules, they are always larger than $\bar{M}_n$ and $\bar{P}_n$.

The breadth of the MW distribution can have an important effect on the properties of a polymer and is often critical to achieving satisfactory performance of a coating. The ratio $\bar{M}_w/\bar{M}_n$ is widely used as an index of the breadth of distribution. In the case of high MW polymers, $\bar{M}_w/\bar{M}_n = \bar{P}_w/\bar{P}_n$, but in the case of oligomers, differences in end groups can be significant and affect the equality of the ratios. These ratios are called *polydispersity* (PD), or sometimes, *polydispersity index* (PDI). We use the symbols $\bar{M}_w/\bar{M}_n$ and $\bar{P}_w/\bar{P}_n$. The ratios provide a convenient way to compare the MW distributions of different polymers. However, one must be cautious in the use of a single value to describe a possibly

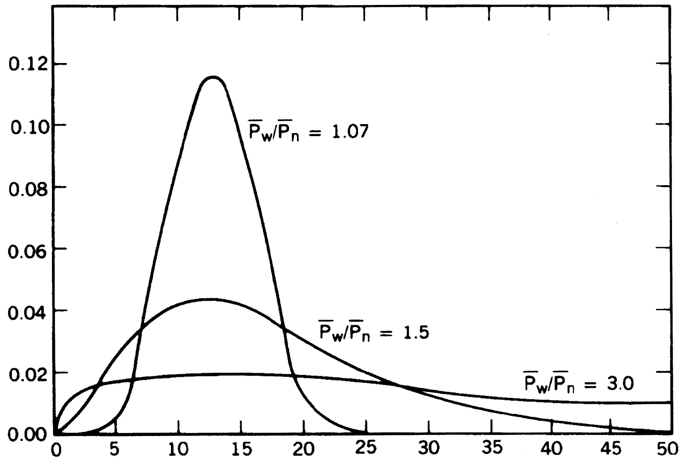
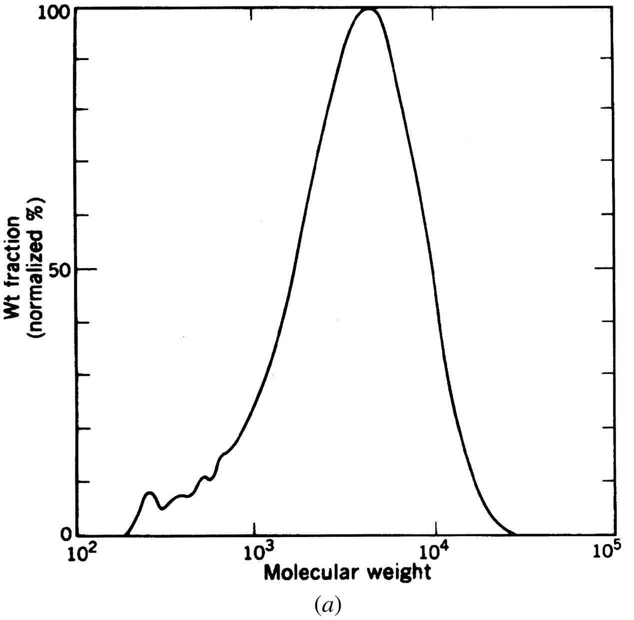


Figure 2.1. *Degree of polymerization distribution plots calculated for three types of chain-growth polymers.* $\bar{P}_w/\bar{P}_n = 1.07$ *is for an ideal anionic polymerization,* $\bar{P}_w/\bar{P}_n$ *is 1.5 for an ideal free radical polymerization with termination by combination, and* $\bar{P}_w/\bar{P}_n$ *is 3.0 for a typical free radical polymerization.* $\bar{P}_n$ *is 12 for all plots, and* $\bar{P}_w$ *is 12.84, 18, and 36, respectively. (From Ref. [4], with permission.)*



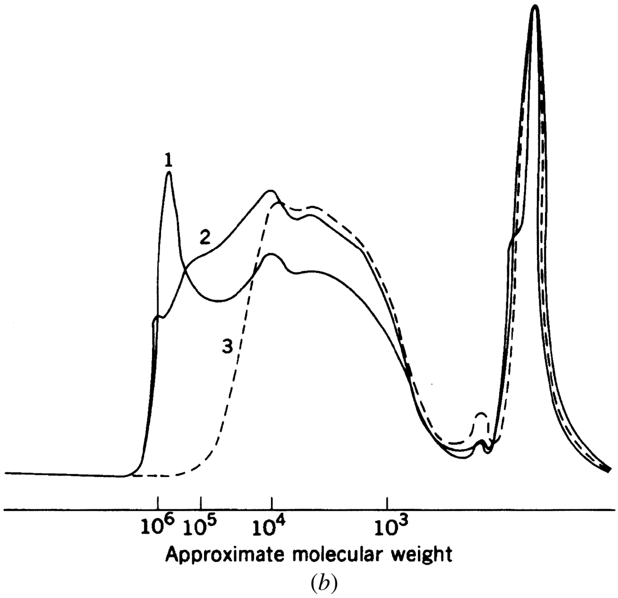


Figure 2.2. *(a) Molecular weight distribution of a typical polyester resin (from Ref. [5], with permission); (b) molecular weight distributions of three alkyd resins, as measured by GPC with a UV detector (from Ref. [6], with permission).*

complex distribution. As shown in Figures 2.1 and 2.2, synthetic polymers commonly have broad distributions of MWs. As $\bar{M}_w/\bar{M}_n$ increases, the fractions of polymer at the extremes above and below the number average MW increase. Even the oligomer with a number average of 12 mers and with $\bar{M}_w/\bar{M}_n = 1.07$ has substantial numbers of molecules containing 7 to 18 mers, and a polymer with a more typical $\bar{M}_w/\bar{M}_n = 3$ has molecules spanning several orders of magnitude of MW.

$\bar{M}_n$ is the MW of most importance for relating stoichiometric ratios of reactants and for comparing certain physical properties. $\bar{M}_w$ often proves more useful than $\bar{M}_n$ when considering the relationship between MW and many physical properties of polymers, including some of the properties that are crucial to coating performance.

MW measurement is difficult and beyond the scope of this book to discuss in detail. (See Ref. [4] for a discussion of the various ways of determining $\bar{M}_w$ and $\bar{M}_n$.) In practice, most scientists in the coatings field use *gel permeation chromatography* (GPC), more properly called *size exclusion chromatography* (SEC), to measure MWs. In this convenient method, a dilute solution of an oligomer or a polymer is pumped at high pressure through a series of columns containing porous gels. The molecules are “sorted” by sizes, with the largest ones coming out first and the smaller ones, which are slowed by entering and leaving more of gel pores, coming out later. The concentration of polymer in the solvent is analyzed as it leaves the column and is plotted as a function of time. A computer program compares the plot to plots of standard polymers of known MWs and calculates $\bar{M}_n$, $\bar{M}_w$, and several other quantities that characterize the polymer. The results appear precise, but they are not accurate; errors of $\pm 10\%$ can be expected, and much larger errors are possible. Errors can result because the MW is not measured directly—instead, the size of the polymer molecules in solution is measured—and from differences in detector response to different compositions. Despite its inaccuracy, GPC is useful, especially for comparing polymers of similar structure.

The $\bar{M}_n$ of oligomers can be measured accurately using colligative methods such as freezing point depression and vapor pressure osmometry. However, the accuracy decreases as MW increases, and colligative methods are of little use above $\bar{M}_n = 50{,}000$. Mass spectroscopic methods are available that can accurately measure the MWs of individual molecules in oligomers and even in fairly high polymers. (In Section 10.2 we give examples.)

Some polymers and oligomers have MW distributions approaching the idealized distributions shown in Figure 2.1, as illustrated by the GPC trace of a polyester oligomer in Figure 2.2(*a*). However, many polymers used in coatings have complex distribution patterns, as exemplified by the alkyds in Figure 2.2(*b*). The $\bar{M}_w$ and $\bar{M}_n$ can be calculated for an entire trace or for portions of complex traces. But such polydispersity numbers must be used with caution for complex traces.

The MW of resins is an important factor affecting the viscosity of coatings made with solutions of the resins: Generally, the higher the MW, the higher the viscosity. The MW of oligomers used in higher-solids coatings is especially critical. It is often desirable to make oligomers with as narrow a range of MW as possible, since this minimizes the amount of very low and very high MW resin. The low MW fraction is generally undesirable from the standpoint of film properties, whereas the high MW fraction increases resin solution viscosity disproportionately. However, alkyd resins having broad, complex MW distributions may perform better than alkyds with similar compositions having narrow distributions [6].

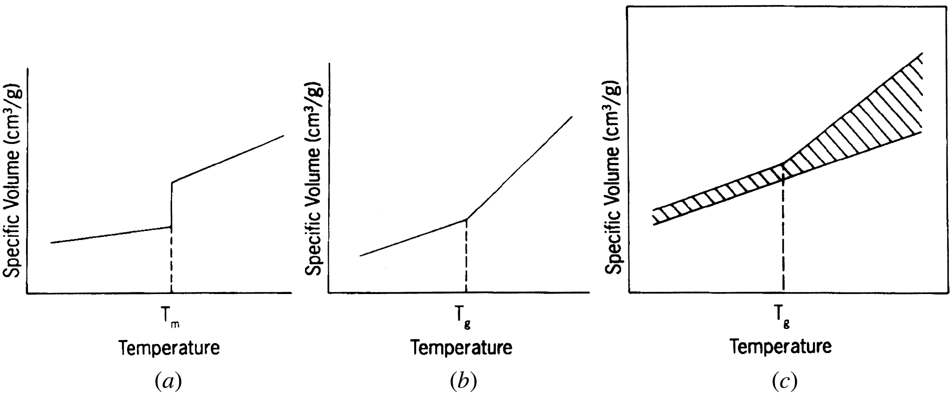
MW is often a critical factor controlling the strength of films that are not cross-linked. In general, the higher the MW, the higher the tensile strength of such films, at least up to a point. The acrylic copolymer in automotive acrylic lacquers must have an $\bar{M}_w$ greater than about 75,000 for acceptable film properties but less than 100,000 for acceptable application properties. For other lacquers the MWs required depend on polymer composition and application methods. Film property considerations argue in favor of using high MW polymers in formulating coatings, but viscosity considerations favor low MWs. As is often the case in coatings, compromises are needed.

An important advantage of many waterborne coatings is that MW of the polymer generally does not affect viscosity directly, since the polymers are dispersions of polymer particles rather than solutions.

2.1.2. Morphology

Morphology is the study of the physical forms of materials. Like MW, morphology is more complex with polymers than with small-molecule substances. Pure small molecules generally solidify to crystals if the temperature is sufficiently low. In contrast, few synthetic polymers crystallize completely, and many do not crystallize at all. Non-crystalline materials that appear to be solids are called *amorphous solids*. There are at least two reasons that synthetic polymers are at least partly amorphous. In general, synthetic polymers are not pure compounds, so it is difficult to achieve the completely regular structure characteristic of a crystalline material. In addition, the molecules are so large that the probability of complete crystallization is low. Part of a molecule can associate with part of a different molecule or with another part of the same molecule, reducing the odds of pure crystal formation. However, small crystalline domains are common in synthetic polymers; polymers with fairly regular structures, usually homopolymers, are most likely to crystallize partially. In these crystalline domains, fairly long segments of molecules associate with each other in a regular way. The remaining parts of the same molecules are unable to fit together regularly and remain amorphous. Whereas polymers used in fibers and films (e.g., polyethylene and nylon) are often partly crystalline, polymers used in coating applications are, with few exceptions, completely amorphous.

Amorphous materials behave quite differently from crystalline materials. An important difference is shown in Figure 2.3(*a*) and (*b*), which compare schematically changes in specific volume of crystalline and amorphous materials with temperature. In the case of a pure crystalline material, as temperature increases, initially there is a slow increase in specific volume, owing to increasing vibrations of the atoms and molecules. Then, at a



(*a*) (*b*) (*c*)

Figure 2.3. *Specific volume as a function of temperature for (a) a crystalline material and (b) an amorphous material; (c) free volume within an amorphous material as a function of temperature. Units of specific volume are volume per mass (usually, cm^3 g^1). (Adapted from Ref. [3], with permission.)*

specific temperature, the substance melts. The melting point T_m is the lowest temperature at which the vibrational forces pushing molecules apart exceed the attractive forces holding them together in crystals. With almost all substances (water is a notable exception), the molten compound occupies more volume at the same temperature than do the crystals; because the molecules are freer to move in a molten compound, they "bounce" their neighbors out of the way, leading to an abrupt increase in specific volume at T_m. Above T_m, the specific volume of a liquid increases slowly with further increase in temperature.

Amorphous materials behave differently, as shown in Figure 2.3(*b*). Starting from a low temperature, there is a slow increase in specific volume as temperature increases, but there is no temperature at which an abrupt change in volume occurs, there is no melting point. Rather, there is a temperature at which there is a change in the rate of increase of specific volume with temperature. Above that temperature, the thermal expansion coefficient is larger than below it. This change of slope is not a phase change; it is a second-order transition; that is, there is a discontinuity in a plot of the *derivative of volume change* as a function of temperature. The temperature at which it occurs is called the *glass transition temperature*, T_g. T_g is properly defined as the temperature at which there is an increase in the thermal expansion coefficient. By comparison, T_m is a first-order transition; that is, there is a discontinuity in change of volume as a function of temperature corresponding to the solid–liquid phase change. Unfortunately, T_g is often improperly defined as the temperature below which a material is brittle and above which it is flexible. Although there are many cases when this is true, there are cases when this definition is misleading (Section 4.2). Perhaps part of the reason for the misunderstanding is the connotation of the word *glass*, which we associate with a brittle material. Like all amorphous materials, glasses undergo a second-order transition. In fact, the phenomenon was first observed in the study of glasses—hence the name *glass transition temperature*. The idea has proliferated that T_g is a phenomenon associated only with polymers. This assumption is not true; many small molecules can be supercooled without crystallization to form amorphous glasses that have a T_g. For example, the T_g of *m*-xylene is 125 K [7]. The T_g is always lower than T_m. Partially crystalline polymers show both a T_m and a T_g.

What is happening physically at T_g? As an amorphous material is heated, atoms in the molecules vibrate with increasing energy, colliding with neighbors and shoving molecules apart for brief periods of time. At T_g, a few of the short-lived "holes" between the molecules become large enough that an adjacent molecule or a segment of a polymer molecule can fit between two molecules. Thus, T_g can be considered the lowest temperature at which segments of polymer molecules can move with some facility relative to neighboring segments. The increase in coefficient of thermal expansion above T_g results from the greater degree of freedom available to the molecule segments. The larger volume between molecules gives more degrees of freedom, so the same increase in temperature gives a greater increase in volume. As the temperature rises, the specific volume increases, but there is no more material—just the same material occupying more space. What is in this "extra" volume? Nothing. It is called *free volume*, represented by the hatched area in Figure 2.3(*c*). The molecular motions involved can be detected by spectroscopic techniques such as solid state nuclear magnetic resonance (NMR), and change as polymers are heated through T_g [8,9].

Although it is difficult to overemphasize the importance of the concepts of T_g and free volume in coatings science, our understanding of these parameters and our ability to measure them are limited. T_g values of a material that are determined by different methods may not agree with each other; one must be careful in comparing T_g values of different materials to be sure that they are based on consistent test methods. The classical method of measuring T_g is *dilatometry* (measurement of specific volume as a function of temperature). More commonly, it is measured by *differential scanning calorimetry* (DSC) or by *dynamic mechanical analysis* (DMA) (Section 4.5). The measured T_g depends on the measurement method and the conditions under which the measurement was made. Heating rate is an important variable. The faster the rate of heating during the determination, the higher the apparent T_g. When free volume is small, the rate of movement of molecules or segments is slow. If the rate of heating is slow, there is more time for movement, and, hence expansion, and the measured T_g is lower. (See Ref. [10] for further discussion of methods of measuring T_g.)

Some scientists argue that T_g is not a real thermodynamic parameter. They point out that if the determination of specific volume were done at a slow enough heating rate, no transition would be observed and that rather than two straight lines, as shown in Figure 2.3(*c*), there would be a smooth curve. Despite this controversy, T_g is a very useful concept and is well understood in qualitative terms. Relationships between polymer structure and T_g are understood well enough that it is often possible to make reasonable predictions of T_g from knowledge of composition and $\bar{M}_n$. Important factors affecting the T_g of thermoplastic polymers include:

1. *Number average MW.* T_g increases with increasing $\bar{M}_n$, approaching a constant value at $\bar{M}_n$ in the range 25,000 to 75,000, depending on the polymer structure. It is logical that T_g is related to $\bar{M}_n$ because decreasing $\bar{M}_n$ results in an increasing fraction of chain ends to chain middles, since chain ends have more freedom of movement than chain middles. The relationship of T_g to $\bar{M}_n$ is approximated by the equation

$$T_g = T_{g\infty} - \frac{A}{\bar{M}_n}$$

where $T_{g\infty}$ is the T_g at infinite MW and A is a constant (T_g is in Kelvin).

2. *Polymer backbone flexibility.* T_g is affected by the ease of rotation about bonds in the polymer backbone. For example, the siloxane bond, Si—O—Si, rotates easily; the T_g of poly(dimethylsiloxane) is 146 K (−127°C) [11]. Aliphatic polyethers such as poly(ethylene oxide), $(\text{—CH}_2\text{—CH}_2\text{—O—})_n$, also have low T_g, generally in the range 158 to 233 K, because there is considerable ease of rotation around the ether bond. The T_g of polyethylene varies because although we commonly think of polyethylene as being just chains of methylene groups, the backbone is actually substituted to varying degrees with alkyl side chains such as ethyl groups. Also, most grades of polyethylene are partially crystalline; only the amorphous areas show a T_g. However, all would agree that the T_g of a long linear aliphatic chain is low, perhaps less than 200 K. The presence of rigid aromatic rings in the polymer backbone increases T_g substantially.

3. *Side chains.* Pendant aromatic rings also lead to high T_g, for example, 373 K for polystyrene, since ease of rotation is decreased. Similarly, pendant methyl groups and carboxymethyl groups increase T_g: for example, 281 K for poly(methyl acrylate) and 378 K for poly(methyl methacrylate), which has both groups on alternate carbons of the chain. If the side chains are several atoms long and flexible, they reduce T_g: for example, 219 K for poly(*n*-butyl acrylate). However, if the side chain is short, bulky, and inflexible, it has less effect and in some cases, raises T_g: for example, 314 K for poly(*t*-butyl acrylate).

TABLE 2.1. Glass Transition Temperatures (°C) for Homopolymers of Various Monomers

Monomer	Methacrylate	Acrylate	Monomer	Methacrylate	Acrylate
Free acid	185	106	*n*-Tridecyl[a]		−46
Methyl	105	9	*iso*-Tridecyl		−39
Ethyl	65	−23	2-Hydroxyethyl	55	
I*so*propyl	81	−8	2-Hydroxypropyl	73	
n-Butyl	20	−54	Other monomers		
Isobutyl	53	−40	Styrene	100	
t-Butyl	114	74	Vinyl acetate	29	
n-Hexyl	−5	−57	Vinyl chloride	81	
2-Ethylhexyl	−10	−50	Vinylidene chloride	−18	
iso-Decyl		−30			

[a] Mixture of C_{12-14}.

Care must be taken when comparing T_g values to be sure that the determinations have been done under consistent conditions and that the MWs are high enough to eliminate MW effects. Table 2.1 gives the T_g of high MW homopolymers of a group of acrylic and methacrylic esters and of other monomers commonly used as comonomers in polymers for coatings [11–13].

Copolymers have T_g values intermediate between those of the homopolymers. It is common to use the *Fox equation* to estimate the T_g of copolymers: where w_1, w_2, w_3, etc. are the weight fractions of the various monomers in the copolymer and T_{g1}, T_{g2}, T_{g3}, etc. are the T_g (Kelvin) of their high MW homopolymers.

$$\frac{1}{T_{g(\text{copolymer})}} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} + \frac{w_3}{T_{g3}} + \cdots$$

Somewhat better approximations can be calculated using a different mixing equation, also devised by Fox, in which v_1, v_2, v_3, etc. are the volume fractions from the various monomers in the copolymer:

$$T_{g(\text{copolymer})} = v_1 T_{g1} + v_2 T_{g2} + v_3 T_{g3} + \cdots$$

This equation is not widely used because some of the homopolymer densities needed to calculate v_1, v_2, v_3, etc. are not readily available.

Gupta [14] reports an extensive study of the estimation of T_g of acrylic copolymers. He recommends use of the *van Krevelen equation* for estimation of T_g:

$$T_g = \frac{Y_g}{M}$$

where M is the MW of the repeat unit and Y_g is a molar glass transition factor. Gupta's values for the T_g of *n*-butyl methacrylate (10°C) and of 2-ethylhexyl acrylate (−63°C) vary considerably from the values given in Table 2.1, illustrating that different values are often found in the literature.

The T_g of cross-linked polymers is controlled by four factors and their interactions: T_g of the segments of polymer between the cross-links, the cross-link density (XLD), the presence of dangling ends, and the presence of cyclic segments [15]. Although generalized equations showing the relationships of these factors with T_g have been developed, the complex relationships are not fully understood. The T_g of the polymer segments between cross-links is governed by the chemical structures of the resin and the cross-linking agent, by the ratio of these components, and by the extent of the cross-linking reaction. The factors discussed in connection with thermoplastic polymers apply in terms of their effects on the T_g of the segments of cross-linked polymer chains. Since cross-links restrict segmental mobility, T_g increases as cross-link density increases. On the other hand, T_g decreases with an increasing proportion of dangling ends—that is, chain segments with unreacted cross-link sites.

Solutions of polymer in solvent and of solvent in polymer have T_g values intermediate between the T_g of the polymer and that of the solvent. The T_g of solutions increases with increasing polymer concentration. When the weight fraction of solvent w_s is less than about 0.2, a simple mixing equation gives reasonable correlation between experimental and predicted results [16]: Over a wider range of concentrations, this simple equation gives poor correlations.

$$T_{g(\text{solution})} = T_{g(\text{solution})} - k w_s$$

For solutions of oligomeric *n*-butyl methacrylate in *m*-xylene [7], Eq. 2.1 gives a good fit between observed and predicted data over the entire range from pure solvent to solvent-free oligomer. Here, w_s and w_o are weight fractions and T_{gs} and T_{go} are the T_g of the solvent and the oligomer, respectively. Although Eq. 2.1 accurately describes a limited number of oligomer and polymer solutions, its generality is not fully established.

$$\frac{1}{T_{g(\text{solution})}} = \frac{w_s}{T_{gs}} + \frac{w_o}{T_{go}} + K w_s w_o \tag{2.1}$$

An excellent general review of glass transition is available in Ref. [17]. A review of free volume considerations in coatings may be found in Ref. [18].

2.2. POLYMERIZATION

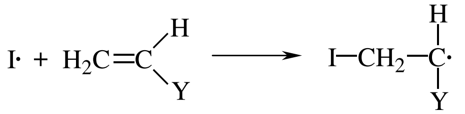
There are two major classes of polymerization reactions: *chain-growth* and *step-growth.* The common denominator of chain-growth polymerization is that reactions are chain reactions. Frequently, chain-growth polymerization is called *addition polymerization*, but this terminology is inadequate. While all chain-growth polymerizations involve addition reactions, not all addition polymerizations involve chain-growth reactions—some are step-growth reactions.

2.2.1. Chain-Growth Polymerization

Chain-growth polymerization, initiated by free radicals, is the most commonly used chain-growth polymerization for making polymers for coatings. Its mechanisms and kinetics have been studied extensively. Reference [19] gives an extensive review of the topic, especially the kinetics of the reactions. Free radical chain-growth polymerizations of most interest to coating applications are *solution polymerization* (Chapter 8) and *emulsion polymerization* (Chapter 9). A related process of importance in coatings is the autoxidation involved in cross-linking drying oils and drying oil derivatives (Chapter 14). The discussion in this section applies to solution polymerization, although many of the principles are also true for emulsion polymerization.

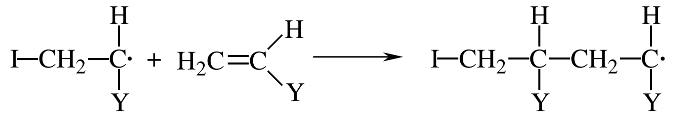
Three types of chemical reactions—*initiation*, *propagation*, and *termination*—are always involved in chain-growth polymerization; and a fourth, *chain transfer*, often plays a significant role. Initiation occurs when an *initiator* (I) reacts to form an initiating free radical (I·) (Eq. 2.2), which, in turn, adds rapidly to a monomer molecule to form a second free radical (Eq. 2.3):

$$I_2 \longrightarrow I\cdot \qquad (2.2)$$



$$I\cdot + H_2C{=}C\begin{matrix}H\\Y\end{matrix} \longrightarrow I{-}CH_2{-}\overset{H}{\underset{Y}{C}}\cdot \qquad (2.3)$$

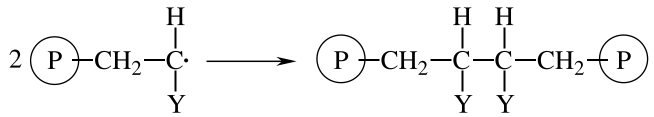
The polymer chain grows by the propagation reaction, in which the monomer free radical adds to a second monomer molecule to extend the chain while forming a new free radical:



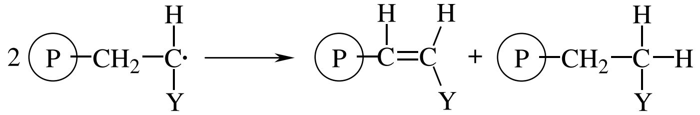
$$I{-}CH_2{-}\overset{H}{\underset{Y}{C}}\cdot + H_2C{=}C\begin{matrix}H\\Y\end{matrix} \longrightarrow I{-}CH_2{-}\overset{H}{\underset{Y}{C}}{-}CH_2{-}\overset{H}{\underset{Y}{C}}\cdot \qquad (2.4)$$

Propagation reactions are very fast, so fast that a chain with hundreds of mers can grow in a fraction of a second. At any moment, the concentrations of monomer and polymer greatly exceed the concentration of growing polymer molecules (ca. 10^{-6} ML^{-1}). (Exceptions are controlled free radical polymerizations, Section 2.2.1.1.)

The final stage is termination of the growing chain. Two common types of termination reactions are *combination* (Eq. 2.5) and *disproportionation* (Eq. 2.6). In most free radical–initiated polymerizations, the rate of propagation (Eq. 2.3) is faster than the rate of initiation, which is limited by the rate of Eq. 2.2.



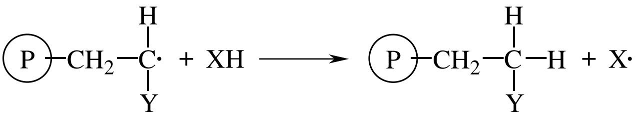
$$2\,Ⓟ{-}CH_2{-}\overset{H}{\underset{Y}{C}}\cdot \longrightarrow Ⓟ{-}CH_2{-}\overset{H}{\underset{Y}{C}}{-}\overset{H}{\underset{Y}{C}}{-}CH_2{-}Ⓟ \qquad (2.5)$$



$$2\,Ⓟ{-}CH_2{-}\overset{H}{\underset{Y}{C}}\cdot \longrightarrow Ⓟ{-}\overset{H}{C}{=}C\begin{matrix}H\\Y\end{matrix} + Ⓟ{-}CH_2{-}\overset{H}{\underset{Y}{C}}{-}H \qquad (2.6)$$

where Ⓟ- represents an attached polymer chain.

Side reactions also occur; among the most important are chain transfer reactions, in which the free radical on the end of the propagating polymer chain abstracts a hydrogen atom from some substance X—H present in the polymerization reaction mixture:

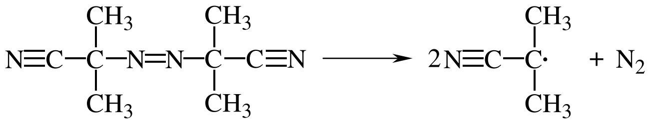


$$Ⓟ{-}CH_2{-}\overset{H}{\underset{Y}{C}}\cdot + XH \longrightarrow Ⓟ{-}CH_2{-}\overset{H}{\underset{Y}{C}}{-}H + X\cdot \qquad (2.7)$$

The net effect of chain transfer is to terminate the growing chain while generating a free radical, which may start a second chain growing. X—H may be a solvent, a monomer, a molecule of polymer, or a *chain transfer agent*, a reactant that is added to the polymerization reactants to cause chain transfer. When chain transfer is to a solvent or a chain transfer agent, MW is reduced. When chain transfer is to a polymer molecule, growth of one chain stops but a branch grows on the polymer molecule; the result is a higher $\bar{M}_w/\bar{M}_n$.

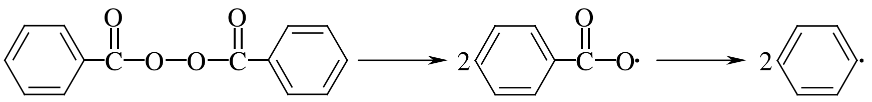
Note that the structures of the propagating polymer chains show substitution on alternate carbon atoms. This structure results from the favored addition of free radicals to the CH_2 end of the monomer molecules: *head-to-tail addition*. With almost all monomers, head-to-tail addition predominates, but a small fraction of *head-to-head addition* occurs. The result is a polymer with most of the substitution on alternating carbons in the chain, but with a few chain segments having substitution on adjacent carbons. The effect of a small fraction of head-to-head structure is generally negligible but sometimes has significant consequences for exterior durability and thermal stability.

Initiators, incorrectly called catalysts, are used in low concentration [usually in the range 1 to 4 wt% (weight percent), but sometimes higher when low MW is desired]. A variety of free radical sources has been used. Two classes of initiators are used most often: azo compounds such as azobisisobutyronitrile (AIBN) and peroxides such as benzoyl peroxide (BPO) or *t*-amyl peracetate. AIBN is fairly stable at 0°C but decomposes relatively rapidly when heated to 70 to 100°C to generate free radicals. A substantial fraction of the resulting radicals initiate polymerization, although some combine to form a coupling product. The half-life of AIBN is about 5 hours at 70°C and about 7 minutes at 100°C.

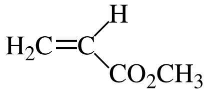


$$\mathrm{N{\equiv}C-\underset{CH_3}{\overset{CH_3}{C}}-N{=}N-\underset{CH_3}{\overset{CH_3}{C}}-C{\equiv}N \longrightarrow 2N{\equiv}C-\underset{CH_3}{\overset{CH_3}{C}}\cdot \quad + N_2}$$

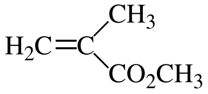
BPO decomposes at similar temperatures—its half-life is about 20 minutes at 100°C. The reactive benzoyloxy free radical generated can initiate polymerization; also, it can dissociate (rapidly at higher temperatures, such as 130°C) to yield a very highly reactive phenyl free radical and CO_2:



A range of monomers is capable of propagating a free radical–initiated chain reaction. Most are alkenes having an electron-withdrawing group; methyl acrylate (MA) and methyl methacrylate (MMA) are important examples:



MA



MMA

Copolymers containing a preponderance of acrylic and methacrylic ester monomers are called *acrylic polymers*, or often, just *acrylics*. They are used extensively in coatings. Control of MW and MW distribution is critical in preparing polymers for coatings. There are four major factors that affect MW with the same monomer, initiator, and solvent:

1. *Initiator concentration.* The higher the initiator concentration, the lower the MW. When the initiator concentration is higher, more initiating free radicals are generated to react with the same total amount of monomer. More chains are initiated and terminated; the $\bar{M}_n$ and $\bar{M}_w$ of the polymer produced are lower.
2. *Temperature.* At higher temperatures, more initiator is converted into initiating free radicals in a given time, increasing the concentration of growing chains and the probability of termination. As with increasing initiator concentration, the result is lower $\bar{M}_n$ and $\bar{M}_w$.
3. *Monomer concentration.* The higher the monomer concentration, the higher the $\bar{M}_n$ and $\bar{M}_w$. The highest MW is obtained in a solvent-free reaction mixture. With the same concentration of growing free radical ends, a higher monomer concentration increases the probability of chain growth relative to termination.
4. *Solvent concentration.* The higher the solvent concentration, the lower the $\bar{M}_n$ and $\bar{M}_w$. Higher solvent concentration leads to lower monomer concentration, reducing MW as described previously. Furthermore, most solvents undergo chain-transfer reactions to varying extents, which also reduce MW.

To the extent that any of these factors change during a polymerization process, $\bar{M}_n$ and $\bar{M}_w$ of the polymer molecules also change. The usual result is broader MW distribution. Changes in monomers also produce changes in MW distribution. Consider the difference between MA and MMA. Since the free radicals at the ends of growing chains of poly(methyl methacrylate) (PMMA) are sterically hindered, termination by combination is impeded, and termination by disproportionation predominates. On the other hand, with MA, a major fraction of the termination reactions occur by combination. Theoretical calculations show that for high MW polymers, the lowest $\bar{M}_w/\bar{M}_n$ attainable with termination by combination is 1.5, while the minimum with termination by disproportionation is 2.0. In actual polymerization processes, $\bar{M}_w/\bar{M}_n$ is usually higher, although with very high initiator concentrations, polydispersities tend to be lower. No basic studies have been reported to account for the low polydispersities with high initiator concentrations. It is speculated that lower polydispersity with high initiator concentration reflects the resulting higher rate of initiation relative to propagation, which is expected to promote “living polymerization,” as discussed in Section 2.2.1.1.

Chain transfer to polymer must also be considered. This reaction occurs to a degree in the polymerization of MMA but is more important in the polymerization of MA. The hydrogen on the carbon to which the carboxymethyl group is attached is more susceptible to abstraction by free radicals than is any other hydrogen in PMA or PMMA. The new free radical on the PMA chain can now add to a monomer molecule, initiating growth of a branch on the original polymer molecule. The result is a polymer containing branched molecules and having a larger $\bar{M}_w/\bar{M}_n$ than predicted for ideal linear polymerization. In extreme cases, chain transfer to polymer results in very broad MW distributions and, ultimately, to formation of gel particles through cross-linking.

Branching can also result from the abstraction of hydrogen atoms from a polymer chain by initiating free radicals. Phenyl free radicals from high temperature decomposition of BPO are so reactive that they will abstract almost any aliphatic hydrogen, leading to substantial branching. BPO at high (e.g., 130°C) temperature is a good choice when branching is desired, but in most cases it is desirable to minimize branching. In these cases, azo initiators such as AIBN, or aliphatic peroxy initiators, are preferred over BPO. Initiator residues remain attached to the polymer chain ends. For high MW polymers, they have a negligible effect on most properties; for oligomers, they may have an appreciable effect, particularly on exterior durability (Section 8.2.1).

MW and MW distribution also depend on solvent structure. For example, substituting xylene for toluene and keeping other variables constant leads to a decrease in MW. Since each xylene molecule has six abstractable hydrogen atoms, whereas toluene has only three, the probability of chain transfer increases and average MW decreases. To prepare a low MW polymer or oligomer, one can add a compound that undergoes facile hydrogen abstraction as a chain-transfer agent. If the hydrogen atoms are readily abstracted, the addition of even relatively low concentrations of a chain transfer agent can lead to a substantial reduction in MW. Mercaptans (RSH) are widely used as chain-transfer agents. Other variables affecting MW and MW distribution are the decomposition rate of the initiator and the reactivity of the resulting free radicals. To achieve a low $\bar{M}_w/\bar{M}_n$, concentrations of reactants must be kept as constant as possible through the polymerization. It is undesirable to simply charge all of the monomers, solvents, and initiators into a reactor and heat the mass to start the reaction. This procedure is sometimes used in small scale laboratory reactions, but never in production. At best, it yields a high $\bar{M}_w/\bar{M}_n$; at worst, the reaction may run violently out of control, because free radical polymerizations are highly exothermic. Instead, one charges some of the solvent into the reactor, heats to reaction temperature, and then adds monomer, solvent, and solutions of initiator to the reactor at rates such that the monomer and initiator concentrations are kept as constant as possible. Adding monomer at a rate that maintains a constant temperature leads to a fairly constant monomer concentration. The appropriate rate of addition of the initiator solution can be calculated from the rate of its decomposition at the temperature being used. Keeping solvent concentration constant is more complex since as the polymerization proceeds, polymer is accumulating; in a sense, the polymer becomes a part of the "solvent" for the polymerization. Solvent is added at a decreasing rate so that the other concentrations stay as constant as possible. Perfect control is not possible, but careful attention to detail makes an important difference in the $\bar{M}_w/\bar{M}_n$ of the polymer produced.

Copolymerization of mixtures of unsaturated monomers further complicates the situation. The rates of reaction involved in the various addition reactions depend on the structures of the monomers. If the rate constants for all of the possible reactions were the same, the monomers would react randomly and the average composition of molecules of substantial length would all be the same. However, the rate constants are not equal. If polymerization is carried out by putting all of the reactants in a flask and heating, the first molecules formed would contain more than proportional amounts of the most reactive monomer, and the last molecules formed would have an excess of the least reactive monomer. This situation is usually undesirable. Such effects have been studied extensively, and equations have been developed to predict the results with different monomer combinations. (See Ref. [19] for a detailed discussion of copolymerization.) In actual practice, the problem is somewhat less complex. Reactions are not run in bulk, but rather, as mentioned above, monomers, solvent, and initiator solution are added gradually to the reaction mixture. If the additions are carefully controlled so that the rate of addition equals the rate of polymerization, copolymers having reasonably uniform composition that corresponds to the feed ratio are obtained with most monomers. This procedure, called *monomer-starved conditions*, results in polymerization under conditions in which the concentration of monomers is low and fairly constant. Further process refinements are possible by adding individual reactants or mixtures of reactants in two or three streams at different rates. Computer modeling of the processes can help achieve the desired results.

2.2.1.1. Controlled Free Radical Polymerizations For several decades, considerable effort has been directed to the preparation of acrylic polymers with narrow MW distributions. This can only be accomplished by finding chain-growth polymerization processes in which the rate of initiation is much faster than the rate or propagation and the rates of termination reactions are very slow. Under these circumstances, all polymer chains start growing early in the process and grow at about the same rate under about the same conditions. In these processes the polymer chain ends often remain reactive after all monomer has been consumed, in which case they are called *living radical polymerizations*. Early efforts focused on *anionic polymerizations* and *group transfer polymerizations*. More recently, attention has shifted to *controlled free radical polymerizations* (CFRP). There has been controversy about how to define living radical polymerizations and about nomenclature in general. A sensible proposal is that if after all monomer has been consumed, polymerization continues when additional monomer is supplied, the polymerization is living [20].

All CFRP methods mediate the rate of propagation by including some substance that bonds reversibly to the radical at the growing end of the polymer chain. It is possible to slow the propagation rate by many orders of magnitude, satisfying the kinetic requirements for living polymerization. Since these polymerizations are free radical processes, they are relatively insensitive to impurities with active hydrogens and can be used to copolymerize monomers with active hydrogens. These methods enable preparation of block, alternating block, and gradient copolymers by sequential addition of monomers; and they can be adapted to synthesize a limitless variety of linear, graft, and star polymers, copolymers, and *macromonomers* (polymerizable oligomers or polymers) from most of the common acrylic and styrenic monomers. The extensive literature about CFRP processes lacks consistency about how the processes are named. One way to classify them is as follows:

1. *Stable free radical polymerization* (SFRP), also called *nitroxide-mediated polymerization* (NEM), in which polymerization is mediated by nitroxide compounds [21].
2. *Reversible addition-fragmentation chain transfer polymerization* (RAFT), which involves mediation by certain dithioesters or xanthates (trithiocarbonates) [22].
3. *Transition metal–mediated living radical polymerizations* (TMMLRP), two methods can be distinguished, although some authors lump them together:
    a. *Atom transfer radical polymerization* (ATRP), in which the mediator is a metal salt, often of copper, with a carefully chosen organic ligand and an organic halide that can undergo a redox reaction with the metal to trigger the polymerization [23–25].

b. *Catalytic chain transfer polymerization* (CCTP), which uses conventional initiator, usually an azo type, in the presence of a chelated cobalt (or other) metal salt. CCTP is especially useful for preparing macromonomers, and it yields products with relatively little color [26,27].

TMMLRP methods have thus far been the primary techniques used in work aimed at coating applications. Much information on other techniques has been published, and there is a book covering a symposium on controlled free radical polymerizations [28]. Another source is Ref. [29]. The various processes, with an emphasis on ATRP, are discussed in a review paper. It emphasizes the importance of interrelationships among monomer, halogen compound, and concentrations on control of the polymerization. Possible application to the preparation of oligomers for UV curing is also discussed [30].

Recent patents and journals are rich with examples of CFRP synthesis of acrylic polymers; a few examples are mentioned here. ATRP is used for preparation of an acrylic resin for use in powder coatings [31]. A reactor is loaded with toluene, $CuBr_2$, Cu powder, 2,2′-bipyridyl, diethyl 2-bromo-2-methylmalonate, MMA, BMA, and *t*-BMA, heated for 4 hours at 85°C, cooled, and filtered. After solvent removal by distillation, the residue is dissolved in dioxane, 1 M aqueous HCl is added and the solution is refluxed for 4 hours to hydrolyze the malonate ester groups. The solution is cooled, neutralized with Na_2CO_3, filtered, and the solvent and water are distilled off to give a solid resin that is pulverized. The resin had a $\bar{P}_w/\bar{P}_n$ of 1.25 compared with 1.95 for a similar resin made by conventional free radical polymerization. The melt viscosity at 180°C of the ATRP polymer was 11.2 Pa•s, compared with 57.2 Pa•s for the conventional resin. A powder coating using bis(*N*,*N*-di-2-hydroxyethyl) adipamide as a cross-linker was compared with a similar powder coating made with the conventional free radical copolymer. The ATRP powder coating gave cured films with better leveling than the conventional polymer and had superior storage stability. The lower melt viscosity due to the narrow MW distribution resulted in better leveling. The reduced amount of very low MW molecules reduced the fusion of powder particles during storage.

Block acrylic copolymers prepared by ATRP are useful aqueous pigment dispersants [23], as are graft copolymers made with CCTP [32]. See Section 21.3.1 for further examples and discussion of the use of the copolymers in pigment dispersion.

An acrylic resin prepared by CFRP is being used in automotive clear coats. The solids of the SuperSolids^{TM} clear coat are reported to be 65%, with the possibility of future coatings having up to nearly 90%. At the same time, the scratch and mar resistance are substantially higher. Dupont was awarded the EPA clean air achievement award for the work [33].

High-solids acrylic block copolymers, including ones in which HEA is a comonomer, have been synthesized by CFRP using a mediating nitroxy. The oligomers obtained have narrow MW distributions and hence low viscosities for their MW [34].

2.2.2. Step-Growth Polymerization

A second class of polymerization that is important in the coatings field is *step-growth polymerization*. As the name indicates, the polymer is built up a step at a time. The term *condensation polymerization* has been used for this process because early examples involved condensation reactions, reactions in which a small molecule by-product such as water is eliminated. Although both terms are still used, *step-growth polymerization* is more appropriate because many step-growth polymerizations are not condensation reactions.

Step-growth polymerization reactions are used in coatings in two ways. One is in the preparation of resins for use as vehicles, and the other is for cross-linking after a coating has been applied to a substrate. In this introductory section, polyester formation is used to illustrate the principles involved; polyesters are discussed more broadly in Chapter 10.

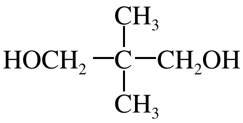
Of the many reactions that form esters, three are commonly used in making step-growth polymers and oligomers for coatings: direct esterification of an acid with an alcohol, transesterification of an ester with an alcohol, and reaction of an anhydride with an alcohol. The first two of these reactions proceed rapidly only at elevated temperature, and process temperatures of 200°C and higher are common.

When one of the reactants is monofunctional, polymer cannot form. If, however, both reactants have two or more functional groups, a polymer can be made. When all monomers are difunctional, linear polymers form. Linear step-growth polymers are commonly used in fibers, films, and plastics, but their use in coatings is restricted to low-MW oligomers. Most polyester resins used in coatings have relatively low MWs and are branched resins made using at least one monomer with three or more functional groups. After application of the coating, the terminal groups on the branch ends are reacted with a cross-linker to form the cured coating.

When a difunctional acid (AA) reacts with a difunctional alcohol (BB) in a direct esterification reaction, the MW builds up gradually. Under ideal conditions, polymer chains averaging hundreds of mers per molecule can be made, but this can occur only if (1) the reactants AA and BB contain no monofunctional impurities, (2) exactly equimolar amounts of AA and BB are used, (3) the reaction is driven virtually to completion, and (4) side reactions are negligible. If one reactant is present in excess, terminal groups of the excess monomer predominate. The MW of the completely reacted system is progressively lower as the difference from equal equivalents is increased. For example, if 7 mol of dibasic acid are completely reacted with 8 mol of a dihydroxy compound (a diol), the average molecule will have terminal hydroxyl groups, as shown in the following equation (here, for convenience, AA and BB represent both the reactants and the mers in the polymer):

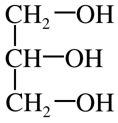
$$7AA + 8BB \longrightarrow BB\left(AA{-}BB\right)_6 AA{-}BB + 14H_2O$$

The symbol F is used for the functionality of monomers, which is the number of reactive groups per molecule, for example:



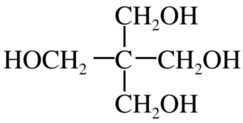
$$\begin{array}{c} CH_3 \\ | \\ HOCH_2-C-CH_2OH \\ | \\ CH_3 \end{array}$$

Neopentyl glycol



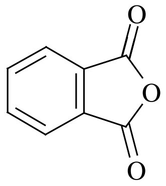
$$\begin{array}{l} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array}$$

Glycerol

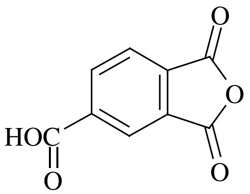


$$\begin{array}{c} CH_2OH \\ | \\ HOCH_2-C-CH_2OH \\ | \\ CH_2OH \end{array}$$

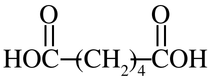
Pentaerythritol



Phthalic anhydride



Trimellitic anhydride



$$HO\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}OH$$

Adipic acid

Note that the anhydride groups in phthalic anhydride and trimellitic anhydride count as two functional groups since they can form two ester groups during polymerization.

The average functionality, represented by $\bar{F}$, of a mixture of monomers containing equal equivalents of hydroxyl and carboxyl groups is calculated as follows:

$$\bar{F} = \frac{\text{total equivalents}}{\text{total moles}}$$

Most coating polyester resins are hydroxy-functional and are made using monomer mixtures with excess hydroxyl groups. Some of the hydroxyl groups have no carboxyl groups to react with, so the equation must be modified to reflect only the total number of equivalents that can react. In a resin with excess hydroxyl groups prepared from dicarboxylic acids, the total equivalents that can react correspond to twice the number of equivalents of carboxylic acid groups:

$$\bar{F} = \frac{\text{total equivalents that can react}}{\text{total moles}} = \frac{2(\text{equiv of COOH})}{\text{total moles}}$$

A simple formulation for a polyester oligomer is given in Table 2.2.

A further type of functionality important in designing resins is the functionality of the resin. To distinguish this functionality from that of the monomers and the monomer mixture, the symbol f is used. Since almost all coating resins are made using some triol or tetrol, one generally uses a number average functionality $\bar{f}_n$:

$$\bar{f}_n = \frac{\text{number of functional groups in a sample}}{\text{number of molecules in the sample}}$$

The value of $\bar{f}_n$ can be calculated from $\bar{M}_n$ and the number of functional groups per sample weight obtained by analysis.

Esterification of a carboxylic acid with an alcohol is acid catalyzed. In the absence of a strong acid catalyst, the rate r is approximately third order in reactants: with one carboxyl group reacting with the alcohol and a second catalyzing the reaction. Since water is generally removed rapidly from the reaction mixture, it is reasonable to use Eq. 2.8, which disregards the reverse reaction.

$$r = k[\text{RCOOH}]^2[\text{R}'\text{OH}] \tag{2.8}$$

Because of the second order dependence on acid concentration, the rate decreases precipitously as reaction proceeds. For example, polyesterification of equal moles

TABLE 2.2. Polyester Formulation

Component	Moles	Equivalents
Adipic acid	0.9	1.8
Phthalic anhydride	0.9	1.8
Neopentyl glycol	1.0	2.0
Glycerol	1.0	3.0
	3.8	8.6

$F = 8.6/3.8 = 1.89$

of diethylene glycol with adipic acid at 160°C without a catalyst is 60% complete in 1 hour but requires 27 hours to reach 94.5% conversion and would require years to reach 99.8% conversion [35]. The reaction is catalyzed by strong acids. In many cases, conventional strong acids cause side reactions and discoloration, so the most appropriate catalysts are organotin compounds such as monobutyltin dioxide, or titanate esters. It has been shown that both the organotin compound and carboxylic acid act as catalysts [36].

The kinetics of ideal step-growth polyesterification for difunctional reactants can be analyzed in terms of p, the fractional extent of reaction; n_p, the number fraction of differing degrees of polymerization; P_n, the degree of polymerization; and w_p, the weight fraction of molecules [37]. As p increases, the degree of polymerization builds up slowly at first—at

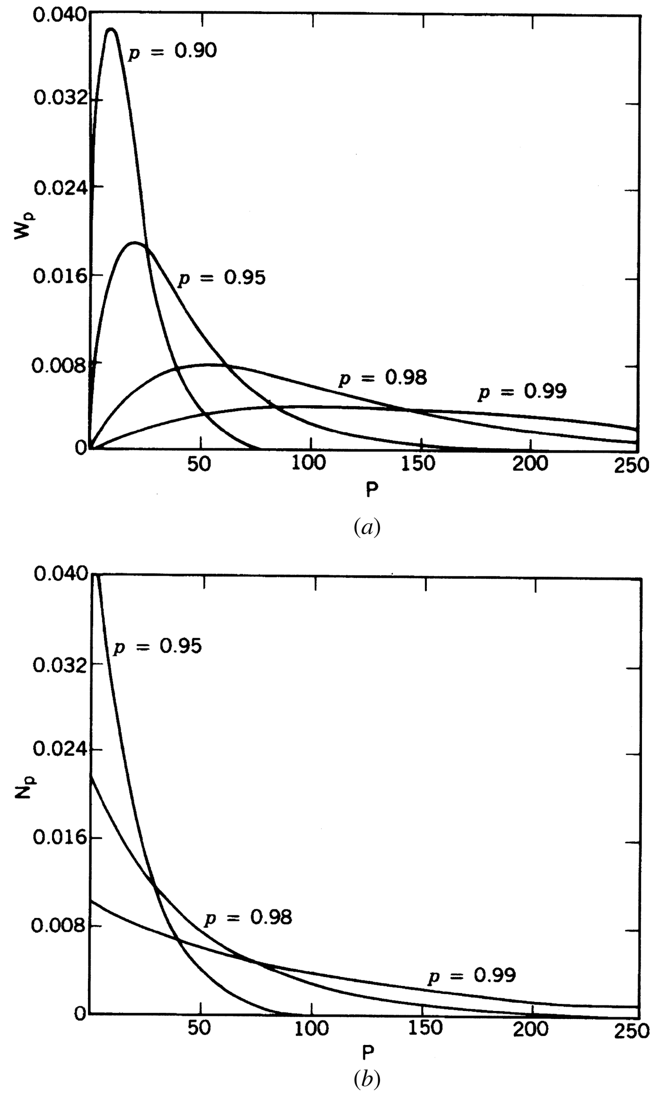


Figure 2.4. *(a) Weight fraction distribution* w_P *of molecules in a linear step-growth polymer for several extents of reaction* p*; (b) number, or mole fraction, distribution* n_P*. (From Ref. [37], with permission.)*

$p = 0.5$ (corresponding to 50% conversion), $\bar{P}_n$ is only 2, $\bar{P}_n$ is only 10 at $p = 0.9$, and $p = 0.998$ is required to reach a $\bar{P}_n$ of 500. Thus, with difunctional monomers, high MW can only be attained when the COOH/OH mole ratio is 1.00 and when esterification is driven beyond $p = 0.99$. This is difficult because of the decreasing reaction rate at high values of p. Note that as shown in Figure 2.4(*a*), the number of unreacted monomer molecules remains higher than that of any other single species in the reaction mixture, no matter how high p becomes. As shown in Figure 2.4(*b*), $\bar{P}_n$, the peak of the P distribution curve, reaches substantial values only at high p values. In the case of high MW linear polymers, under ideal conditions, the $\bar{M}_w/\bar{M}_n$ obtained in step-growth polymerizations is 2.

2.3. FILM FORMATION

Most coatings are liquids with a viscosity appropriate for the application method, generally in the range 0.05 to 1 Pa•s at high shear rates. After application, the liquid is converted to a *dry* (i.e., solid) *film*. In powder coatings, the powder is liquefied after application and then converted to a solid film. The chemical and physical changes that occur in this process are called *film formation*, a process that is critical to the ultimate appearance and performance of the coating.

If the applied coating were crystalline, there would be no difficulty in defining a solid film. The film would be solid if the temperature were below its freezing point; however, binders of coatings are almost always amorphous, with no melting point and no sharp demarcation between a liquid and a solid. A useful definition of a solid film is that it does not flow significantly under the pressures to which it is subjected during use. Thus, one can define whether a coating is a solid under a set of conditions by stating the minimum viscosity required such that flow does not exceed a specified extent under specified pressure and time. For example, it is reported that a film is *dry-to-touch* if its viscosity is greater than about 10^3 Pa•s [38]. However, if the definition of a solid is that the film resists *blocking*—that is, sticking together when two coated surfaces are put against each other for 2 seconds under a pressure of 1.4 kg cm^{-2} (20 psi)—the viscosity has to be greater than about 10^7 Pa•s.

For thermoplastic binders, we can use this information to predict polymer structures that could meet such tests. Using a simplified form (Eq. 2.9; in the equation, T is in Kelvin) of the Williams–Landel–Ferry (WLF) equation (Section 3.4), using "universal constants" and assuming that the viscosity at T_g is 10^{12} Pa•s, one can estimate the T_g of a binder required so that a film does not flow under some set of circumstances:

$$\ln \eta = 27.6 - \frac{40.2(T - T_g)}{51.6 + (T - T_g)} \tag{2.9}$$

Using Eq. 2.9, we can estimate the appropriate $(T - T_g)$ value required for a film to be dry-to-touch, that is, to have a viscosity of 10^3 Pa•s. The $T - T_g$ value calculated is 54°C, which corresponds to a T_g of -29°C for a film to be dry-to-touch at a temperature T of 25°C. The T_g calculated for block resistance (at 1.4 kg cm^{-2} for 2 s at 25°C, i.e., for a viscosity of 10^7 Pa•s) is 4°C. Because there is considerable variation in the WLF universal constants, these T_g values are not exact, but they can serve as a formulation guide. Since we have a reasonable idea of the relationships between structure and T_g (Section 2.1.2), we can approximate the requirements to make a binder with the viscosity necessary to pass a particular test. If the coating has to pass a test at a temperature higher than 25°C, the T_g of the binder must be higher, since the free volume dependence is on $T - T_g$. If the pressure to which the film is to be subjected is higher or the time under pressure is to be longer, the T_g must be higher.

2.3.1. Film Formation by Solvent Evaporation from Solutions of Thermoplastic Binders

Films can be formed in a variety of ways. One of the simplest is to dissolve a polymer in solvent(s) at a concentration needed for application requirements, apply the coating, and allow the solvent to evaporate. Let us illustrate with a copolymer of vinyl chloride, vinyl acetate, and a hydroxyl-functional vinyl monomer with an $\bar{M}_n$ of 23,000 that is reported to give coatings with good mechanical properties without cross-linking [39]. The T_g of the copolymer is reported to be 79°C. A solution in methyl ethyl ketone (MEK) with a viscosity of 0.1 Pa•s required for spray application would have about 19 NVW (nonvolatile weight, i.e., wt% solids) and about 12 NVV [nonvolatile volume, i.e., volume percent (vol%) solids]. MEK has a high vapor pressure at room temperature and evaporates rapidly from a thin layer. In fact, a sizable fraction of the MEK evaporates from the atomized spray droplets between the time they leave the spray gun and the time they reach the substrate. As solvent evaporates from a film, viscosity increases, and the film will be dry-to-touch soon after application. Also, in a short time, the coating will not block under the conditions mentioned previously. Nevertheless, if the film is formed at 25°C, the "dry" film contains several percent of retained solvent. Why?

In the first stage of solvent evaporation from a film, the rate of evaporation is essentially independent of the presence of polymer. The evaporation rate depends on the vapor pressure at the temperature, the surface area/volume ratio, and the rate of air flow over the surface. However, as solvent evaporates, viscosity increases, T_g increases, free volume decreases, and the rate of loss of solvent becomes dependent on how rapidly solvent molecules can diffuse to the surface of a film so that they can evaporate. The solvent molecules must jump from free volume hole to free volume hole to reach the surface. As solvent loss continues, T_g increases, free volume decreases further, and solvent loss slows. If the film is formed at 25°C from a solution of a polymer that, when solvent free, has a T_g greater than 25°C (in this example, it is 79°C), the film retains considerable solvent even though it is a hard "dry" film. Solvent slowly leaves such a film, but it has been shown experimentally that 2 to 3% of solvent remains after several years at ambient temperature. To assure nearly complete removal of solvent in a reasonable period of time requires baking at a temperature significantly above the T_g of the solvent free polymer. Solvent loss from films is discussed in more detail in Section 18.3.4.

2.3.2. Film Formation from Solutions of Thermosetting Resins

A drawback of solution thermoplastic polymer–based coatings is that the MWs required for film properties require high solvent levels (on the order of 80 to 90 vol%) to achieve the viscosity for application. Less solvent is needed for a coating based on solutions of lower-MW thermosetting resins. After application, the solvent evaporates, and chemical reactions cause polymerization and cross-linking to impart good film properties. Many combinations of chemical reactions are used in thermosetting coatings, as discussed in

Chapters 8 to 17. A critical aspect of the design of a coating is the selection of components that give required mechanical properties (Chapter 4). In this section we cover only the general principles of cross-linking reactions.

A problem with all thermosetting systems is the relationship between coating stability during storage and the time and temperature required to cure a film after application. Generally, it is desirable to be able to store a coating for many months, or even several years, without a significant increase in viscosity resulting from reaction during the storage period. On the other hand, after application, one would like to have the cross-linking reaction proceed rapidly at the lowest possible temperature.

As formulations are shifted to higher solids to reduce VOC emissions, there are higher concentrations of functional groups and there is greater difficulty in formulating storage stable coatings. The problem results not only from the presence of less solvent, but also from the lower MWs and lower equivalent weights needed to achieve a cross-linked film of acceptable cross-link density. Both factors increase the concentration of functional groups in a stored coating. Concentration of reactants in a film increases after application and evaporation of solvent, which increases reaction rates, but since the MW is lower, more reactions must occur to achieve the desired cross-linked film properties.

What controls the rate of a reaction? We can consider this question broadly as a reaction between two groups, represented by the symbols A and B, that react to form a cross-link A–B:

$$\mathrm{A + B \longrightarrow A - B}$$

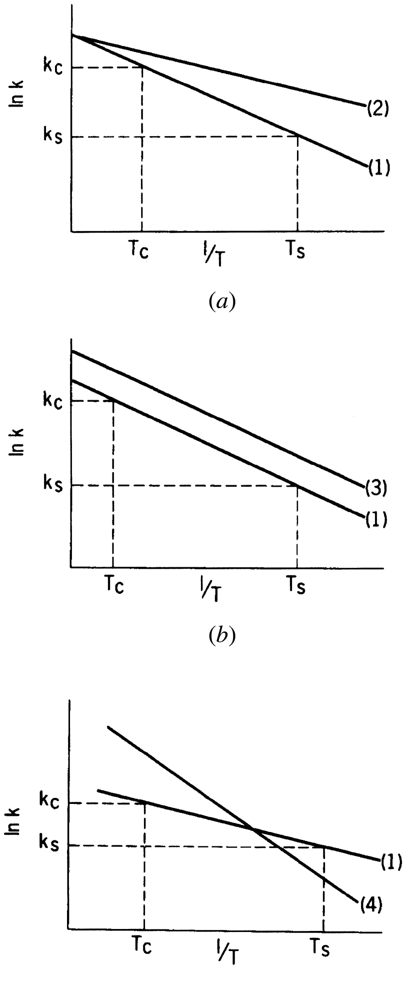
In the simplest cases, one can express the rate of reaction r of A and B as where k is the rate constant for the reaction between A and B by Eq. 2.10 at a specified temperature, and [A] and [B] represent the concentration of the functional groups in terms of equivalents per liter. The rate constant is the reaction rate when [A] × [B] equals 1 equiv.^{2} L^{-2}.

$$r = k[A][B] \tag{2.10}$$

To minimize the temperature required for curing while maintaining adequate storage stability, it is desirable to select cross-linking reactions for which the rate depends strongly on temperature. This dependence is reflected in the rate equation by the dependence of k on temperature. It is commonly taught in introductory organic chemistry classes that rate constants double with each 10°C rise in temperature. That generalization is true for only a limited number of reactions within a narrow temperature range near room temperature. A better estimate, but still an estimate, of the temperature dependence of k is given by the *empirical Arrhenius equation* where A is the *preexponential term*, E_a is the thermal coefficient of reactivity (commonly labeled *activation energy*), R is the gas constant, and T is temperature (in Kelvin).

$$\ln k = \ln A - \frac{E_a}{RT} \tag{2.11}$$

Reaction rate data that fit the equation give straight lines when ln k is plotted against $1/T$, as illustrated in Figure 2.5. As seen in plot (*a*) of competing reactions (1) and (2), where $A(1) = A(2)$ and $E_a(1) > E_a(2)$, the temperature dependence of rate constants



(*a*)

(*b*)

(*c*)

Figure 2.5. *Arrhenius plots for competing reactions: (a)* A*(1) =* A*(2),* $E_a(1) > E_a(2)$*; (b)* A*(3) >* A*(1),* $E_a(1) = E_a(3)$*; (c)* A*(4) >* A*(1),* $E_a(4) > E_a(1)$*. (From Ref. [40], with permission.)*

increases with increasing values of E_a. However, the rate of reaction (2) is slower than that of reaction (1) at all temperatures. This effect can be counteracted by selecting a reaction with a higher A value, as shown in plot (*b*), where $A(3) > A(1)$ and E_a for the two reactions is equal. If both A and E_a are sufficiently greater for one reaction than for another, the rate constant at storage temperature could be smaller while the rate constant at a higher temperature could be larger, as shown schematically in plot (*c*) [40].

Term A is controlled predominantly by entropic factors, or more specifically, by changes in randomness or order, as the reaction proceeds to the activated complex in the transition state. Three important factors are: (1) unimolecular reactions tend to exhibit larger A values than those with a higher molecular order; (2) ring opening reactions tend to have high A values; and (3) reactions in which reactants become less polar exhibit larger A values. The importance of these factors (in particular, factor 3) depends on the reaction medium; accordingly, solvent selection can have a significant effect on storage stability.

Although unimolecular reactions are desirable for high *A* values, cross-linking reactions are necessarily bimolecular. A way around this problem is to use a *blocked* reactant BX that thermally releases a reactant B by a unimolecular reaction—most desirably, with ring opening and decreasing polarity—followed by cross-linking between A and B:

$$\mathrm{BX} \rightleftharpoons \mathrm{B} + \mathrm{X}$$

$$\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{A} - \mathrm{B}$$

Another approach is to use a blocked catalyst CX, where C catalyzes the cross-linking of A and B:

$$\mathrm{CX} \rightleftharpoons \mathrm{C} + \mathrm{X}$$

$$\mathrm{A} + \mathrm{B} \xrightarrow{\mathrm{C}} \mathrm{A} - \mathrm{B}$$

An important consideration is that the cross-linking reaction, which follows unblocking, should be faster than the reverse reaction, which regenerates the blocked reactant or catalyst. Although one often encounters "threshold" or "unblocking" temperatures for reactions in the literature, such minimum reaction temperatures do not exist in the kinetics of reactions. Reactions proceed at some rate at any temperature. Threshold or unblocking temperatures are actually the temperatures at which some observable extent of reaction has occurred within a specified time interval.

These concepts are helpful for understanding the differences we see between storage stabilities, but another reason for understanding these kinetic considerations is that they can be used to predict whether any chemical reaction will ever be found to meet some combination of stability and cure schedule that might be desired for a coating. Pappas and Hill have carried out calculations to permit such predictions [25,41]. They made a set of reasonable assumptions about reactive group concentrations during storage and in the applied film, permissible degrees of reaction during storage, and required extents of reaction during curing. Using these assumptions, they calculated the ratio of rate constants needed to permit any time of storage with any time of curing. In turn, this allowed calculation of E_a and *A* values as a function of any combination of storage and curing temperatures. Kinetic parameters calculated for unimolecular blocked reactant systems that proceed 5% over a six-month period at 30°C (storage temperature) and 90% in 10 minutes at various curing temperatures are listed in Table 2.3.

TABLE 2.3. Kinetic Parameters as a Function of Cure Temperature

T (°C)	A (s^{-1})	E_a ($\mathrm{kJ\ mol}^{-1}$)[a]
175	10^{10}	109
150	10^{12}	121
125	10^{17}	146
100	10^{24}	188

Source: Ref. [40].

[a] 1 kJ = 0.239 kcal.

Rate constants and kinetic parameters are independent of concentration for unimolecular reactions but not for bimolecular reactions. Kinetic parameters calculated for bimolecular (i.e., second order) reactions using concentrations corresponding to high-solids coatings were of similar magnitude to those for unimolecular reactions. Although the values in Table 2.3 represent order of magnitude calculation, they provide useful guidelines for avoiding development projects aimed at impossible goals and provide insights for design of thermosetting coatings. Kinetic parameters are known for many chemical reactions. As a point of reference, a reasonable upper limit of A values for unimolecular reactions is $10^{16}\ \mathrm{s}^{-1}$, which corresponds to an upper value for the frequency of simple vibrations. For bimolecular reactions, A values tend to be less than $10^{11}\ \mathrm{L\ mol^{-1}\ s^{-1}}$, an upper limit for the rate constant of diffusion, which must precede reaction. However, as shown in Table 2.3, a coating stable at 30°C would require an A value of $10^{24}\ \mathrm{s}^{-1}$ if it were to cure within 10 minutes at 100°C. No such reaction is known or even conceivable. Users would like to have package stable coatings that cure in a short time at 80°C, a convenient temperature for low pressure steam heat, but it is pointless to pursue this goal via kinetic control. That is not to say that it is impossible to make such a coating: It means that the problem must be solved by an approach other than kinetic control.

Storage life can be extended by refrigeration, but users are seldom willing to incur the expense. More reactive combinations can be used in *two package coatings*, in which one package contains a resin with one of the reactive groups and the second package contains the component with the other reactive group. Alternatively, the second package could contain a catalyst for the reaction. The packages are mixed shortly before use. Two package coatings are often called *2K coatings*, and single package coatings are sometimes called *1K coatings*. The K stands for the German word for *component*. Two package coatings are used on a large scale commercially, but they pose substantial extra problems for the user; mixing and cleaning equipment take extra time, material is usually wasted, they are generally more expensive, and there is a chance of error in mixing. Even 2K coatings have the analogous problem of *pot life*: that is, the length of time after the two packages are mixed that the viscosity stays low enough for application. Pappas and Hill have made similar calculations of A and E_a values for the shorter times involved [41].

There are several approaches to increasing package stability while permitting cure at ambient or moderately elevated temperature. One or more of these approaches are included in the discussions of many of the cross-linking reactions that are covered in later chapters. The following list gives some of the approaches to solving this "impossible" problem:

1. Use of a radiation-activated cross-linking reaction instead of a thermally activated reaction.
2. Use of a cross-linking reaction requiring an atmospheric component as a catalyst or reactant; reactions involving oxygen or water vapor in the air are examples. The same principle is involved in passing a coated article through a chamber containing a catalyst vapor.
3. Use of a volatile inhibitor that works when the coating is stored in a closed container but volatilizes after application as a thin film, permitting the reaction to proceed. Examples include use of a volatile antioxidant in a coating that dries by oxidation, and use of oxygen as an inhibitor in a composition that cures anaerobically.

4. Use of a cross-linking reaction that is a reversible condensation reaction involving loss of a volatile reaction product; some of the monofunctional volatile reactant can be used as a solvent in the coating. The equilibrium of the reaction favors the non-cross-linked side during storage but shifts to the cross-linked side after application, when the solvent evaporates. A similar approach can be used with blocked reactants and catalysts in which the blocking group is volatile.

5. Use of an encapsulated reactant or catalyst, whereby the capsules are ruptured during application. Encapsulation has been useful in adhesives but has not been very useful in coatings because residual capsule shells interfere with appearance and/or performance.

6. Use of a reactant that undergoes a phase change. Although there are no threshold temperatures for kinetic reactions, phase changes can occur over narrow temperature ranges. A crystalline blocked reactant or catalyst, insoluble in the vehicle, could give an indefinitely stable coating; heating above the melting point permits the unblocking reaction to occur, releasing a soluble reactant or catalyst. Over a somewhat wider temperature range, the same idea can be used for an amorphous blocked reactant, having a T_g about 50°C above the storage temperature and perhaps 30°C below the desired cure temperature.

Another consideration in selecting components for thermosetting coatings is the potential effect of the availability of free volume on reaction rates and reaction completion. For reactions to occur, the reacting groups must diffuse into a reaction volume to form an activated complex that can then form a stable bond. If the diffusion rate is greater than the reaction rate, the reaction will be kinetically controlled. If the diffusion rate is slow compared to the kinetic reaction rate, the rate of the reaction will be mobility controlled. The major factor controlling the diffusion rate is the availability of free volume. If the reaction is occurring at a temperature well in excess of T_g, the free volume is large and the rate of reaction is controlled by concentrations and kinetic parameters. If, however, the temperature is well below T_g, the free volume is so limited that the polymer chain motions needed to bring unreacted groups close together are very slow, and reaction virtually ceases. At intermediate temperatures, the reaction can proceed, but the reaction rate is controlled by the rate of diffusion—that is, by the mobility of the reactants.

Since cross-linking starts with low MW components, T_g increases as the reaction proceeds. If the reaction temperature is well above the T_g of the fully reacted polymer, there will be no mobility effect on the reaction rate. However, if, as is often the case in ambient cure coatings, the initial T_g is below the ambient temperature and the T_g of the fully reacted polymer is above the ambient temperature, the reaction rate will become mobility controlled as cross-linking proceeds. As further reaction occurs, cross-linking may essentially stop before reaching completion. As T_g increases toward the temperature at which the reaction is occurring, reactions become slower. When T_g equals T, reactions become very slow, and vitrification (glass formation) is said to occur. Unless the experiment is continued for a relatively long time, the reactions have been said to cease [42]. However, with extended reaction times, it can be seen that reactions continue slowly. One paper [43] reports that reaction rate constants drop by about three orders of magnitude when T_g equals T, but that the reaction continues at a slow rate until T_g increases to

$T + 50°C$ [43]. It is interesting to consider the similarity of this value to the universal B constant of 51.6 in the WLF equation (Eq. 2.9). $T_g - B$ is the temperature at which viscosity goes to infinity and free volume theoretically approaches zero, corresponding to a T_g of $T + B$. The effect of variables on mobility control of reaction rates has been studied by Dusek and Havlicek [44]. In the reaction of bisphenol A diglycidyl ether and 1,3-propanediamine, they determined the effects of temperature, polymer–solvent interaction, and solvent volatility on reaction rates and extent of reaction. They also reviewed the theories involved.

It seems reasonable for a formulator to assume that cross-linking reactions begin to slow as T_g increases to about 10°C below the curing temperature and get progressively slower until T_g is about 50°C above the curing temperature, where reaction essentially ceases. The slow rates of reaction mean that properties of many ambient cure coatings can change substantially for several weeks or even months. Caution is required, since T_g values are dependent on the method of determination and the rate of heating used. For this purpose, T_g values obtained at very slow rates of heating and at low rates of application of stress are most appropriate. It has been pointed out that if reactions are very fast, equilibrium T_g may not be reached [44]. Another factor that may affect the development of mobility control is the size of the diffusing reactants. Small molecules may diffuse more readily to reaction sites than functional groups on a polymer chain. Water plasticizes coatings such as polyurethanes and epoxy–amines, lowering their T_g.

If the initial reaction temperature is well below the T_g of the solvent-free coating, it is possible that little or no reaction can occur after solvent evaporation and that a "dry" film forms merely due to solvent evaporation, without much cross-linking. The result is a weak, brittle film. One must be careful when defining what is meant by a dry film, especially when dealing with ambient temperature cure coatings. One consideration is whether the film is dry-to-handle. This stage could be reached with little cross-linking if the T_g of the solvent free binder is high enough. Another consideration is whether some required extent of cross-linking has occurred. This must be tested by some method other than hardness, most easily by determining resistance to dissolution or by the extent of solvent swelling (Section 4.2).

Mobility control is less likely to be encountered in baking coatings because in most cases, the final T_g of the film is below the baking temperature. Furthermore, the T_g is usually well above ambient temperatures, so even if there are some unreacted groups, reactions do not continue after cooling to ambient temperature. In moderate temperature cure powder coatings, mobility control of reaction can be a limitation, since the initial T_g of the reactants has to be above 50°C so that the powder will not sinter during storage (Section 28.3). To achieve a high extent of reaction, the baking temperature must be above the T_g of the fully reacted coating. Gilham and co-workers have studied factors influencing reaction rates in high T_g epoxy–amine systems; Gilham's work is summarized in Ref. [45], with a focus on its applicability to powder coatings.

2.3.3. Film Formation by Coalescence of Polymer Particles

In contrast to the processes of film formation from solutions of thermoplastic or thermosetting polymers, dispersions of insoluble polymer particles form films by coalescence (fusion) of particles. After application and loss of volatile components, the particles form a continuous film. The largest volume of coatings having such binders are latexes, which are a dispersion of high MW polymer particles in water (Chapter 9).

For a given latex, the lowest temperature at which coalescence occurs sufficiently to form a continuous film is called its *minimum film formation temperature* (MFFT); some authors call it the *minimum filming temperature* (MFT). MFFT is measured by placing samples on a heated metal bar with a temperature gradient. A major factor controlling MFFT is the T_g of the polymer in the particles. The T_g of poly(methyl methacrylate) (PMMA) is about 105°C, and one cannot form a useful film from a PMMA latex at room temperature; instead, one gets a layer of material that powders easily. Many latexes are designed to have layers of material with different T_g values within each particle (Sections 9.1.3 and 9.2), making it difficult to relate MFFT directly to T_g.

The mechanism of film formation from latexes has been studied extensively, but is still not fully understood. Film formation is divided into three overlapping steps:

1. *Evaporation* of water and water-soluble solvents that leads to a close packed layer of latex particles
2. *Deformation* of the particles from their spherical shape that leads to a more or less continuous but weak film
3. C*oalescence* a relatively slow process in which the polymer molecules *interdiffuse* across the particle boundaries and entangle, strengthening the film

As water evaporates, the particles come closer together, becoming close packed. The internal phase volume of a latex film is highly dependent on particle size distribution: The broader the distribution, the higher the internal phase volume.

As the particles become close packed, the polymer particles are deformed. It has been proposed that as the particles approach each other, the spaces between them act like the equivalent of a capillary, and capillary forces apply pressure to the close packed particles, leading to deformation. It is estimated that such forces may generate as much as 3.5 MPa (5000 psi) where latex particles touch [46].

T_g of the latex particles is an important factor controlling the rates of particle deformation. Surfactant stabilizers can increase water absorption and also act as plasticizers for the polymer [47,48]. In general, higher surfactant content further reduces MFFT. Structure of the surfactant also affects MFFT; for example, nonyl phenol ethoxylates with fewer than 9 ethoxylate units reduced MFFT further than those with 20 or 40 units. Lower T_g particles have a lower modulus—that is, they are softer (Section 4.2) and hence are more easily deformed. For latex coatings, which are baked, the T_g is commonly above ambient temperature, and coalescence does not fully occur prior to baking. When water is evaporated, the latex particles become a layer of close packed spheres. Sulfate groups from the polymerization initiator can form H-bonds between spheres, thereby raising the T_g. The MFFT of latex particles can be affected by water, which can act as a plasticizer [48]. Reduction of T_g is largest with hydrophilic polymers. It has been shown that MFFT can be reduced by as much as 5°C by forming the film in a humid atmosphere [49].

Deformation of the close packed particles increases the area of contact between particles and promotes coalescence. For coalescence to occur it is necessary to overcome the stabilizing repulsion. Although capillary forces may be a factor, Croll points out that the time span during which the forces are high is very short [46]. His data on drying rates support a proposal of Kendall and Padget that a major driving force for coalescence is surface free energy reduction [47]. The surface area of a coalesced film is only a small fraction of the surface area of the particles, so the driving force resulting from reduction in surface area must be large. Other workers strongly adhere to the position that capillary pressure is the dominant driving stress for film formation [50]. Probably both forces are involved, with capillary pressure an important factor in deformation and surface free energy reduction for coalescence [51,52].

Consistent with the differences in surface area, small particle size latexes form films at somewhat lower temperatures than larger particle size latexes [51]. However, it has been shown that this is not always the case [53]. With other latexes, larger size promotes coalescence. Still other work indicates that there is no effect of particle size on MFFT. Since broader distribution of particle size increases close packed volume fraction, it leads to more rapid film formation. Possibly, these different conclusions are caused not just by particle size, but also by particle size distribution and differences in the compositions of the latexes used. It is speculated that the larger proportion of surface active material in small particle size latexes may also play a role.

With the large number of variables involved in coalescence, one would expect interactions among the different variables. The rate of interdiffusion is driven primarily by $T - T_g$. Adequate interdiffusion will occur only when the T_g of the particles is lower than the temperature at which the film is to be formed. Theoretical and experimental studies of coalescence suggest that it is only necessary for the molecules to interdiffuse a distance comparable to the radius of gyration of one molecule to develop maximum film strength [54]. This distance is considerably less than the diameter of a typical latex particle. The rate of interdiffusion is directly related to T_g and is therefore controlled by free-volume availability [54]. The major factor affecting free volume is the difference between the temperature of film formation and the T_g of the particles. Presumably, the T_g of the material near the surface of the original particle is most important. As a general rule, coalescence will not occur unless the temperature is at least slightly higher than T_g. Latexes for paints are generally copolymers of acrylic and vinyl esters that have a T_g well below room temperature so that they can coalesce readily within the usual range of application temperatures.

Most studies of the mechanism of film formation use carefully prepared uniform films that are dried in a laboratory under conditions of intermediate humidity and little air flow over the surface. Real-life conditions are quite different; the latex has been formulated into a paint with pigments and many additives, and dried under a wide variety of conditions, In many cases, film thickness is not uniform. A further complication is that water evaporation is seldom uniform across the entire area of a film. Instead, a drying front starts, perhaps at a thin spot, and spreads laterally across the panel [55]. Both water and polymer particles move sideways near the drying front, and smaller particles appear less likely to give uniform films. The practical implications of this finding are only partly understood. If exterior house paint is applied on a hot windy day with low humidity, film formation is very poor.

Plasticizers, which dissolve in the polymer, can be added to lower the T_g and MFFT of the formulation. Since nonvolatile plasticizers permanently reduce T_g, most latex paints contain volatile plasticizers, which are called *coalescing solvents*, although they accelerate deformation as well as coalescence. A coalescing solvent must be soluble in the polymer and have a low, but appreciable evaporation rate. It acts as a plasticizer to lower the MFFT, but after the film has formed, it diffuses to the surface of the film and evaporates. Since free volume in the film is relatively small, the rate of loss of the last of the coalescing solvent is very slow. Although the films feel dry in a short time, they will still block for days, or even weeks, after application. Effects of coalescing solvents on film formation have been studied quantitatively using fluorescence decay measurements to follow the extent of polymer diffusion in films as they coalesce [56]. The efficiency of coalescing solvents varies over a wide range; an example of a relatively efficient solvent is the acetate ester of propylene glycol monobutyl ether (P*n*BA) [57]. The rate of evaporation from films also varies; for example, dipropylene glycol dimethyl ether leaves a film more rapidly than does P*n*BA, but somewhat more is required for film formation [57]. A widely used coalescing solvent is Texanol, the isobutyric ester of 2,2,4-trimethylpentane-1,3-diol.

Although films form rapidly from latexes when the temperature is above MFFT, complete coalescence is a relatively slow process; in many cases, the film probably never equilibrates to become completely uniform. The rate of equilibration is affected by $T - T_g$. From the standpoint of rapid coalescence, it is desirable to have a latex with a T_g well below the temperature at which the film is to be formed. There are review papers that discuss factors affecting development of the cohesive strength of films from latex particles [54,58]. The extent of coalescence has been studied using small-angle neutron scattering, direct energy transfer of particles labeled with fluorescent dyes, and scanning probe microscopy [59,60].

Usually, architectural paints are formulated so that film formation occurs at temperatures as low as 2°C. Film formation at such a low temperature requires a low-T_g latex. However, as discussed in the introductory paragraphs of Section 2.3, $T - T_g$ also affects whether the film obtained will be solid. It was estimated that for a film to withstand the relatively mild blocking test described, $T - T_g$ would have to be on the order of 21°C. If the film is to be exposed to the blocking test when the temperature is 50°C (not an unreasonable expectation during direct exposure to summer sun), the T_g should be about 29°C or higher. Thus, the paint formulator is faced with a difficult challenge to design a system that can form a film when applied at 2°C, yet resist blocking at 50°C.

Coalescing solvents help solve this problem, but environmental regulations are limiting permissible emissions of volatile organic compounds (VOC). A second approach is to design latex particles so that there is a gradient of T_g from a relatively high T_g in the center of the particles to a relatively low T_g at the outer periphery [61] (Sections 9.1.3 and 9.2). The low T_g of the outer shell permits film formation at low temperature. Over time, the T_g of the coalesced film approaches the average T_g of the total polymer. This higher average T_g reduces the probability of blocking. Relatively small amounts of coalescing solvents can be sufficient with such a latex. A third approach is to use blends of high and low T_g latexes, which can reduce MFFT without the presence of coalescing solvents [62]. It has been proposed that the films contain particles of high T_g polymer dispersed in a matrix of lower T_g polymer, reinforcing the matrix, increasing its modulus, and hence, decreasing blocking. There must be an adequate ratio of the soft polymer to the hard polymer so that the soft polymer forms a continuous film enclosing the hard particles. These studies were done without pigment; it would be interesting to compare the results with films made with a low T_g polymer with an equal volume content of pigment, which can also reinforce a film. A fourth approach involves use of core–shell latexes [63] (Section 9.1.3).

Polyurethane dispersions (PUDs) have low MFFT values in relation to dry film T_g owing to the plasticizing effect of hydrogen bonding with water. Accordingly, coalescing solvents, which are generally required for film formation of latexes at low temperatures, are not needed with PUDs. When PUDs are used with high T_g acrylics, MFFT is reduced without reducing hardness (Section 12.7.2).

Although the majority of latexes are thermoplastic polymer latexes, there are applications for thermosetting latexes as well. An excellent and extensive review has been published [64]. In many cases, two package coatings are required, but they are useful only for industrial applications; a few stable systems have been developed that can be used for architectural paints. (See Section 9.4 for further discussion and examples.) Cross-linked films have better mechanical properties and increased resistance to solvents. In general, a lower T_g latex can be used in coatings, which permits coalescence without addition of a coalescing solvent and/or at lower film formation temperatures. Film properties depend on the relative rate of interdiffusion between polymer particles and the rate of cross-linking. If the rate of cross-linking is fast compared to the rate of diffusion, cross-linking within particles will occur and interfere with good film formation. If the rate of cross-linking is slow, achievement of desirable film properties may take excessive time. A balance between the two is needed. In some cases the functional groups on a latex particle are on the particle surface, and an external cross-linker serves to cross-link the particles together. In other cases the functional groups are on the same polymer and interdiffusion is required to bind the particles together.

Winnik [65] has reviewed the literature on thermosetting latexes and experimental results related to the importance of the rate of interdiffusion and cross-linking in films of thermosetting latexes. To develop good properties, significant interdiffusion must occur before extensive cross-linking. The rate of interdiffusion is controlled by $T - T_g$ and the chain length of the latex. Thus, thermosetting latexes are designed with lower MW, which both reduces T_g and shortens chain length. Straight chains diffuse more rapidly than branched chains.

Most studies of the mechanism of film formation have been done with latexes, not with fully formulated paints. It is to be expected that other components of paints, such as pigments, pigment dispersing agents, and water soluble polymers used as thickening agents, among others, affect MFFT, rate of film formation, and blocking resistance. (See Chapter 31 for further discussion of latex paints.)

Other types of coatings that involve coalescence of particles are discussed in later chapters, including aqueous polyurethane dispersions, organosols, water-reducible resins, and powders.

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3

Flow

Rheology is the science of flow and deformation. In this chapter we deal only with the flow of relatively liquid materials; deformation of relatively solid materials are discussed in Chapter 4. Flow properties of coatings are critical for the proper application and appearance of films. For example, in brush application of a paint, the flow properties govern settling of pigment during storage, how much paint is picked up on the brush, film thickness applied, leveling of the applied film, and control of sagging of the film. Depending on how stress is applied to a fluid, there are several types of flow. Of major importance in coatings is flow under shear stress. We consider shear flow first and then, more briefly, other types of flow.

3.1. SHEAR FLOW

To understand and define *shear flow*, consider the model shown in Figure 3.1. The lower plate is stationary, and the upper parallel plate is movable. The plates are separated by a layer of liquid of thickness x. Force F is applied to the top movable plate of area A, so the plate slides sidewise with velocity v. The model assumes that there is no slip at the interfaces and that there is no fluid inertia. When the plate moves, the liquid near the top moves with a velocity approaching that of the movable plate, and the velocity of the liquid near the bottom approaches zero. The velocity gradient dv/dx for any section of the liquid is constant and, therefore, equals v/x. This ratio is defined as *shear rate* $\dot{\gamma}$. The units of shear rate are reciprocal seconds, s^{-1}.

$$\dot{\gamma} = \frac{dv}{dx} = \frac{v}{x}; \qquad \text{units: cm s}^{-1}/\text{cm} = \text{s}^{-1}$$

Organic Coatings: Science and Technology, Third Edition, by Zeno W. Wicks, Jr., Frank N. Jones, S. Peter Pappas, and Douglas A. Wicks

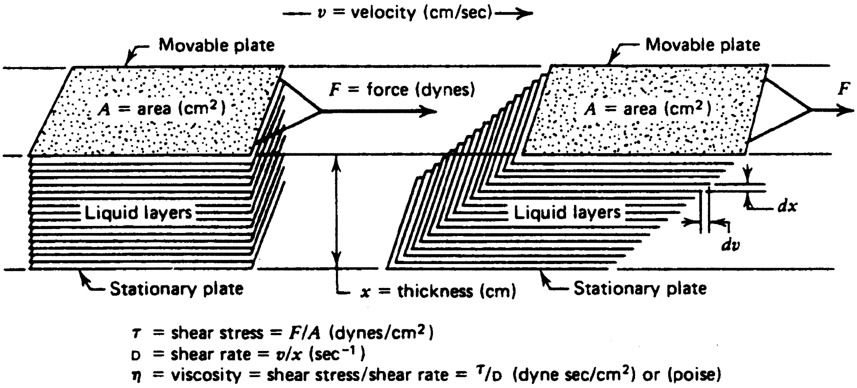

Figure 3.1. *Model of shear flow of an ideal liquid. (In current usage, the symbol for shear stress is σ and its units are Pa, the symbol for shear rate is $\dot{\gamma}$ and the units of η are Pa·s) (From Ref. [1], with permission.)*

Force F acting on top plate of area A results in *shear stress*, σ. The units of shear stress are pascal (Pa).

$$\sigma = \frac{F}{A}; \qquad \text{units: m} \cdot \text{kg} \cdot \text{s}^2\,\text{m}^{-2} = \text{N m}^{-2} = \text{Pa}$$

A liquid exerts a resistance to flow called *viscosity*, η, defined as the ratio of shear stress to shear rate. This type of viscosity is correctly called *simple shear viscosity*, but since it is the most widely encountered type of viscosity, it is usually just called *viscosity*. The separation of molecules in flow dissipates energy, primarily as heat. Thus, viscosity is the energy per unit volume dissipated to attain a unit velocity gradient. The units are pascal seconds (Pa•s). The older and still commonly used unit is the poise (P). One Pa•s equals 10 P, and 1 mPa•s equals 1 cP.

$$\eta = \frac{\sigma}{\dot{\gamma}}; \qquad \text{units: Pa/s}^{-1} = \text{Pa}\cdot\text{s}$$

When a liquid flows through a hole or a capillary, part of the energy is diverted into kinetic energy; then the resistance to shear flow is called *kinematic viscosity*, ν, with units of $\text{m}^2\,\text{s}^{-1}$, formerly stokes, where $1\ \text{m}^2\,\text{s}^{-1} = 10^4$ stokes. When the acceleration results from gravity, kinematic viscosity equals simple shear viscosity divided by the density, ρ, of the liquid:

$$\nu = \frac{\eta}{\rho}; \qquad \text{units: m}^2\,\text{s}^{-1}$$

3.2. TYPES OF SHEAR FLOW

When the ratio of shear stress to shear rate is constant, liquids are *Newtonian* and viscosity is independent of shear rate (or shear stress). A plot of shear rate as a function of shear stress is linear [Figure 3.2(*a*)], and the slope equals the inverse of viscosity. Such plots

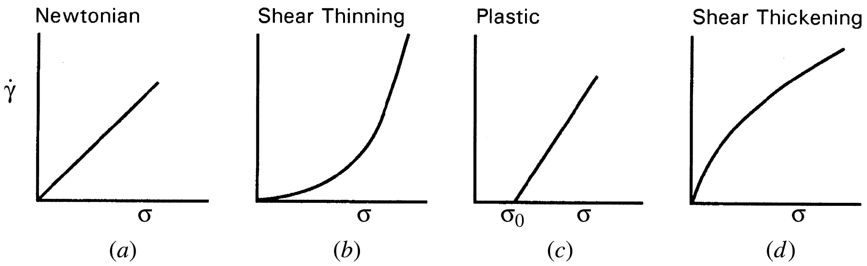

Figure 3.2. *Plots of flow of various types of liquids.*

also appear in the literature with axes opposite to those shown; then the slope is the viscosity. Newtonian flow is exhibited by liquids composed of miscible small molecules. Many solutions of oligomeric resins also approximate Newtonian flow.

Many liquids are non-Newtonian; that is, the ratio of shear stress to shear rate is not constant. One class of non-Newtonian liquids exhibits decreasing viscosity as shear rate (or shear stress) increases; these liquids are *shear thinning*. As stress is applied, the molecules line up parallel to the direction of flow, reducing the energy required to displace them further. In the case of liquids with a disperse phase, the particles line up as bead chains again reducing the energy required to displace them further. Shear thinning has been called *shear-induced order*. When the molecules or particles are all aligned in the direction of flow the viscosity is again independent of shear rate and the curve becomes linear [Figure 3.2(*b*)].

In some cases, no detectable flow occurs unless a minimum shear stress is exceeded. Such materials exhibit *plastic flow* and are sometimes called *Bingham bodies*. The minimum shear stress required is called the *yield value*, or *yield stress*, and is designated by the symbol σ_0.

$$\sigma - \sigma_0 = \eta_p \dot{\gamma}$$

A schematic flow diagram is shown in Figure 3.2(*c*). The yield value depends strongly on the rate at which stress is increased. The faster the rate of stress increase the higher the measured value that will be obtained. It is fairly common to extrapolate the linear part of the curve to the intercept with the shear stress axis and call the intercept a yield value.

Another class of liquids exhibits increasing viscosity as shear rate (or shear stress) increases. A schematic plot of such behavior is given in Figure 3.2(*d*). Such liquids are *shear thickening*. Shear thickening has been called *shear-induced disorder*. If shear thickening liquids also increase in volume under shear, they are called *dilatant fluids*. Dilatant fluids have dispersed phases that become less ordered and hence occupy more volume. Examples are pigment and resin dispersions in which the dispersed phase is sufficiently concentrated so that the particles approach being randomly close packed. If sufficient stress is applied for flow, microscopic voids are created, increasing the volume and increasing the energy necessary to induce flow. Thus, the viscosity increases. Another example is quicksand. See Ref. [2] for a discussion of factors affecting dilatant flow.

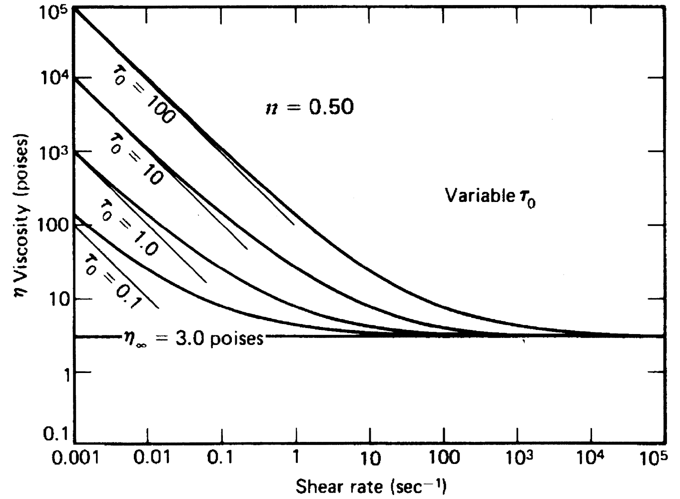

Figure 3.3. *Casson plot of viscosity as a function of shear rate, showing the dependence τ_0 with constant η and η_∞. (From Ref. [1], with permission.)*

The *Casson equation* linearizes the viscosity/shear rate data of shear thinning or thickening fluids:

The slope of the line is the yield stress, and extrapolation gives the viscosity at infinite shear rate η_∞.

$$\eta^n = \eta_\infty^n + \frac{\sigma_0^a}{\dot{\gamma}} \tag{3.1}$$

In many cases, the value of n is 0.5, and commonly, the Casson equation is shown with just the half-power relationship. In plots of log viscosity against shear rate, the degree of curvature is related to the value of σ_0. In Figure 3.3 the values of η and η_∞ are held constant to show the effect of changes in τ_0 on flow response [3]. For a Newtonian fluid, τ_0 equals zero and the plot is a straight line parallel to the shear rate axis.

Some fluids show time or shear history dependence of viscosity, as illustrated in Figure 3.4(*a*). The curves in the figure result from shear stress readings taken at successively higher shear rates to some upper limit (right-hand curve), followed immediately by shear stress readings taken at successively lower shear rates (left-hand curve). At any shear rate on the initial curve, the stress would decrease with time to an equilibrium value between the two curves; that is, the viscosity would decrease. On the other hand, if such a system had been exposed to a high rate of shear and then the shear rate decreased, the shear stress would increase to an equilibrium value as the measurement was continued; that is, the viscosity would increase with time. This behavior is called *thixotropic flow*. Thixotropic fluids are shear thinning fluids; their viscosity is also dependent on time and prior shear history. All thixotropic fluids are shear thinning fluids, but not all shear thinning systems are thixotropic. Unfortunately, the term *thixotropy* is often improperly used as a synonym for *shear thinning*.

Thixotropy usually results from reversible formation of a structure within a fluid; an example is association of dispersed particles held together by weak forces. Thixotropic structure is broken down by applying shear for a sufficient time, and the structure reforms over

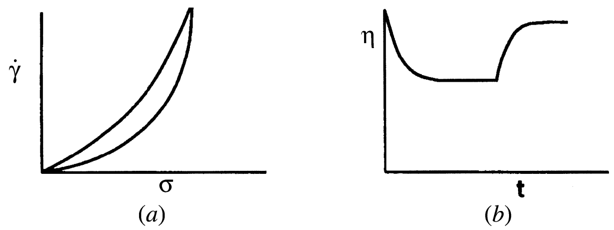

Figure 3.4. *Plots of systems exhibiting thixotropic flow. (a) The curve to the right is based on readings taken as the shear rate was being increased, and the curve to the left is based on readings taken as the shear rate was then being decreased. (b) The viscosity drops as shear continues, then increases as the shear rate is decreased.*

time when shear is stopped. Some thixotropic fluids undergo viscosity reduction to equilibrium values in short time periods and recover their viscosity rapidly when shearing is stopped; others change more slowly with time. In early work, areas within hysteresis loops were compared, as shown in Figure 3.4(*a*). However, the areas of such loops depend on the shear history, the peak shear, and the time intervals between successive measurements. Another way to represent the effect is to plot the viscosity at a series of shear rates as a function of time, as illustrated in Figure 3.4(*b*). The time for recovery after shifting from a high shear rate to a lower shear rate is a useful method for comparing different paints. In many coatings, thixotropic flow is desirable since it controls sagging, leveling, and pigment settling. It is desirable to formulate a coating so that the rate of recovery is rapid enough to avoid sagging but slow enough to permit leveling.

Additives to impart thixotropy to coatings have been developed. Clays treated with quaternary ammonium compounds, which form salts with the clay platelets and make them organophilic, are widely used in solventborne coatings. Attapulgite clay is used in both solventborne and waterborne coatings. The needles of this clay associate with each other, providing an increase in viscosity that reverses with agitation. In waterborne coatings, the clay also acts by absorbing water to make swollen particles that distort in shape with stress. Fine particle size silica has been used for many years. Castor oil derivatives and powdered polyethylene are effective thixotropic agents in baking coatings. Polyamides such as alkyds made with aminoalcohols are used as thixotropes especially in Europe. Basic calcium sulfonate derivatives are liquid thickeners that do not reduce gloss and retain their effectiveness when a coating is heated. They are particularly useful in moisture-curable urethane coatings since their basicity neutralizes the CO_2 produced by reaction with water hence reducing the bubbling problem as well as imparting thixotropy. In latex-paints, hydroxyethyl cellulose is widely used. Reference [4] provides a review of thixotropes and additives for modifying paint flow.

Rheologists frequently discuss the properties of such systems in terms of viscoelasticity; that is, their flow is a combination of viscous flow and elastic deformation. (Viscoelasticity is discussed in Section 4.2.) Such interpretations are valid and useful, but they have seldom been applied in the coatings industry. Time dependency can best be measured in terms of viscoelasticity (see Refs. [3] and [5] for such analyses). Increasing use of viscoelastic flow analysis can be expected in the future.

Another way to show the effect of shear on a thixotropic fluid is by a different type of Casson plot, as shown in Figure 3.5. The square root of the viscosity is plotted against the square root of the reciprocal of the shear rate; the steeper the slope, the greater the degree

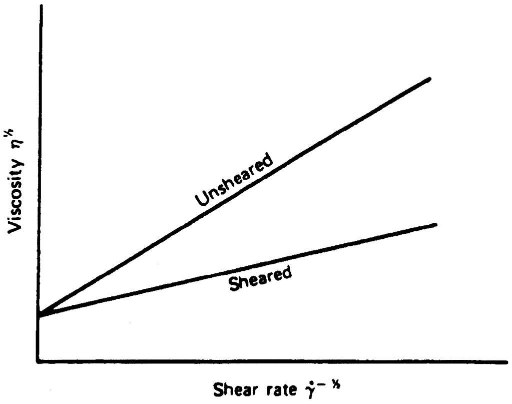

Figure 3.5. *Casson plots of a sheared and an unsheared thixotropic coating. The degree of divergence gives an estimate of the degree of thixotropy. (From Ref. [6], with permission.)*

of shear thinning. If the sample had been sheared until all of the thixotropic structure was broken down, and if the measurements could be made before any structure buildup occurred, the plot would be linear and parallel to the x axis. Although comparisons of the differences between the slopes of such lines give a qualitative expression of the extent of thixotropy, the slopes of the curves are dependent on prior shear history, the rate of acceleration of shear, and the length of time that the sample was exposed to the highest shear rate.

3.3. DETERMINATION OF SHEAR VISCOSITY

A variety of instruments is available to determine viscosity. They vary in cost, time required for measurements, operator skill required, susceptibility to abuse, precision, accuracy, and ability to measure shear rate variability or time dependency effects. Data obtained on the same sample with different instruments and by different operators with the same instruments can vary substantially, especially for shear thinning liquids at low rates of shear [7]. Some of the variation can result from lack of attention to details, especially temperature control and possible solvent loss; major errors can result from comparing samples that have had different shear histories.

Temperature must be carefully controlled. Since viscosity depends strongly on temperature, it is critical that the sample has reached a constant, known temperature before measurement. When high viscosity fluids are sheared at high shear rates, heat is evolved and the temperature of the sample increases unless the heat exchange efficiency of the viscometer is adequate. If viscosities are determined as both shear rate and temperature are increasing, it may be impossible to tell whether or not a fluid is shear thinning.

Viscometers can be divided into three broad classes: (1) those that permit quite accurate viscosity determinations, (2) those that permit determination of reasonable approximations of viscosity, and (3) those that provide flow data marginally related to viscosity. Space limitations restrict our discussion to major examples of each class. The general references at the end of this chapter are good sources of further information.

3.3.1. Capillary Viscometers

Figure 3.6 shows an example of a *capillary viscometer* [8]. The time required for a known amount of liquid to flow through a capillary tube is measured. Although viscosities can be calculated based on the diameter of the capillary, usually each instrument is standardized with liquids of known viscosity; then, calculation is based simply on instrument constants and time.

Flow is usually driven by gravity, so kinematic viscosity is measured. Simple shear viscosity can be calculated by correcting for density. Capillary viscometers with a range of diameters permit the determination of viscosities from 10^{-7} to $10^{-1}\,\mathrm{m}^2\,\mathrm{s}^{-1}$. For liquids with a density of 1, these values correspond to a range of 1 mPa•s to 1000 Pa•s.

Capillary viscometers are the instruments of choice for research work, since the accuracy attained is high. They are applicable only to Newtonian fluids and are not appropriate for routine work, because determinations are relatively time consuming especially when temperature dependence of viscosity data is desired. Temperature equilibration is slow because of the relatively large sample sizes and the low rate of heat transfer by glass. Capillary viscometers are particularly appropriate for use in determining the viscosity of volatile liquids or solutions containing volatile solvents, since they are essentially closed systems.

Various modified capillary viscometers are available that overcome limitations of the standard types. Vacuum viscometers are available in which the sample is sucked up into the tube. The time to pass from the lower marker to the upper one is measured. Since the flow rate is not affected by gravity, density does not affect the time, and viscosity is

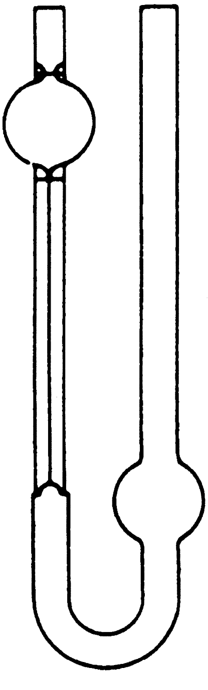

Figure 3.6. *Ostwald capillary viscometer. (From Ref. [8], with permission.)*

measured in Pa•s, avoiding the need to determine density. Similar viscometers can be used for opaque liquids since the passage of liquid from the lower mark to the upper mark can easily be seen.

3.3.2. Rheometers

For non-Newtonian liquids, including pigmented liquids, the highest accuracy over a wide range of shear rates is obtained with rotational rheometers, exemplified by *cone and plate rheometers*. A schematic diagram is shown in Figure 3.7. The sample is placed on the plate, which is then raised to a level with a small clearance from the cone. The cone can be rotated at any desired number of revolutions per minute (rpm) and the torque is measured. The angle of the cone is designed to make the shear rate constant throughout the sample in the gap. Shear rate is proportional to the rpm, and shear stress is related to the torque. Temperature is controlled by passing temperature-controlled water through the plate; temperature control problems are minimized by the small sample size.

A variety of rheometers are available, varying in the range of shear rates that can be used and the time required to increase or decrease shear rate. (See the general references and Refs. [6] and [8] for further discussion.) The least expensive instruments are sufficiently rugged, simple to use, and fast enough for quality control applications. The most versatile ones are sensitive scientific instruments requiring skill in use and are most appropriate for research applications. In some instruments, the edge of the liquid sample is exposed to the atmosphere, and volatiles can evaporate. When rheometers are used with solutions containing volatile solvents, the cone and plate unit should be shrouded in an atmosphere saturated with solvent vapor. Two types are available:

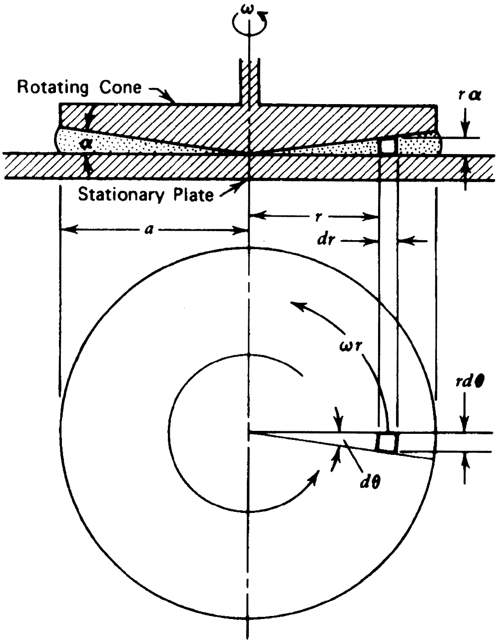

Figure 3.7. Cone and plate viscometer geometry. (From Ref. [1], with permission.)

controlled strain and controlled stress instruments. The latter type offers advantages for coatings, as it is generally superior for measurements at very low shear rates.

The viscosity of highly viscous materials can be determined at high rates of shear by the use of *mixing rheometers*, which are small, heavy-duty mixers. The test sample is confined to a relatively small space and subjected to intense mixing by dual rotors in the form of sigma-shaped blades. A dynamometer measures the work input through a reaction torque that is converted to a strip chart readout. The speed is set by a tachometer. The newer instruments are computerized. These instruments were originally designed for studying the molding of plastics, but are also used in studying the effect of pigments on viscosity. Heat buildup can be substantial with high viscosity fluids. A micro twin screw rheometer is available in which the rpm of the screws can be varied over a wide range, permitting measurement of shear stress as a function of rpm.

3.3.3. Rotating Disk Viscometers

Rotating disk viscometers, such as a Brookfield Viscometer, have a motor that rotates a disk immersed in a liquid over a range of rpm, and the resulting torque is measured. A schematic diagram is shown in Figure 3.8. The instruments must be calibrated with standards. Measurements should be made in a container of the same dimensions as that in which the standardization is carried out, since the distance of the disk below the surface of the liquid, above the bottom of the container, and from the side walls can affect the response. In reporting results, the rpm setting should always be specified. The instruments are sturdy and relatively inexpensive, although they must be recalibrated periodically. When used properly, they provide relatively accurate viscosity measurements for Newtonian liquids. For non-Newtonian liquids, the viscosity reading represents an average response corresponding to the viscosities resulting from a span of shear stresses.

Rotating disk viscometers can detect whether a liquid is shear thinning or shear thickening by measurements carried out at different rpm settings. They can detect thixotropy by a change in response over time at the same rpm setting. Useful comparisons of the

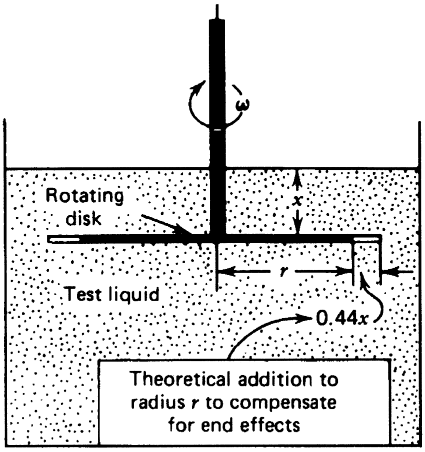

Figure 3.8. *Disk viscometer. (From Ref. [1], with permission.)*

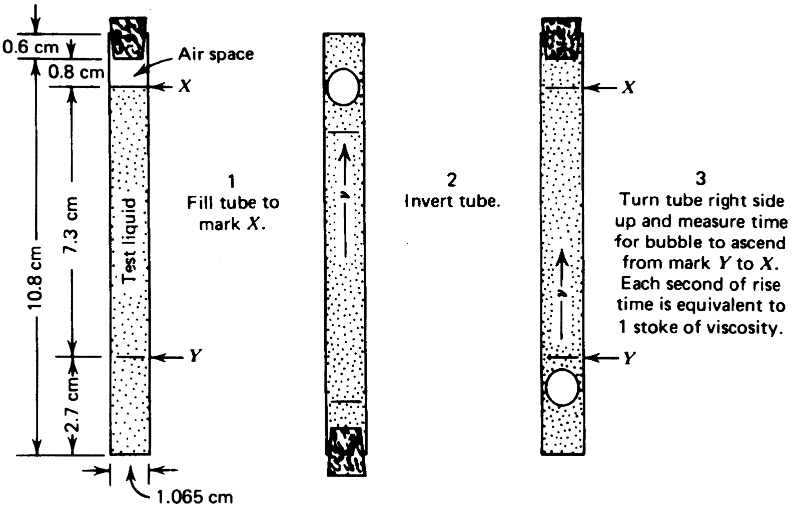

Figure 3.9. *Determination of viscosity with a bubble tube. (From Ref. [1], with permission.)*

thixotropic properties can be obtained by applying a high shear rate, then suddenly reducing the rate of shear to a lower value and measuring the time required for the viscosity to reach equilibrium at that lower rate.

3.3.4. Bubble Viscometers

Bubble viscometers are widely used in quality control to approximate the viscosity of solutions of resins (Section 15.6.2). The measurement is based on the rate of rise of an air bubble in a tube of liquid; the higher the viscosity, the slower the bubble rises. A glass tube is filled with a liquid to a graduation mark and stoppered so that a definite amount of air is enclosed at the top, as shown in Figure 3.9. The tube is placed in a thermostatic bath and kept there long enough for the temperature to equilibrate. Equilibration is slow, but is essential if meaningful measurements are to be made. The tube is then inverted, and the time required for the air bubble to travel between two calibration marks on the tube is measured. Provided that the length of the bubble is greater than its diameter, the rate of rise is independent of the bubble size. The density of the liquid affects the rate of rise of the bubble, so kinematic viscosity is measured. Sets of standard tubes are designated as A, B, C, and so on; after Z, tubes are designated as Z_1, Z_2, and so on. Kinematic viscosities range from about 10^{-5} to 0.1 $m^2\ s^{-1}$. Bubble viscometers are appropriate only for Newtonian, transparent fluids. They are low in cost and simple to use. If the bubble has a tail, the resin is approaching gelation.

3.3.5. Efflux Cups

The most widely used control device for measuring flow of industrial coatings, especially for spray application, is the *efflux cup*. A variety of efflux cups are used. (Refs. [6] and [8] provide a comparison of about two dozen that are used commercially.) A schematic diagram of one of the most common efflux cups, the Ford No. 4 cup, is shown in

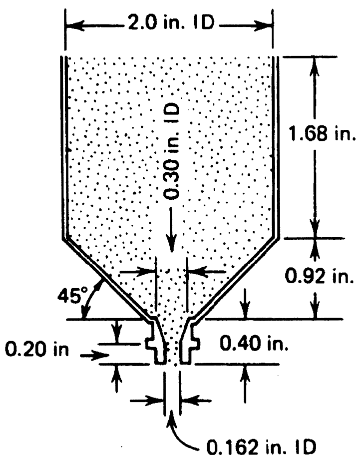

Figure 3.10. *Ford No. 4 efflux cup. (From Ref. [1], with permission.)*

Figure 3.10. One holds a thumb over the hole in the bottom of the cup, fills the cup with coating, removes the thumb, and then times when the stream of coating flowing through the hole breaks. The result is expressed in seconds. The data should not be converted into kinematic viscosity numbers, since a significant amount of the force is converted into kinetic energy, especially with low viscosity coatings. The method is not appropriate for non-Newtonian liquids, although efflux cups are frequently used for coatings that exhibit a small degree of shear thinning. Despite their limitations, efflux cups are useful quality control devices. They are low in cost, rugged in construction, and easily cleaned. Results are simply and quickly obtained, but reproducibility is poor, reportedly only in the range 18 to 20% [8].

The proper way to use an efflux cup to control viscosity for spraying, for example, is to adjust the viscosity of the coating by solvent addition until the coating sprays properly, and then measure the time it takes to flow through the efflux cup. This time can then be used as the standard for spraying that particular coating through that spray gun at that distance from the object being sprayed. Proper efflux cup flow times for spraying vary with different coatings for a given application system and with different application systems for a given coating.

3.3.6. Paddle Viscometers

In the United States, the most widely used viscometer in architectural paint formulation is the *Stormer Viscometer*. The instrument paddle is immersed in the paint and rotated at 200 rpm. The force required to maintain this rotation rate is measured by adding weights to a platform at the end of a cord over a pulley connected to the paddle by a geartrain. A schematic diagram is shown in Figure 3.11. The weight loaded is converted into *Krebs units* (KU) by an arbitrary conversion scale. Originally, a KU value of 100 was supposed to correspond to a good brushing consistency. In current practice, paints are usually formulated with somewhat lower KU values. The instrument is of little utility with Newtonian fluids, and the readings have no real meaning for non-Newtonian

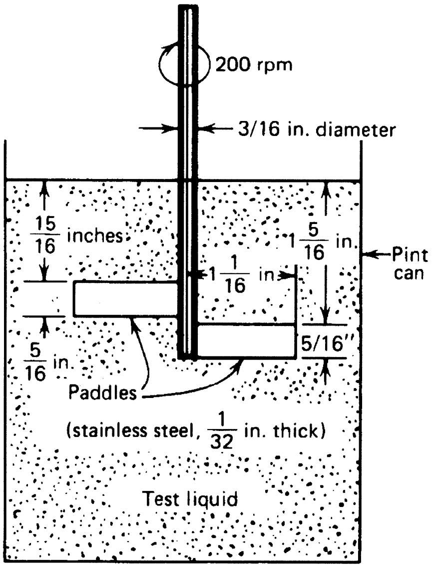

Figure 3.11. Paddle viscometer. (From Ref. [1], with permission.)

fluids, typical of most architectural paints. Even when used only for quality control, a paddle viscometer is not very satisfactory.

The proper way to establish the flow properties for a trade sales paint is to apply it with a brush or roller and adjust it until the best compromise of such properties as ease of brushing, leveling, sagging, settling, and so on, has been achieved. Having done this work, a quality control test can be set up. Appropriate quality control instruments are cone and plate viscometers (some of which are low cost) or, lacking that, rotating disk viscometers. Stormer Viscometers are widely used, but that does not make them satisfactory. The director of research of a large manufacturer of trade sales paints in the United States said some years ago that the Stormer Viscometer was responsible for setting back the formulation of one-coat hiding latex paints by 20 years.

3.4. SHEAR VISCOSITY OF RESIN SOLUTIONS

The viscosity of liquids depends on free volume availability. To put it somewhat simplistically, there are free volume holes opening and closing rapidly in a liquid; molecules move randomly through these free volume holes. When a stress is applied, movements in the direction that relieves the stress are favored, and the liquid flows. Therefore, factors that control viscosity of resin solutions are those that control the availability of free volume. Many coatings are based on solutions of polymers or oligomers. The variables affecting the flow behavior of these concentrated solutions are not fully understood. The variables that govern the flow of very dilute polymer solutions have been studied extensively and are better understood. Factors affecting the flow of dilute solutions are discussed in Section 3.4.2, and factors affecting the flow of more concentrated solutions are discussed in Section 3.4.3.

3.4.1. Temperature Dependence of Viscosity

Temperature dependence of viscosity for a range of low molecular weight (MW) resins and their solutions has been shown to fit a *Williams–Landel–Ferry* (WLF) *equation* [9–12] (Section 2.3): where T_r, the reference temperature, is the lowest temperature for which experimental data are available and η_r is the viscosity at the reference temperature, T_g. Except for very dilute solutions, data fit Eq. 3.2 when the reference temperature is T_g and the viscosity at T_g is assumed to be 10^{12} Pa•s [9].

$$\ln \eta = \ln \eta_r - \frac{c_1(T - T_r)}{c_2 + (T - T_r)} \cong 27.6 - \frac{A(T - T_g)}{B + (T - T_g)} \tag{3.2}$$

For higher MW polymers at temperatures above $T_g + 100°C$, the temperature dependence of viscosity approximately fits an Arrhenius equation, shown in Eq. 3.3, where E_v is the activation energy for viscous flow. (Note that the Arrhenius A value is not the same as the constant A in Eq. 3.2.)

$$\ln \eta = K + \frac{B}{T} = \ln A + \frac{E_v}{RT} \tag{3.3}$$

Using the data available for low MW resins and their solutions, Arrhenius plots of ln η as a function of $1/T$ have been found to be curved and not linear [9,11]. On the other hand, the data do fit a WLF equation. From a practical viewpoint, the differences in the models are small if the temperature range is small. However, over a wide range of temperatures, the differences are relatively large. Figure 3.12 shows plots of the temperature dependence of viscosity of commercial standard liquid bisphenol A epoxy resin (Section 11.1.1), calculated from both Arrhenius and WLF equations, together with experimental data points; the data fit the WLF equation.

A major factor controlling the viscosity of resin solutions is $T - T_g$, but it is not the only factor. When the differences between T_gs are small, differences in WLF constants A and B may overshadow the small difference in $T - T_g$. Constant A depends on the difference in thermal expansion coefficients above and below T_g, but no studies have been reported on the structural factors that control these coefficients. Constant B is the value of $T_g - T$ at which viscosity goes to infinity. The *universal value* of this constant is 51.6°C, but the "constant" varies considerably with composition. No studies have been reported on the relationship between structure and the value of constant B.

Generally, in designing resins, it is reasonable to predict that a lower T_g will lead to a lower viscosity of the resins and their solutions. (See Section 2.1.2 for a discussion of the factors controlling the T_g of polymers.) Linear poly(dimethylsiloxanes) have low T_gs and low viscosities. Linear polyethylene glycols have almost as low T_gs and viscosities. Poly(methyl methacrylate) resin solutions have higher T_g values and viscosities than those of comparable poly(methyl acrylate) resin solutions. BPA epoxy resins have higher T_g values and viscosities than those of corresponding hydrogenated derivatives. Exceptions to this generalization on the effect of T_g have been reported for some high-solids acrylic resins (Section 8.2.1). Acrylic resins made with a comonomer that has a bulky group, such as 3,3,5-trimethylcyclohexyl methacrylate [13] or isobornyl methacrylate [14], are reported to have low viscosities at high solids even though their homopolymers have high T_g values; no explanation of this effect has been advanced.

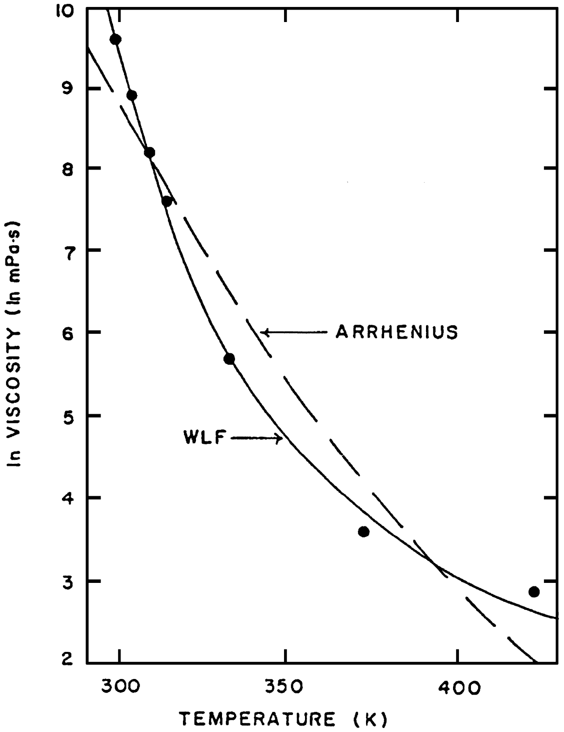

Figure 3.12. *Viscosity dependence of standard liquid BPA epoxy resin on temperature. (From Ref. [9], with permission.)*

3.4.2. Dilute Polymer Solution Viscosity

Measurement of viscosities of very dilute solutions of polymers played an important part in the early development of polymer science, since they were the earliest method of estimating MWs. If the concentration of a solution is low enough that individual polymer molecules and their associated solvent molecules are isolated from each other, the *relative viscosity* (η_r) of the solution can be expressed by the empirical *Huggins equation* where [η] is *intrinsic viscosity* (sometimes called the *limiting viscosity number*) and C is the concentration of the polymer solution, expressed as weight of polymer per unit volume of polymer solution. Relative viscosity is the ratio (it is unitless) of solution viscosity to viscosity of the solvent. In recent literature, the units of C most commonly used are grams of polymer per milliliter of solution, but in older literature, g dL^{-1} is common, so one must be careful to check units. When C is expressed in g mL^{-1}, the units of intrinsic viscosity are mL g^{-1}. Intrinsic viscosity is obtained by extrapolating a plot of ln η_r/C as a function of C to zero concentration. It is related to the hydrodynamic volume of the sphere swept out by an isolated polymer molecule and its associated solvent as it moves through a dilute solution. Further information on the Huggins equation and a table with data covering [η] for a large number of polymers with various solvents and temperatures may be found in Ref. [15].

$$\ln[\eta]_r = [\eta]C + [\eta]^2C^2 \qquad (3.4)$$

Intrinsic viscosity depends on temperature. As temperature increases, the coil size of the polymer molecule usually increases, more solvent is entrapped, and intrinsic viscosity increases. Intrinsic viscosity is also affected by solvent–polymer interactions. The greater the extent of solvent association with a polymer molecule, the more the coil expands, and therefore, the higher the intrinsic viscosity. Intrinsic viscosity depends on MW: The higher the MW, the larger the intrinsic viscosity. Another factor is the rigidity of the chain. Everything else being equal, polymers with flexible, randomly kinked chains have lower intrinsic viscosities than those with rigid, rod-like structures. The relationship between intrinsic viscosity and molecular weight M is expressed by the *Kuhn–Mark–Houwink–Sakurada equation*:

$$[\eta] = KM^a \tag{3.5}$$

in which K and a are constants.

If the solvent is too poor or the temperature is too low, the polymer molecules precipitate rather than staying in solution. The combination of minimum temperature and poorest solvent that just maintains solubility is called the *theta condition* (θ). Under theta conditions, intrinsic viscosity $[\eta]_\theta$ is at a minimum. If the chains are flexible, as for example with acrylic polymers, $[\eta]_\theta$ is proportional to the half-power of MW, as shown in Eq. 3.6. Note that Eqs. 3.5 and 3.6 are based on polymers that have narrow MW distributions.

$$[\eta]_\theta = K_\theta M^{1/2} \tag{3.6}$$

In better solvents the isolated polymer coils expand, intrinsic viscosity increases, and the exponent a in Eq. 3.5 increases to as high as 0.78 for flexible polymers, and even higher for rigid polymers. In THF, branched poly(methyl methacrylate) (PMMA) has been shown to have an intrinsic viscosity of 0.40 compared to 0.688 for linear PMMA [16]. The lower value of a is attributed to the lower hydrodynamic volume of the branched polymer solvent swollen molecules.

3.4.3. Concentrated Polymer Solution Viscosity

Concentrated solutions of polymers behave quite differently than dilute solutions. There have been relatively few fundamental studies of the factors controlling the viscosity of more concentrated solutions of polymers and resins, such as those used in the coatings field. Several empirical relationships have been proposed, such as the concentration dependence of relative viscosity: In which w_r is the weight fraction resin and the k values are constants.

$$\ln \eta_r = \frac{w_r}{k_1 - k_2 w_r + k_3 w_r^2} \tag{3.7}$$

Nonlinear regression analysis of the limited number of sets of data that were available in the literature in 1985 fits Eq. 3.7 over a wide range of concentrations [9]. Even with this many constants, there is some systematic deviation from the model at very low concentrations. Constant k_1 is the reciprocal of *weight intrinsic viscosity*, $[\eta]_w$ which although formally unitless, is based on the number of grams of solution containing a gram of resin. Weight intrinsic viscosity can be converted to the more familiar volume intrinsic viscosity $[\eta]$ by dividing by the density of the solution at the concentration $w_r = k_1$. No physical significance of the other two constants, k_2 and k_3, has been elucidated; they are presumably related to further solvent–resin interactions and to free volume availability.

Over narrower ranges of concentration, the experimental data reasonably fit the simpler Eq. 3.8. The even simpler Eq. 3.9 has been used extensively to calculate approximate relative viscosities over a narrow range of concentrations with viscosities from around 0.01 to 10 Pa•s.

$$\ln \eta_r = \frac{w_r}{k_1 - k_2 w_r} \tag{3.8}$$

$$\ln \eta_r = \frac{w_r}{k_1} = [\eta]_w w_r \tag{3.9}$$

As explained in Section 3.4.2, relative viscosity of dilute solutions of polymers increases as the solvent gets "better." However, in concentrated solutions, relative viscosity is higher in poor solvents than it is in good solvents. In the few cases reported in the literature, log of relative viscosity increases with the square root of MW of resins dissolved in good solvents at these higher concentrations [9,17]. It has been postulated that intrinsic viscosities of oligomers exhibit theta condition response; that is, the relative viscosity of oligomer solutions is proportional to the square root of MW [18]: as shown in Eq. 3.10. This relationship appears to be true for solutions in good solvents of resins having relatively narrow MW distributions and viscosities between about 0.01 and 10 Pa•s; but further research is needed.

$$\ln \eta_r = K w_r M^{1/2} \quad \text{or} \quad \ln \eta = \ln \eta_s + K w_r M^{1/2} \tag{3.10}$$

As shown in Eqs. 3.7 to 3.10, the viscosity of the solvent is a factor affecting the viscosity of resin solutions. At first glance it might appear that a small difference in the viscosity of the solvent would have a trivial effect on the much higher viscosity of the resin solution. However, there are examples in which solvents differ in viscosity by as little as 0.2 mPa•s, whereas 50 wt% resin solutions in those same solvents differ in viscosity by as much as 2 Pa•s.

Also important are the effects of resin–solvent interactions. In good solvents, there are stronger interactions between solvent molecules and resin molecules than in poor solvents. In very dilute solutions, this means that the chains become more extended and sweep out larger hydrodynamic volumes in good solvents than in poor solvents. However, in more concentrated solutions, resin molecules are constrained by the hydrodynamic volumes swept out by neighboring resin molecules. If interaction between solvent and resin is stronger than resin–resin interactions, the molecules can flow easily through the hydrodynamic volumes swept out by other molecules (provided that the free volume is adequate). On the other hand, if resin–resin interactions are stronger, more or less transient clusters of resin molecules form, and the viscosity is higher. In solutions containing good solvents, flow is generally Newtonian. In many cases, flow of more concentrated resin "solutions" in poor solvents behave somewhat like dispersed systems; they are non-Newtonian because shear can break up or distort resin clusters.

Although the difference in the viscosity of resin solutions in good and poor solvents is reasonably well understood, there is little definitive work in the literature on comparisons between solutions in various good solvents in which some of the solvents are “more good” than others. Erickson studied relative viscosities of solutions of several low MW resins in a range of solvents [19]. He concluded that relative viscosities decrease as one changes from a very good solvent to a good solvent, pass through a minimum, and then increase rapidly in very poor solvents. As can be seen in Eqs. 3.7 to 3.9, which relate relative viscosity to concentration, the hydrodynamic volume of the isolated resin molecule and its associated solvent molecules is a factor in determining the viscosity not just of very dilute solutions, but also of more concentrated ones. In changing from a very good to a good solvent, the equations predict that intrinsic viscosity, and hence relative viscosity, should decrease; this prediction conforms with Erickson’s hypothesis. The range of error in Erickson’s work is not small enough to establish his conclusions beyond doubt. He may well be right, but there is need for further research.

Solvent effects on hydrogen bonding between resin molecules can be substantial. Figure 3.13 shows the viscosities of solutions of an acrylated epoxidized linseed oil in three solvents chosen because of their similar viscosities but very different hydrogen-bonding characteristics [20]. The resin molecules have multiple hydroxyl groups. Note that the viscosities of the solutions in xylene are highest. Xylene is a poor hydrogen-bond

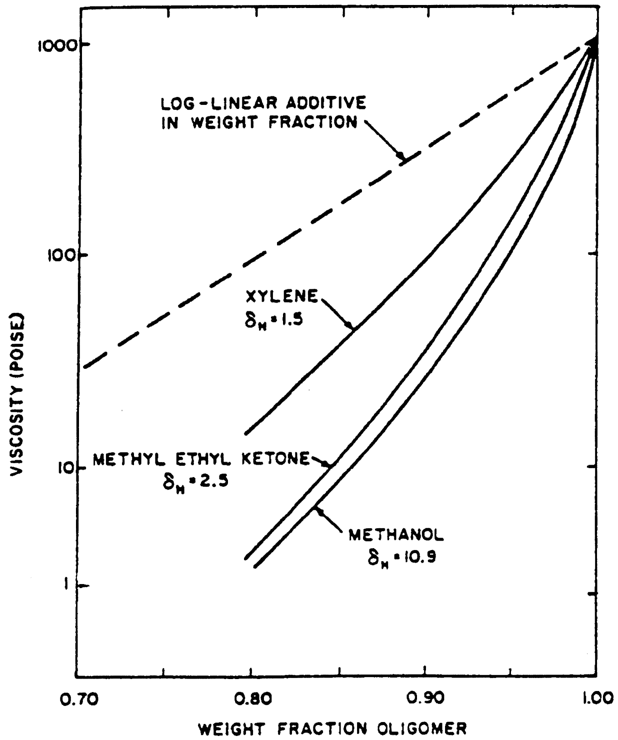

Figure 3.13. Viscosity reduction of a hydroxy-functional UV-curable oligomer with xylene, MEK, and methyl alcohol compared to the viscosity predicted if the viscosity reduction were a log-linear additive relationship by weight. (From Ref. [20], with permission.)

acceptor and hence promotes intermolecular hydrogen bonding between the resin molecules. Methyl ethyl ketone (MEK) is a good hydrogen-bond acceptor and reduces the viscosity more effectively than xylene by reducing intermolecular hydrogen bonding. Although methyl alcohol is a much stronger hydrogen-bonding solvent than MEK, it is only marginally better at reducing viscosity. Methyl alcohol is both a hydrogen-bond donor and acceptor. Possibly, methyl alcohol can bridge resin molecules by functioning as a hydrogen-bond donor with one resin molecule and a hydrogen-bond acceptor with the other; such bridging would counteract the effectiveness of viscosity reduction.

Intermolecular hydrogen bonding between carboxylic acid groups is particularly strong. Correspondingly, solvent effects on the viscosity of carboxylic acid–substituted resins are particularly large [21]. It has been known for many years that simple carboxylic acids, such as acetic acid, exist as dimers in poor hydrogen-bond acceptor solvents such as benzene, whereas the dimers are dissociated in good hydrogen-bond acceptor solvents such as acetone. The effect in resin solutions was demonstrated in a study of a primarily monocarboxylic acid–substituted acrylic oligomer [22]. Relative viscosity in xylene was higher than in methyl isobutyl ketone (MIBK). MW, as determined by vapor pressure depression, was lower in acetone than in benzene. In xylene, hydrogen bonding between carboxylic acid molecules was promoted; in MIBK, the predominant hydrogen bonding is between ketone and carboxylic acid groups rather than between carboxylic acids.

Another solvent effect on viscosity is the solvent T_g. The T_g of resin solutions depends on the concentration and the T_g of both the resin and the solvent. This effect has been recognized in the addition of plasticizers to polymers, but has not been widely studied in resin solutions having concentrations and viscosities in the range of interest for coatings. In one study it was found that the data fit Eq. 3.11, where T_{gs} is the T_g of the solvent and T_{gr} is the T_g of the solvent-free resin [9]. In this study, Eq. 3.11 fits the data over the entire range of concentrations from pure solvent to pure resin. Equation 3.11 needs to be tested with other systems.

$$\frac{1}{T_g} = \frac{w_s}{T_{gs}} + \frac{w_r}{T_{gr}} + k w_r w_s \tag{3.11}$$

The relationships are further complicated because solvent–resin interactions can be further affected by resin MW and the number of polar groups per molecule. For example, consider the data in Table 3.1 on the viscosity of solutions of a pair of styrene/allyl alcohol (SAA) copolymers in methyl ethyl ketone (MEK) and toluene

TABLE 3.1. Effects of Molecular Weight and Functional Group Content on Viscosity

Characteristic	SAA-I	SAA-II
$\bar{M}_n$	1600	1150
$\bar{M}_w/\bar{M}_n$	1.5	1.5
OH content (wt%)	5.7	7.7
Viscosities (mPa·s)		
80 wt% in MEK	10,000	6500
70 wt% in MEK	300	230
60 wt% in MEK	80	65
50 wt% in MEK	34	30
50 wt% in toluene	760	3840

[20]. SAA-I has a higher MW, but a lower functional group content than SAA-II. In MEK, an effective hydrogen-bond acceptor, the effect on viscosity of the OH content is diminished so that the higher MW of SAA-I results in a somewhat higher viscosity then that of SAA-2. In toluene, which does not hydrogen bond effectively, the difference in OH content dominates over the difference in molecular weight, so that the SAA-II solutions have the higher viscosity. Comparison of the 50 wt% solutions in MEK and toluene shows that the hydrogen-bonding solvent is more effective for viscosity reduction of both SAAs. See Table 18.6 in Section 18.4 for examples of effects of solvents on the viscosity of solutions of a high-solids acrylic resin.

The viscosity of mixtures of hydrogen-bond acceptor solvents such as ketones and esters are reported to be nearly ideal in their effects on viscosity; that is, the viscosity of a mixture can be estimated quite well by calculating the weighted average viscosity from those of the components [23]. However, in the case of mixing alcohols with other solvents, the viscosities of mixtures varied substantially from ideal behavior. The deviation can be attributed to reduction of intermolecular hydrogen bonding of alcohols by the other solvents, and was particularly pronounced when water was one of the solvents in a mixture. Although these results with solvent mixtures add to our understanding of the effects of intermolecular interactions on viscosity, they are not directly applicable to the problem of mixed solvent effects on the viscosity of resin solutions. Since most resins have multiple hydrogen-bond donor and acceptor sites, the interactions with solvent are greater and more complex than in solvent blends. Little work has been published on this important question. In one paper, the authors suggest that the “best” solvent in the mixture dominates in determining the effect on the intrinsic viscosity of the resin solution [24]. The rationale is that the “best” solvent interacts most strongly with resin molecules, hence controls the degree to which the resin molecules are extended. It is hoped that further research will be reported on the effects of mixed solvents on resin solution viscosity.

In reducing viscosity to spray viscosity by adding solvent to a coating, it is desirable to have an equation that combines the effects of temperature and concentration on viscosity. For the limited ranges of temperature and concentration involved, Eqs. 3.3 and 3.9 can be combined to give such a relationship [25]. (In Eq. 3.12, log of solvent viscosity is combined into constant K.)

$$\ln \eta = K + \frac{B}{T} + \frac{w_r}{\mathrm{k}_1} \tag{3.12}$$

Flow within coatings during film formation has a major influence on final film appearance and uniformity. It has proven to be a very difficult area to study because of the many variables involved, including nonuniformities within the forming film. Progress is being made, however. For example, Eley and Schwartz used mathematical modeling and numerical simulation to develop a theory that correlated with the behavior of two architectural paints [26].

3.5. VISCOSITY OF LIQUIDS WITH DISPERSED PHASES

Since many coatings contain dispersed pigment and/or resin particles, it is important to consider the effect of dispersed phases on the viscosity of liquids. When a small amount of a dispersed phase is present, there is only a small effect on viscosity (unless the dispersed phase is flocculated); however, as the volume of dispersed phase increases, there is a sharply increasing effect. More energy is used to rotate particles, and the presence of the particles interferes increasingly with the ability of other particles to move. When the system becomes closely packed with particles, the viscosity approaches infinity.

Several equations have been developed that model the effect of a dispersed phase on viscosity; the earliest was proposed by Einstein. Here we use a treatment by Mooney [27]. Equation 3.13 is a useful form of the *Mooney equation* for understanding the effects of variables on viscosity: where η_e is the viscosity of the continuous or external phase, K_E is a shape constant, V_i is the volume fraction of internal phase, and ϕ is the packing factor.

$$\ln \eta = \ln \eta_e + \frac{K_E V_i}{1 - V_i/\phi} \tag{3.13}$$

The *packing factor* is the maximum volume fraction of internal phase that can be fit into the system when the particles are randomly close packed and the external phase just fills all the interstices between the particles. When V_i equals ϕ, the viscosity of the system approaches infinity. Figure 3.14 shows an example of a plot of the relationship between log viscosity and V_i for a dispersed-phase system. Two major assumptions are involved in the Mooney equation: (1) the particles are rigid, and (2) there are no particle–particle interactions other than physical collisions.

The shape constant K_E for spheres is 2.5. Some of the particles in coatings are spheres or are reasonably close to being spheres, but many pigments are irregularly shaped. In the case of uniform diameter spheres (i.e., monodisperse systems), the value of ϕ is 0.637. This value is the packing factor that has been calculated for a random mixture of cubical and hexagonal close-packed spheres and has been confirmed experimentally. To the surprise of many people first considering the question, the packing factor of monodisperse spheres is independent of particle size. The packing factor for basketballs is 0.637; the packing factor for marbles is 0.637; the packing factor for monodisperse latex particles is 0.637. However, marbles fit into the interstices between close-packed basketballs, and latex particles fit into the interstices between close-packed marbles. In other words, the packing factor depends strongly on particle size distribution: The broader the particle size distribution, the higher the packing factor.

The viscosity of dispersions of nonrigid particles does not follow the Mooney equation. When a shear stress is applied to such a dispersion (e.g., an emulsion), the particles can distort. When the particles are distorted, the shape constant changes to a lower value and the packing factor increases [28]; both changes lead to a decrease in viscosity. Commonly, such systems are thixotropic. This is logical since depending on the difference between the viscosities of the internal and external phases, there would be time dependency of the distortion of the particles and hence a decrease in viscosity as a function of time at a given shear rate. There are modifications of the Mooney equation that account for viscosities of the two phases, but not time dependency [29]. Time dependency can be studied using viscoelastic deformation analysis [5,6].

Fluids with readily distorted internal phases include emulsions, water-reducible acrylic and polyester resins, urethane dispersions, some latexes in which the outer layer of the latex particles and layers adsorbed on them are highly swollen by water, and some pigment dispersions with comparatively thick adsorbed layers of polymer swollen with

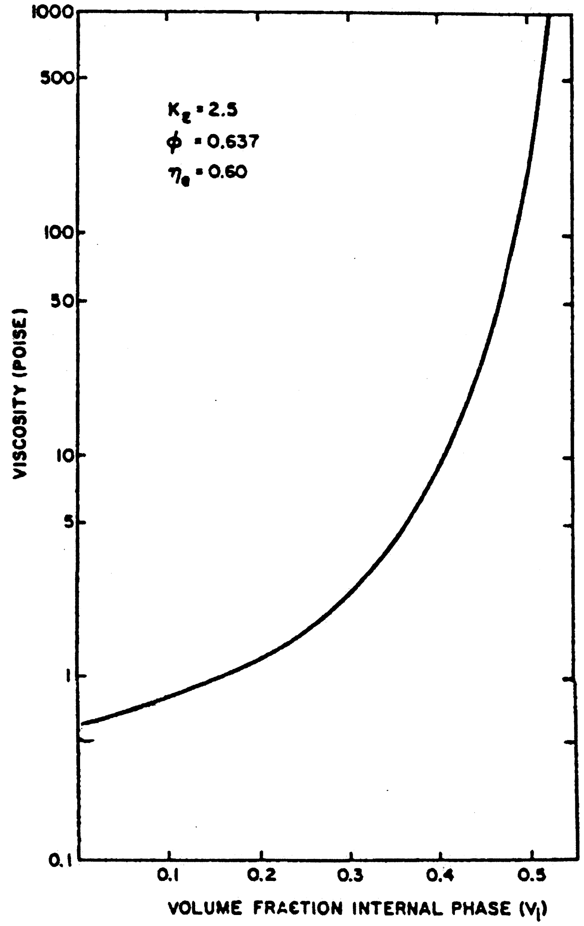

Figure 3.14. Effect of increasing the volume fraction of noninteracting spherical particles on the viscosity of a dispersion. (From Ref. [20], with permission.)

solvent. (See Ref. [2] for a discussion of the effect of adsorbed layers on particles on rheology.)

Although other factors may be involved, many thixotropic agents act by creating a swollen dispersed phase that can be distorted. For example, very small particle size SiO_2 adsorbs a layer of polymer swollen by solvent that is thick compared to the pigment and is distortable in a shear field. Up to a point, the degree of distortion increases as the shear stress increases and/or as the time of shearing increases. When shearing is stopped or decreased, the polymer layers recover their equilibrium shape and viscosity increases. In other cases, lightly cross-linked polymer gel particles are used; the particles swell with solvent, giving a distortable dispersed phase. The shear thinning behavior depends on the particle size, concentration, and internal viscosity of the dispersed phase. Smaller particles lead to higher shear rates for shear thinning. Shear thinning decreases with decreasing concentration and increasing internal viscosity of particles.

The viscosity of dispersions is also affected by particle–particle interactions. If clusters of particles form when stirring of a dispersion is stopped, the viscosity of the dispersion

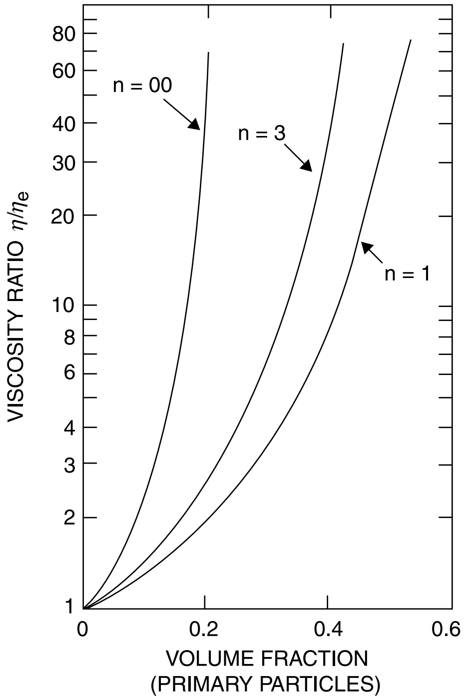

Figure 3.15. *Effect of cluster formation on viscosity. (From Ref. [20], with permission.)*

increases; if these clusters separate again when shear is exerted, the viscosity drops. Examples of such shear thinning systems are flocculated pigment dispersions and flocculated latexes. Another is the *gelation* (really, flocculation) induced by water in coatings containing treated clay dispersions [30]. When clusters of particles form, continuous phase is trapped in the clusters; as a result, at low shear rates, V_i is high. At high shear rates, when the clusters break up, the value of V_i is reduced to just that of individual particles of the dispersion without a trapped continuous phase. As V_i increases, viscosity increases, and vice versa.

One can also consider the dispersion from just the point of view of the V_i of the primary particles only, adjusting the K_E and ϕ in Eq. 3.13 to account for aggregation rather than adjusting the V_i. An example is shown in Figure 3.15. The vertical axis is the ratio of the viscosity of the dispersion to the viscosity of the external phase (η/η_e). The viscosity of the dispersion increases rapidly as the number of particles *n* in aggregates increases.

Polymer solutions containing dispersed phases are complex physical systems whose flow properties are still the subject of continuing research. In this discussion we have used the Mooney equation; alternative treatments, such as those of Krieger and Dougherty [32] and Russel and Sperry [33], are also useful. A detailed analysis of effects of particle interactions on dispersion rheology is included in Ref. [34].

3.5.1. Thickeners for Latex Coatings

Latex paints require a thickener to adjust viscosity. Viscosity of the paint as a function of shear rate particularly affects ease of brushing, film thickness, leveling, sagging, and settling. The viscosity of the external phase controls its rate of penetration into a porous substrate, such as wood. If penetration is rapid, the viscosity of the paint above the porous surface increases rapidly, resulting in poorer leveling. The water soluble polymer hydroxyethylcellulose (HEC) is a widely used thickener. Since high MW HEC leads to increased extensional viscosity, which in turn leads to spattering, larger amounts of medium to low MW HEC have been used (Section 3.6.3). However, latex paints thickened with HEC show a high degree of shear thinning, which may result in the application of thin films of paint.

Progress in minimizing the shear thinning problem has been made with *associative thickeners*. Many kinds are available; all are moderately low MW, hydrophilic polymers with two or more long chain nonpolar hydrocarbon groups spaced along the backbone. Examples include hydrophobically-modified ethoxylated polyurethanes (HEUR), styrene–maleic anhydride terpolymers (SMAT), and hydrophobically-modified alkali-swellable emulsions (HASE). An example of a HASE thickener is a copolymer of MAA/EA/TMI on which the NCO group has been reacted with an ethoxylated stearyl alcohol [35]. Another group is hydrophobically-modified ethoxylated aminoplast (HEAT) polymers.

Use of associative thickeners permits formulation of latex paints that exhibit less shear thinning, so that viscosity at high shear rates can be higher; as a result, thicker wet films can usually be applied [36]. Associative thickeners interact by shared ionic bonds and by absorption of the long aliphatic chains on the surface of latex particles. (The thicker wet film in itself helps promote leveling too, since the rate of leveling depends on wet film thickness, as discussed in Section 24.2.) Low shear viscosity can also be maintained at an appropriate level, as with HEC, for controlling sagging, settling, and penetration into porous surfaces. Combinations of associative thickeners and HEC are sometimes used.

Reynolds has reviewed possible mechanisms of thickening by associative thickeners and factors involved in their use in formulating latex paints [37]. He emphasizes that greater care and skill is required in formulating with associative thickeners than with conventional water-soluble thickeners. The results obtained can be very sensitive to the combination of the particular latex and thickener and to the amounts and types of surfactant present in the formulation [37,38]. It has been shown that formulations with associative thickeners not only level better, but also give somewhat higher gloss [39]. A study of interactions between ethylated octylphenols with various ethoxylation levels and a HEUR and a HEAT associative thickener has been published [40]. The associative thickeners and surfactant with only 4.5 ethoxyl groups were incompatible. Compatibility is particularly important in selecting the surfactant to be used in tint colors for use with paints thickened with associative thickeners.

3.6. OTHER MODES OF FLOW

Although flow from application of shear stress is the most common type of flow encountered in making and using coatings, other modes of flow are sometimes involved.

3.6.1. Turbulent Flow

Turbulent flow occurs at very high rates of shear or in irregularly shaped containers and pipes. At low shear rates, flow occurs in a laminar fashion, as illustrated in Figure 3.1. However, as shear rate increases, a critical point is reached where flow suddenly

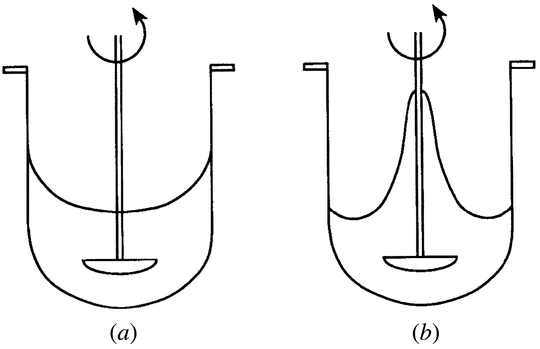

Figure 3.16. (a) Conventional compared to (b) normal-direction flow of liquids on stirring.

becomes chaotic. Laminar flow is disrupted; swirling eddies and vortices occur, and flow changes to turbulent flow. Even with Newtonian fluids, viscosity increases more than proportionally with shear rates above this critical level.

3.6.2. Normal Force Flow

When Newtonian fluids are stirred with a rotary stirrer, the liquid level becomes low in the center near the shaft of the stirrer and high on the walls of the vessel as a result of centrifugal force. This is shown schematically in Figure 3.16(*a*). However, some liquids climb the shaft of the stirrer, as shown in Figure 3.16(*b*), rather than the sides of the vessel. Such flow is normal (perpendicular) to the plane of force. This *normal force flow* behavior is typical of viscoelastic materials and systems that are starting to gel. In the early stages of cooking resins, the flow pattern is as shown in Figure 3.16(*a*), but if cross-linking starts and gelation begins, the flow pattern can change abruptly to that shown in Figure 3.16(*b*). If this occurs, it is time to stop heating and to dump the reaction mixture out as quickly as safely possible before the gel becomes intractable.

Normal force flow effects have been observed in the handling and application of some coatings whose flow is viscoelastic. Under stress, the flow of these coatings has both elastic and viscous components. It seems logical to assume that a significant extent of elasticity could affect atomization in spraying, film splitting in roller coating, and leveling; however, there have been few studies of correlation between normal force flows and coating application [8]. At least part of the reason for the lack of studies is that expensive specialized, instrumentation such as an oscillatory plate rheometer is required for measurements. Unfortunately, even many of those viscometers measure normal force with such poor precision that correlations are not possible.

3.6.3. Extensional Flow

Another mode of flow encountered in some methods of coating application is *extensional flow*, sometimes called *elongational flow*. Extensional flow occurs when fluid deformation is the result of stretching. Various types of stretching are possible. In spin coating, extension occurs in two dimensions. The extensional flow of greatest importance in most other coating processes is uniaxial (i.e., in one direction). In uniaxial flow, the viscosity is properly called *uniaxial extensional viscosity*; we simply use the term *extensional viscosity*, but it should be remembered that there are several types of extensional viscosity.

The difference between extensional flow and shear flow was first observed in fiber drawing. When the fiber material passes through the spinneret, the mode is shear flow. However, as the fiber is pulled after leaving the spinneret, there is no further shearing action; rather, the fiber is extended. The flow is extensional flow, and the resistance to flow is extensional viscosity. The symbol used for extensional viscosity is η_e. In the case of Newtonian fluids, $\eta_e/\eta = 3$.

Extensional flow is encountered when applying coatings by direct roll coating (Section 22.4). The material to be coated is passed through the nip between two rollers, one of which is covered with a layer of coating. Prior to entering the nip, the coating is subject to ambient pressure. As the coating goes through the nip, pressure rises and, as it exits the nip, pressure begins to drop and can drop below ambient pressure. The pressure drop can cause volatilization of solvents and release of dissolved air within the coating, thus causing cavitation. The cavities lead to the formation of ligaments of coating that get elongated under the extensional deformation in the nip exit region. If the extensional viscosity is relatively low, the film splits quickly, leaving a ridged film. However, with higher extensional viscosity, fibers grow; longer fibers tend to split in two places, resulting in formation of droplets, which are thrown out into the air. This is called *misting* or *spattering*. Figure 3.17 shows an extreme case of fiber development in roll coating of paint with an impractically high extensional viscosity [41]. Soules et al. [42] discuss the relationship of variables and extensional viscosity effects in roll coating.

A large fraction of latex flat wall paints is applied by roller. During roller application, latex paints *spatter*, some to a major degree. Paints with high extensional viscosity are likely to spatter severely [43]. Extensional viscosity increases when high-MW water-soluble polymers with very flexible backbones are used as thickeners in a latex paint [41]. As a ligament of the paint is extended, the molecules line up in the direction of extension, leading to increased resistance to the extension. Spattering can be minimized by using low MW water-soluble thickeners with rigid segments in the polymer backbone, such as low MW HEC. Since the selling price of HEC is the same for various MWs, and more low MW polymer is needed to reach the same shear viscosity, paint cost increases when low MW HEC is used. It is common to compromise by using an intermediate MW or a mixture of high and low MW grades of HEC.

Extensional flow can also be encountered in spray application. If, for example, a solution of a thermoplastic acrylic resin with $\bar{M}W$ above about 100,000 is sprayed, instead

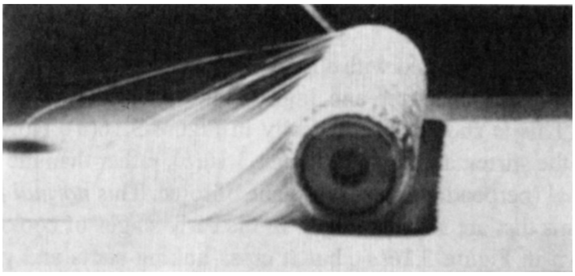

Figure 3.17. *Fiber development in roll coating a high-extensional-viscosity paint. (From Ref. [34], with permission.)*

of droplets coming out of a spray gun orifice, fibers emerge. As the fiber extends, the mode of flow is extensional. The behavior is called *cobwebbing*. Although cobwebbing is undesirable when painting a car, it can give a desirable effect for applying decoration to a Christmas tree. Soules et al. [44] discuss other possible extensional viscosity phenomena in spray application. High extensional viscosity of latex paints that are airless sprayed results in large particle size droplets and hence poor film appearance [45]. Fernando et al. [45] also provide a review of various aspects of extensional viscosity effects in coatings.

Measuring extensional (elongational) viscosity of liquids is difficult. One way is by forming a fiber, wrapping it around a drum, and measuring the rate of extension and the force required for further extension. In another adaptation of this method, the drum is replaced with a vacuum nozzle that is vertically aligned with the nozzle that pumps the fluid. Opposing jet viscometers are a second type of instrument. A third type is the screen viscometer, a simple device that involves flow of a polymer solution through a stack of screen [46]. ASTM is said to be developing a method that employs a screen viscometer. Recently, commercial instruments for measuring extensional viscosity have become available.

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4

Mechanical Properties

4.1. INTRODUCTION: GENERAL COMMENTS ON TESTING OF COATING FILMS

The critical properties of most coating films relate to their ability to withstand use without damage. The range of potential mechanical damage is large. The coating on the outside of an automobile should withstand being hit by a piece of flying gravel without film rupture. The coating on the outside of a beer can must be able to withstand abrasion when cans rub against each other during shipment in a railroad car. The coating on wood furniture should not crack when the wood expands and contracts as a result of changing temperatures during winter shipment or due to swelling and shrinkage resulting from changes in the moisture content of the wood. The coating on aluminum siding must be flexible enough to withstand fabrication of the siding and must resist scratching during installation on a house. In addition, many coatings must also withstand the effects of weather (Chapter 5), retain adhesion (Chapter 6), and protect metals from corrosion (Chapter 7).

In the introductory part of this chapter we discuss all aspects of durability, including the complexities of developing, evaluating, and testing coatings. Development of coatings with adequate durability is made complex by the wide range of conditions to which coatings are exposed. It is safe to generalize that the only way to know how a coating will perform in actual use is to apply the coating to the final product, use the product over its lifetime, and see whether the coating performs satisfactorily. But in many cases, the lifetime of the product can be very long. The coating on the outside of an automobile should maintain its integrity and appearance for well over five years. The coating on furniture should perform satisfactorily for 20 or more years. No laboratory tests are available that permit satisfactory product performance predictions for many applications; however, the formulator must have some way of judging the merits of a new formulation.

Organic Coatings: Science and Technology, Third Edition, by Zeno W. Wicks, Jr., Frank N. Jones, S. Peter Pappas, and Douglas A. Wicks

The most powerful tool is a data bank of field use performance of previous formulations. Formulators have made judgments about the effects of formulation changes on durability based on their years of experience; experienced formulators try to pass on their accumulated experience to novice formulators. Historically, new formulations were relatively small modifications of formulations with known field performance. If the change was significant, initial field use was usually limited. In the automobile field, for example, after a promising new formulation had been developed, it was common to coat just a few cars with it. Then, the next year, if no problems were encountered, the new formulation might be adopted for one color on one model of automobile. The following year, the use might be extended to three or four colors on two or three models. Finally, if all of this history was satisfactory, the new formulation might be widely adopted. This gradual approach to formulating and testing worked quite successfully. However, in recent years, there has been pressure to accelerate the process. This has resulted from increasing performance requirements, pressures to reduce costs, and the need to meet regulation requirements. Reduction of VOC emissions has been a major driving force; but other factors, such as increasing recognition of possible toxic hazards, especially from long term exposure to relatively low levels of some chemicals, have required changes in relatively short time spans.

Increasingly, databases created from actual field use are being accumulated. For example, for many years, teams of representatives of automobile manufacturers and suppliers have surveyed cars in parking lots in various parts of the country. The serial number, which can be seen through the windshield, permits identification of the coatings on that car. In other fields, performance of pipelines, exterior siding, and offshore oil rigs are monitored. Abrasion resistance of exterior beer can coatings can be related to shipment variables. Computers make possible analysis of masses of data correlating actual performance with coating composition and application variables. The computer makes available to all formulators in a company all records, rather than just the memory of one formulator. Data on coatings that fail are as important as data on coatings that are satisfactory. More use of this approach in the future is critical to future progress in formulating superior coatings. A word of caution: Some technical people think only in terms of maximizing performance, but economic factors are important as well. It is foolish to apply an expensive coating that will last 20 years on a product that will last only five years. A five-year life coating can be fully satisfactory and usually costs less than a 20-year life coating.

Accumulating a database takes time. Meanwhile, formulators need tools to work with. The formulator has three kinds of needs when considering the mechanical properties of films. To select the most appropriate components of the coating, the formulator needs to understand the relationships between composition and properties; research instruments can help develop this understanding. Laboratory tests are needed to follow the effects of changes in formulation. Quality control tests are needed to compare production batches to a standard. The accuracy and the appropriate uses of laboratory and quality control tests are often quite limited. Unfortunately, many people working with coatings do not appreciate the limitations of the tests they use. It is common for formulators and users of coatings to assume that an empirical quality control test or an accelerated laboratory test that has been correlated with use performance for one type of coating can predict performance for coatings of a different type. That is almost never the case.

Dickie has proposed a methodology for systematic consideration of the factors involved in service life prediction [1]. He suggests that predictive models can provide the framework for assessing the importance and relevance of available information and may give insight as to what information may be missing from the evaluation of a given material or application. A monograph by Martin et al. [2] provides a discussion of the problems of predicting service lives and proposes reliability theory methodology for database collection and analysis.

4.2. BASIC MECHANICAL PROPERTIES

Understanding relationships between composition and basic mechanical properties of films can provide a basis for more intelligent formulation. Most coating formulators were educated as chemists, not as engineers, and few have had any education on mechanical properties. Terms such as *loss modulus*, *storage modulus*, and *tan delta* may have little meaning to chemists, but such concepts have been used for many years in the plastics, rubber, and fiber industries in developing products with superior performance. Because of the diversity of coatings, the relatively small volume of most types of coatings, and this lack of understanding of the physical behavior of films, the coatings industry has lagged behind in applying these concepts. In 1977, Hill published a review paper discussing stress analysis as a tool for understanding coatings performance [3]. He did an excellent job of presenting an introduction to stress analysis in terms that a coatings formulator could understand. Much of the information presented had to be based on examples from plastics, rubber, and fiber work; there were few such papers that dealt with coatings at the time. Thirty years later, application of stress analysis to coatings has mushroomed.

Basic to understanding the study of mechanical properties of coatings is a recognition that coating films are *viscoelastic materials*. The mode of deformation of any solid can be elastic and/or viscous. In ideal *elastic deformation*, or *Hookean deformation*, a material elongates under tensile stress in direct proportion to the stress applied in conformance with Hooke's law, as exemplified by a steel spring. When the stress is released, the material returns to its original dimensions essentially instantaneously. An ideal viscous material, a Newtonian fluid, also elongates when a stress is applied in direct proportion to the stress; but in contrast to an ideal elastic material, it does not return to, or even toward, its original dimensions when the stress is released; the deformation is permanent. Almost all coating films are viscoelastic—that is, they exhibit intermediate behavior. Thermoplastic films frequently do not recover their original shape completely after deformation; the viscous flow part of the deformation is permanent. In cross-linked films, if there is no yield point, the recovery of the original dimensions may be complete, even though there was viscous flow. The stress on the cross-links supplies the force to reverse the viscous flow. If there is a yield point, there is partial but incomplete recovery of the original dimensions.

Figure 4.1 shows a schematic plot of the results of a stress–strain test, in which a coating film is elongated (*strain*) at a constant rate and the resulting *stress* is recorded [4]. (Methods for measurement of mechanical properties are discussed in Section 4.5.) By convention, the stress (force per unit of cross-sectional area) is based on the original dimensions. Strain is expressed in terms of percent elongation. The slope A of the initial, essentially straight line, portion of the graph is the *modulus*: that is, the ratio of stress to strain. One must be careful to know how the term *modulus* is used in a specific case. In the initial part of this plot, modulus is independent of strain. However, as strain increases, the ratio is no longer constant, and the modulus depends on the strain. The end of the curve signifies that the sample has broken. This point is defined in

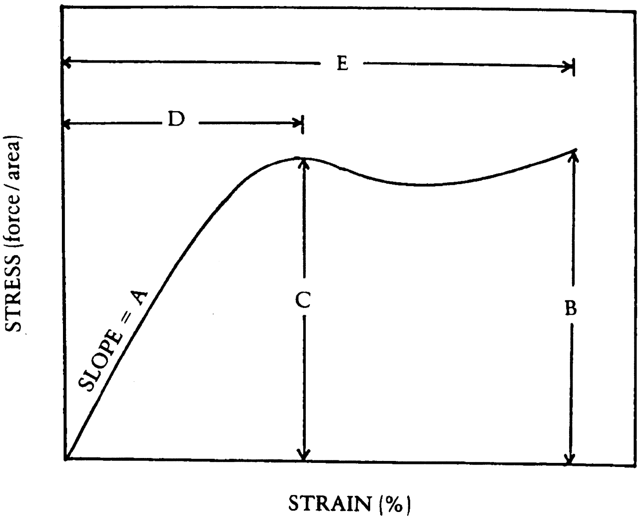


Figure 4.1. *Stress–strain plot. (From Ref. [4], with permission.)*

two ways: (1) *elongation-at-break* is a measure of how much strain (E) is withstood before breaking; and (2) the tensile strength, or *tensile-at-break*, is a measure of the stress (B) when the sample breaks. The area under the curve represents the *work-to-break* (energy vol^{-1}). Quite commonly, as shown in Figure 4.1, at an intermediate strain, the stress required for further elongation decreases. The maximum stress (C) at that point is called the *yield point*. Yield point can also be designated in two ways: *elongation-at-yield* (D) and *yield strength* (C).

An ideal elastic material deforms virtually instantaneously when a stress is applied and recovers its original shape virtually instantaneously when the stress is released. Elastic deformation is, over a wide range, almost independent of temperature. In contrast, viscous flow is time dependent; the flow continues as long as a stress is applied. The rate of deformation depends on the viscosity of the material as well as on the temperature. As a result, viscoelastic deformation is dependent on the temperature and the rate at which a stress is applied. If the rate of application of stress is rapid, the response can be primarily elastic; if the rate of application of stress is low, the viscous component of the response increases and the elastic response is correspondingly lower. Similarly, if the temperature is low, the response can be primarily elastic, whereas at a higher temperature, the viscous response is correspondingly greater.

These differences are illustrated in Figure 4.2(*a*) and (*b*). Plot (*a*) shows, schematically, the results of elongating a film at two different rates at the same temperature. Curve A is the same curve shown in Figure 4.1; curve B results from a more rapid application of stress. In curve A there is time for the sample to undergo some viscous flow along with the elastic deformation. In curve B, the stress was applied at such a rapid rate that there was little time for viscous flow, and the elastic response dominated. Note that as commonly occurs in real samples, elongation-at-break is less, and tensile-at-break is greater, when the rate of application of stress is higher. Plot (*b*) shows the results of pulling the films at the same rate: equal to the slower rate in plot (*a*), but at two different temperatures. Curve A is at the same temperature as in plot (*a*); curve B is at a lower temperature. At the lower temperature, the viscosity was higher, so that even at the slower rate of

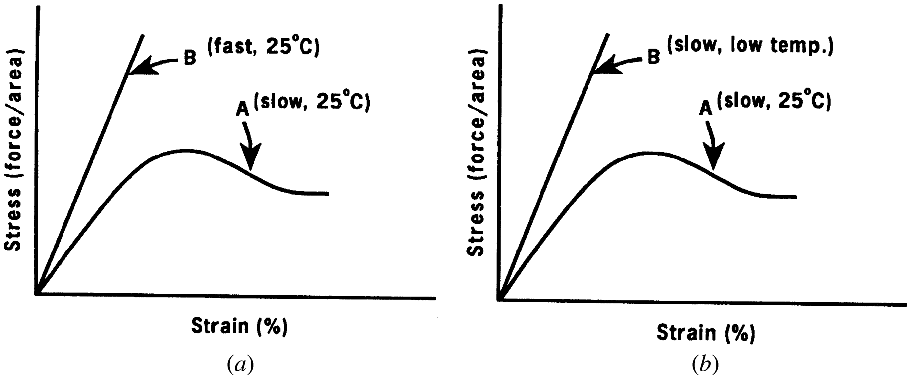


Figure 4.2. Effects of (a) rate of application of stress and (b) temperature on stress–strain responses.

extension, there was essentially no viscous flow, and elastic deformation dominated. At the higher temperature, the viscosity was low enough to permit substantial viscous flow during stretching. As commonly occurs in real samples, elongation-at-break is less and tensile-at-break is higher when the temperature is lower.

Plots (*a*) and (*b*) are identical. The rates of application of stress and temperatures were chosen so that the change in the viscous response would be the same. In viscoelastic materials, the effects of higher rates of application of stress and lower temperatures are in the same directions. It is possible to do time–temperature superpositioning of curves mathematically. If one's instrument cannot operate at as high a rate of application of stress as one would want in order to evaluate stress–strain behavior, one can operate at a lower temperature and then calculate data points at higher stress rates, as discussed in Ref. [4].

Stress–strain determinations are also run in creep or relaxation modes rather than in a tensile mode. In creep experiments, a constant stress is applied and the resulting strain is determined. An ideal elastic material undergoes an instantaneous strain, with stress application at time t_1, that stays constant until the strain is removed at time t_2, as shown in Figure 4.3(*a*). A Newtonian fluid subjected to a creep test shows linearly increasing strain with time, as shown in Figure 4.3(*b*). For a viscoelastic sample, strain is observed to increase over time in a nonlinear manner. Typical responses for cross-linked and thermoplastic coatings (viscoelastic) are shown in Figure 4.3(*c*) and (*d*), respectively. In a relaxation test, one applies an instantaneous strain, elongating the sample, then follows the change in stress with time. The stress stays constant with time for an ideal elastic material, and a Newtonian liquid exerts no stress. For viscoelastic samples, the stress is initially high and drops to lower values (relaxes) with time.

Stress–strain analysis can also be done dynamically by using instruments that apply an oscillating strain at a specific frequency. The stress and strain vary according to sine waves, due to the alternation from the oscillations. The stress and the phase angle difference between applied strain and resultant measured stress are determined. For an ideal elastic material, the maximums and minimums occur at the same angles since there is an instantaneous stress response to an applied strain; the phase shift is 0°. For a Newtonian fluid, there would be a phase shift of 90°. Viscoelastic materials, on the other hand, show an intermediate response, as illustrated in Figure 4.4. If the elastic component is high, the phase shift δ is small; if the elastic component is low compared to the viscous component,

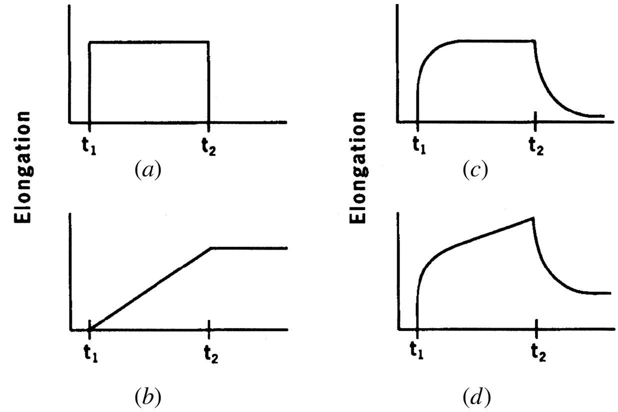
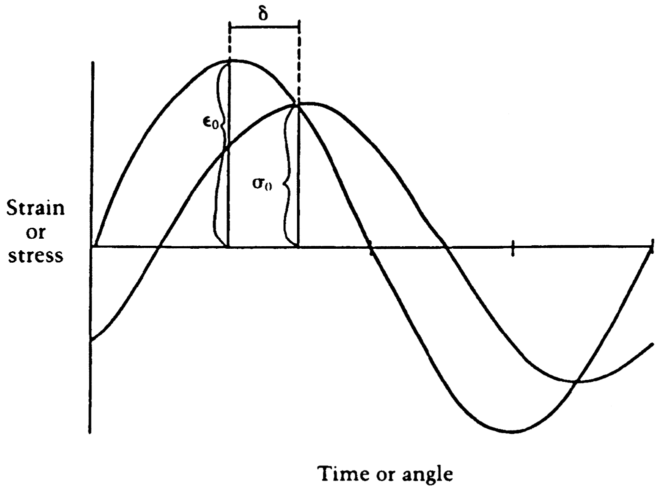


Figure 4.3. *Plots of creep test responses. A constant stress is applied at t_1 and removed at t_2 for (a) an ideal elastic solid, (b) a Newtonian fluid, (c) a viscoelastic sample with cross-links that result in complete recovery, and (d) a viscoelastic sample that shows incomplete recovery. (Adapted from Ref. [4], with permission.)*

the phase shift is large. The phase shift, along with the maximum applied strain ε_0 and the maximum measured stress σ_0, are used to calculate the dynamic properties.

The *storage modulus E′*, also called the *elastic modulus*, a measure of elastic response, equals $(\sigma_0 \cos \delta)/\varepsilon_0$. Its magnitude and physical significance are similar to modulus



$$\text{Storage modulus} = E' = \frac{\sigma_0 \cos \delta}{\epsilon_0}$$

$$\text{Loss modulus} = E'' = \frac{\sigma_0 \sin \delta}{\epsilon_0}$$

$$\text{Loss tangent} = \frac{E''}{E'} = \tan \delta$$

Figure 4.4. *Dynamic mechanical analysis plot as a sinusoidal strain is applied and a sinusoidal stress is determined. (From Ref. [4], with permission.)*

obtained from the initial straight-line slope of a stress–strain curve, such as shown in Figure 4.1. The term *storage modulus* reflects the fact that E' measures the recoverable portion of the energy imparted by the applied strain. The *loss modulus* E'', a measure of the viscous response, equals $(\sigma_0 \sin \delta)/\varepsilon_0$. The term *loss modulus* reflects the fact that viscous flow leads to dissipation (as heat) of part of the energy imparted by the applied strain. The square of the total modulus equals the sum of the squares of the storage and loss moduli. The ratio E''/E' is called the *loss tangent*, since all of the terms cancel except the ratio $\sin \delta/\cos \delta$, corresponding to the tangent of an angle, $\tan \delta$, commonly called *tan delta*.

Dynamic mechanical analysis (DMA) has the advantage over static stress–strain studies, such as that shown in Figure 4.1, that the elastic and viscous components of a modulus can be separated. The frequency of oscillation is a variable related to the rate of application of strain. The higher the frequency, the greater the elastic response: that is, the smaller the phase angle. The lower the frequency, the greater the viscous response: that is, the larger the phase angle. The higher the frequency, the less time there is for viscous flow; hence, elastic response dominates. Similarly, lowering the temperature reduces viscous flow, decreasing the phase angle, and raising the temperature gives greater viscous flow, increasing the phase angle. Generally, it is possible to run experiments over a range of frequencies in dynamic tests that is wider than the range of rates of application of stress possible in linear stress–strain experiments. Furthermore, dynamic testing can be done over a wider range of temperatures and rates of heating. In dynamic tests it is not possible to determine tensile-at-break (tensile strength), elongation-at-break, or work-to-break, since the sample must remain unbroken in order to run the test.

Stress–strain analysis discussed above is based on elongation of samples by application of tensile stress. Oscillating (dynamic) and linear (static) stress–strain analysis can also be carried out by application of shear or compressive forces. In shear tests, the stress is applied sideways—analogous to shear viscosity tests. The ratio of shear stress to shear strain, called *shear modulus*, is represented by the symbol G. For many coatings, the tensile modulus E' equals three times the shear modulus G''. Recall from Section 3.6.3 that the analogous extensional and shear viscosity have the same relationship.

4.3. FORMABILITY AND FLEXIBILITY

In many cases, a coated metal object is subjected to mechanical forces either to make a product, as in forming bottle caps or metal siding, or in use, as when a piece of gravel strikes the surface of a car with sufficient force to deform the steel substrate. To avoid film cracking during such distensions, the elongation-at-break must be greater than the extension of the film under the conditions of fabrication or distortion.

To illustrate some of the variables involved, let us consider the simpler case of a plastic, poly(methyl methacrylate) (PMMA), for which data on stress–strain relationships are available. Tensile stress–strain curves of PMMA ($T_g = 378$ K) as a function of temperature are shown in Figure 4.5. At low temperatures, there is no yield point, the modulus is high, and the elongation-at-break is low. Breakage at low temperature is called *brittle failure*. The terminology confuses some people; at low temperature, PMMA approaches being an ideal elastic material, but its failure is classified as brittle because the

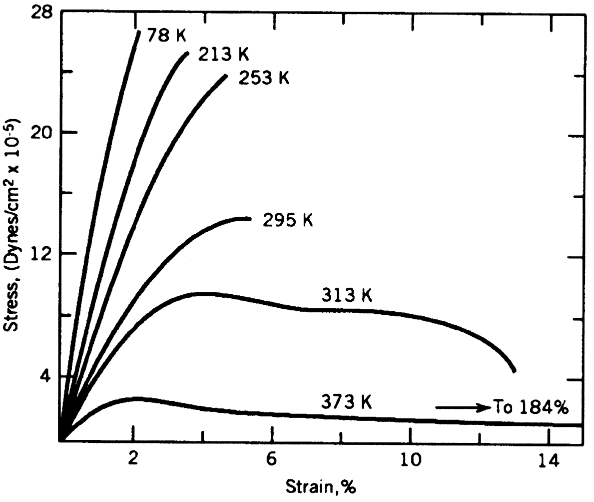


Figure 4.5. *Stress–strain plots of PMMA as a function of temperature. (From Ref. [3], with permission.)*

elongation-at-break is low. At higher temperatures, but still below T_g, greater elongations without breaking are possible, and there is a yield point.

Wu studied the modulus, elongation-at-yield, and elongation-at-break of PMMA and other plastics as a function of temperature [6]. Figure 4.6 shows plots of these three properties versus temperature. The abrupt drop in modulus at T_g is typical of amorphous high molecular weight (MW) thermoplastic homopolymers. Similar data are in the literature for many such polymers. Fewer examples of the plots of elongation-at-break appear. Note that

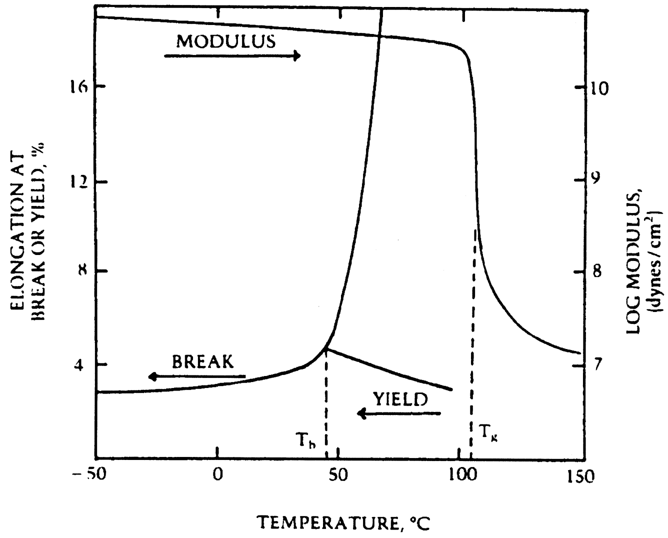


Figure 4.6. *Elongation-at-break and elongation-at-yield as functions of temperature, superimposed on a storage modulus–temperature plot. (From Ref. [5], with permission.)*

elongation-at-break starts to increase rapidly at a temperature below the T_g of PMMA. Wu defines the temperature at the intercept of the elongation-at-break and elongation-at-yield plots as the *brittle–ductile transition temperature*, T_b. (T_b can also be defined as the intercept of plots of tensile strength and yield strength versus temperature.) Below T_b, the polymer is brittle; between T_b and T_g, it is hard and ductile; above T_g, the polymer becomes increasingly soft. Plastics can be deep-drawn above T_b; it is not necessary to be above T_g, which is contrary to the common but erroneous definition of T_g as the temperature below which an amorphous material is brittle.

Copolymers of MMA with methacrylates of longer chain alcohols, such as *n*-butyl methacrylate, have lower T_g and T_b values. There is substantial variation in the difference between T_g and T_b of various thermoplastic polymers, as illustrated by the data in Table 4.1. Since these polymers are viscoelastic, the deformation is dependent on the rate of application of stress as well as on temperature. T_g and T_b are both dependent on the rate of application of stress: The higher the rate, the higher the T_g and T_b values.

Brittle–ductile transition temperature has been studied less with thermosetting systems. The limited data available indicate that polymers with a low degree of cross-linking show a differential between T_b and T_g, but the differential decreases as the cross-link density (XLD) increases. Probably, most thermoset coatings show little, if any, differential between T_g and T_b, but few data have been published. The T_g of cross-linked polymers depends on several factors: structure of the segments between cross-links, XLD, the amount of dangling chain ends, and the extent, if any, of cyclization of the backbone [7].

It has been known for many years that there is a proportional relationship between XLD and the modulus of low XLD elastomers above T_g, but it had been uncertain whether the relationship could be extended to relatively higher XLD coatings. Hill demonstrated that this relationship also holds for melamine–formaldehyde (MF) cross-linked acrylic and polyester coating films [8,9]. The relationship is surprisingly simple, as shown in Eq. 4.1, in which v_e is XLD expressed as the number of moles of *elastically effective network chains* per cubic centimeter of film. An elastically effective network chain is one that is connected at both ends to the network at different junction points: Short cyclical chains and dangling ends are not elastically effective. The terms E and G are tensile and shear storage moduli, respectively. Since E'' and G'' are low at temperatures well above T_g, $E \approx E'$ and $G \approx G'$. It has been suggested that the simple form of Eq. 4.1 is favored when network chains are short and when E' is obtained with very small deformations, as used in DMA [10]:

$$E = 3v_eRT (\text{or } G = v_eRT) \qquad (\text{when } T \gg T_g) \tag{4.1}$$

Thus, at least for the classes of films studied, it is possible to calculate XLD (v_e) from modulus against temperature plots [9]. Note that v_e divided by the film density provides the

TABLE 4.1. Transition Temperatures of Homopolymers

Polymer	T_g (°C)	T_B (°C)	$T_g - T_b$
Polystyrene	100	90	10
Poly(methyl methacrylate)	105	45	60
Poly(vinyl chloride)	80	10	70
Bisphenol A polycarbonate	150	−200	350

moles of network chains per gram. The inverse, grams per mole of network chains, corresponds to the average MW of network chains, frequently called the average MW between cross-links, $\bar{M}_c$. Commonly, $\bar{M}_c$ is erroneously defined and used as the MW per branch point; one must be careful when reading any paper dealing with MW of network chains and XLD. Cross-link density can also be calculated and correlated with XLD measurements by swelling. Correlation is good, although it is necessary to assume an interaction parameter from the extent of swelling of a film by solvent [8]. Although cross-linked films do not dissolve in solvent, solvent does dissolve in a cross-linked film. As cross-links get closer together (i.e., as XLD increases), the extent of swelling decreases.

XLD can also be determined by nuclear magnetic resonance imaging (NMR). The technique has the advantage that one can determine XLD as a function of depth through a film [11]. For example, as expected, the top surface of air dry films of alkyds with only cobalt driers could be seen to have cross-linked selectively. Also, the poor cure of the surface of UV curing films could be seen to be air inhibited.

Equation (4.1) can also be used to predict the storage modulus above T_g from the XLD. In a system with stoichiometric amounts of two reactants whose functional groups react completely, one can estimate the XLD from the equivalent weights and the average functionality. If the reactant mixture contains molecules of several different functionalities, calculation becomes more difficult. A more general approach is provided by the *Scanlan equation*, where ν is moles of elastically effect network chains per cm^3 of polymer film [8]:

$$\nu = \frac{3}{2}C_3 + \frac{4}{2}C_4 + \frac{5}{2}C_5 + \cdots \tag{4.2}$$

The C values are the concentrations of reactants with functionality of 3 to 5 (or more), expressed in units of moles per cubic centimeter of final cured film. The volume of the final film depends on the density of the cured film and loss of volatile by-products of the reaction. Equation (4.2) does not include a term for difunctional reactants because these reactants do not create junction points in a network; they only extend chains. Recent modifications permit consideration of incomplete conversion [10]. Although the Scanlan equation is convenient for stoichiometric reactions, it does not apply to other cases. For non-stoichiometric mixtures and/or incomplete conversion, Miller–Macosko equations are useful general equations. Bauer selected the Miller–Macosko equations as most useful for coatings, gave examples of their applications, and provided a computer program [12].

Properties are affected by the extent to which cross-linking has been carried to completion. Incomplete reaction leads to lower XLD and, hence, lower storage modulus above T_g. The extent of reaction can be followed by determining storage modulus as a function of time [13]. As cross-linking continues, storage modulus increases until a terminal value is reached.

Thus, one can, at least in theory, design a cross-linked network to have a desired storage modulus above T_g by selecting an appropriate ratio of reactants of appropriate functionality. By proper selection of the structures between cross-links and cross-link density, one can design the T_g of the cross-linked network.

Effects related to cross-linking can be achieved by intermolecular hydrogen bonding. For example, the strong hydrogen bonds between urethane groups leads to high abrasion resistance in urethane coatings. When subjected to stress the hydrogen bonds rupture without breaking chemical bonds, relieving the stress. When the stress is released, hydrogen bonds re-form, restoring the original properties.

A related phenomenon results from the presence of mesogenic groups on resins, which when the film is cured, form liquid crystal domains. When stress is applied, the crystal structure can be disrupted, and when the stress is relieved, crystal domains can re-form. The initial examples of such a coating system were prepared by cross-linking a mesogenic diol with hexamethoxymethylmelamine (HMMM) [14]. A variety of resin classes were investigated, including epoxy–amine, polyester, alkyd, and acrylic resins with side chains from *p*-hydroxybenzoic acid. There were non-cross-linked acrylic lacquers, Class I melamine–formaldehyde cross-linked thermosetting coatings, and waterborne coatings. Appropriate levels of mesogenic groups provided both high impact resistance and film hardness, which are generally difficult to achieve in combination [15]. MF resins in which HMMM is reacted with a mesogen such as the hydroxytriphenyl ether of 1,6-hexanediol were used to replace part of the methoxy groups of the HMMM. The resins were tested as coil coating vehicles and showed liquid crystal domains; they provided both high flexibility and hardness [16]. A UV cure coating formulated with an acrylic ester of a mesogenic alcohol also provided both hardness and flexibility [17]. High cost has limited the commercialization of such coatings. Specialty electronic coatings are reported to be in use.

Determination of dynamic mechanical properties has proved to be a valuable tool for studying cross-linking of hydroxy-functional resins with MF resins [8,9]. As the stoichiometric ratio of methoxymethyl groups from the MF resin to hydroxyl groups was raised from values less than 1, the storage modulus above T_g of the fully cured films increased up to the point that the ratio became 1. As discussed in Section 11.3.2, these results show that all of the functional groups on the MF resin can react with hydroxyl groups and the reaction is not limited by steric hindrance, as thought previously. When the amount of MF resin was increased so that excess methoxymethyl groups were present, storage modulus above T_g increased at higher temperatures during dynamic mechanical testing. This behavior is explained on the basis that the excess methoxymethyl groups can undergo self-condensation reactions during testing. The self-condensation reaction is relatively slow and was incomplete during the baking cycle used in preparing the film; hence, the reaction continued at the higher temperatures used in dynamic mechanical analysis, leading to the higher storage modulus. Self-condensation during baking of coatings also occurs when excess MF resin is used; then, the extent of self-condensation increases as baking time and temperature increase.

As done in Figure 4.7, it is common to assign the peak of the tan delta curve as the T_g. Some authors prefer to assign the peak of the loss modulus plot as the T_g. As can be seen, there is a substantial difference between the two. The peak of the loss modulus plot is usually nearer to the T_g determined using DSC. As noted before, T_g is dependent on the rate of heating in DSC (Section 2.1.2) and on the rate of application of stress—the frequency of oscillation—as well as the rate of heating in a dynamic test. This dependence on experimental technique might lead one to wonder if T_g means anything. It does, but one must always be careful to compare T_g values determined in the same way. With regard to fabrication or deformation of coatings, the most relevant T_g is the one determined at a rate of stress application close to the rates of stress encountered in deformation of the coating.

An additional factor that can affect the mechanical properties of polymeric materials is the breadth of the T_g transition region [18]. In some materials, the slope of the transition region is steep, as shown in Figure 4.6. In others, this slope is shallower, as shown in

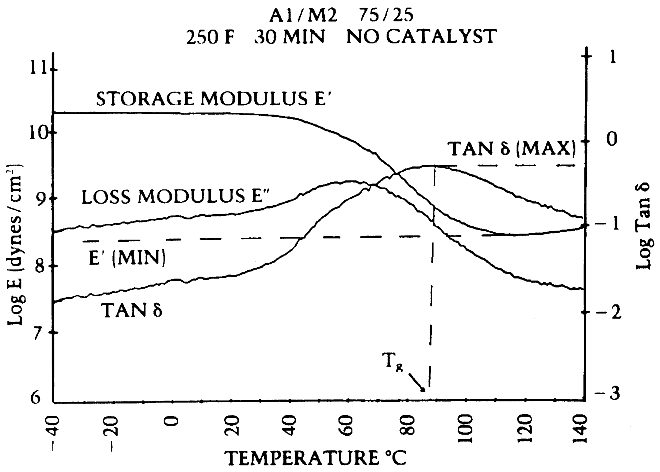


Figure 4.7. Dynamic properties of a highly cross-linked acrylic coating film (solid lines). Dashed lines indicate values E′(min), tan δ(max), and T_g that are measures of the extent of cure. The values of E′(min) and T_g tend to increase, whereas tan δ(max) tends to decrease as the extent of cure increases. (From Ref. [5], with permission.)

Figure 4.7. The same effect can be seen in tan delta plots, which exhibit various breadths. The breadth of the T_g transition region can also be estimated by differential scanning calorimetry (DSC), but dynamic mechanical analysis gives a clearer picture.

Factors controlling the breadth of the T_g transition have been only partly elucidated, but broad tan δ peaks are frequently associated with heterogeneous polymeric materials. Blends of different thermoplastic resins often display two distinct T_g's presumably because of phase separation. Other blends of thermoplastics have a single, often broad, T_g, presumably when phase separation is indistinct or when the phases are very small. For thermosetting polymers, the T_g transition region is generally broader than for thermoplastics, and the breadth may vary considerably. Breadth of the distribution of chain lengths between cross-links is a factor, and blends of thermosetting resins such as acrylics and polyesters often display a single broad T_g transition [9]. As a rule—to which there are probably exceptions—materials with broad and/or multiple T_gs have better impact resistance than comparable polymers with a sharp, single T_g.

Some homogeneous polymers exhibit one or more, usually small, tan delta peaks at temperatures below T_g. These peaks are called *low temperature loss peaks*, or β- and γ-transitions. They are thought to result from the onset of some specific small-scale motions of parts of the polymer molecules as temperature is increased. These transitions have been detected in a number of polymers and, in some cases, related to specific motions of molecule segments [19]. In plastics it is well established that tough, impact-resistant materials generally have low temperature loss peaks; polymers made from bisphenol A (epoxies and polycarbonates) are common examples. It is reasonable to speculate that coatings with low temperature loss peaks may have good impact resistance (if adhesion is good), but the relationship is not well documented in the literature.

Mechanical properties of coatings are generally more complex than those of most plastics. One reason is that coatings are used as thin films on a substrate. Interaction with the substrate affects the mechanical properties of thin films. The substrate can limit the extent of deformation that occurs. The substrate can act as an energy sink to dissipate the energy so that there is less effect on the coating film. Adhesion can have a profound affect on the ability to withstand fabrication. If adhesion is good, the fabrication and impact resistance of the films are almost always superior. Stress within the film can act to pull the film off the substrate. Coatings have been known to pop off postformed metal bottle caps when a jar is sitting on a supermarket shelf. Stress within films can also arise during the last stages of solvent loss and/or cross-linking of films [20]. Solvent loss and cross-linking result in shrinkage. If the shrinkage occurs when the temperature is near the T_g of the film, the resulting internal stresses may persist indefinitely. (See Section 6.2 for a discussion of the effects of internal stresses on adhesion.)

Film thickness is also a factor in the ability of a coating film to withstand fabrication without cracking. Thin films can be used for deeper draws than can thick films. In making coated exterior siding, the hardness of the film can be increased without encountering cracking by limiting the film thickness. Of course, thinner films of pigmented coatings give poorer hiding; a common compromise in this case is at 20- to 25-μm film thickness. Two-piece fish cans are coated as flat sheets with a relatively highly cross-linked phenolic coating that is quite brittle, to minimize swelling with fish oil. Such cans can be formed successfully without cracking only if the film thickness is 5 μm or less.

Pigmentation affects the mechanical properties of films. In many cases, as the pigment volume concentration of films is increased up to the critical pigment volume concentration, the tensile strength of the films increases (Section 21.1). A DMA study of aluminum pigmented base coats showed that the E' increased tenfold as the pigmentation increased in five steps from 0 to 13 PVC [21]. It is also possible that imperfections resulting from some types of pigmentation may lead to crack propagation. In some cases, the storage modulus above T_g is increased by the presence of pigment. For pigmented coatings, one cannot expect a direct proportional relationship between storage modulus (E') above T_g and XLD [8]; however, if the pigment content is constant in a series of films varying in the polymeric portion, the relative values of E' should still indicate relative XLDs for the pigmented films. A study of the effects of pigmentation on mechanical properties of coatings is available. Tan delta is lower, broader, and shifted to higher temperature by pigmentation. E' is increased, but above CPVC it decreases. Tensile strength generally increases with PVC and then drops sharply above CPVC. However, if there is poor bonding between the pigment particles and the resin, as is the case with $CaCO_3$ in an acrylic binder, the tensile strength drops steadily as the PVC increases [22]. (See Section 22.1.1 for further discussion.)

Nano-pigments can have substantial effects on mechanical properties. Nano-pigments are those with small particle size; some authors include those with average particle sizes of less than 100 nm, but more commonly the particle size is below 25 nm. The term is new but nano-pigments have been used in coatings for many years. For example, high strength channel blacks have particle sizes in the range 5 to 15 nm. A review paper on nano-material technology applications in coatings is available [23].

Compared to the effects of conventional pigments, nano-pigments, especially nano-fillers, improve scratch, abrasion, heat, radiation, and swelling resistance, decrease water permeability, and increase hardness, weatherability, modulus, and strain-to-failure while maintaining toughness. These properties reflect the high surface area of nano-pigments, resulting in an increase in adsorption of resin on the pigment surfaces and a larger fraction of immobilized resin. In some cases, the films have two T_gs. Nano-pigments have been shown to increase E' and, in some cases, the T_g of clear-coat films [21]. When the particle size of the pigments is smaller than the wavelength of light, coatings pigmented with nano-pigments are transparent [24]. Ball mills are used to disperse nano(aluminum silicate) in an acrylic resin with a commercial dispersing agent. The dispersion is used in making mar resistant clear coats [25].

The effect of heterogeneity in coating films has been recognized increasingly as an important factor with regard to mechanical properties [26]. Most obviously, as pigment volume concentration (PVC) of a film increases, the elastic modulus increases due to the reinforcing effect of pigments. If the pigment is increased above the critical pigment volume concentration (CPVC), the tensile strength drops precipitously (Chapter 22). The increase in elastic modulus is affected by the aspect ratio of the pigments: fibrous > laminar > spherical. One can obtain significant effects by incorporating elastomeric particles in a coating. The use of a combination of low T_g and high T_g components gives films with higher blocking resistance and longer elongation.

Another important variable can be the timing of fabrication or flexing after curing a coating. It is common for coatings to become less flexible as time goes on. Particularly in air dry coatings, some solvent may be retained in films. Since most coatings have T_g values near or a little above room temperature, solvent loss may be very slow (Section 18.3.4). Solvents generally act as plasticizers, so as solvent is lost, T_g and storage modulus increase and coatings tend to become less flexible. In cross-linkable coatings, if the cross-linking reaction was not complete, the reaction may continue slowly, increasing XLD and, hence, storage modulus and decreasing flexibility. Continued cross-linking is particularly likely to occur in air dry coatings, since reaction rates are likely to become mobility rate controlled, and hence, the last part of the reaction is slow, as discussed in Section 2.1.3. Reactions during the use life of the coating, especially during exterior exposure (Section 5.1), can result in embrittlement. Dynamic mechanical analyses of a variety of clear coats after Florida exposure and QUV testing show the changes in mechanical properties resulting from exposure [27].

Hardening of baked cross-linked coatings over time is also commonly observed. Although in some cases, further volatile loss or continued cross-linking may be responsible, another possible factor is *densification*. If a polymer is heated above its T_g and then cooled rapidly (quenched), the density is commonly found to be lower than if the sample had been cooled slowly. During rapid cooling, more and/or larger free volume holes are frozen into the matrix than with slower cooling, which provides greater chances for molecular motion. On storage, the molecules in quenched films slowly move even though the temperature is somewhat below T_g and free volume decreases, causing densification. Since this process results in changes in properties with ageing with no chemical change, it is also called *physical ageing*. With the decrease in free volume and the increase in density, cracking during fabrication is more likely. This phenomenon has been widely observed in plastics and is increasingly being recognized in coatings. It may occur when coatings are baked on metal at high temperatures and then cooled rapidly after coming out of the oven. It has been suggested that densification may be a common cause of embrittlement during ageing of baked coating films. Greidanus has studied physical ageing at 30°C of polyester/MF films that had been baked at 180°C and then quenched to 30°C [28]. There was a small but reproducible increase in modulus with time at 30°C. The aging rate (i.e., the rate of increase of modulus) decreased with time. If the sample was heated again at 180°C and again quenched to 30°C, the modulus returned to its lower value and underwent physical ageing again. Perara has shown that relative humidity can also affect physical ageing; samples stored at high humidity age more quickly that those stored at 0% RH because of the plasticizing effect of water relaxing the polymer so that it can rearrange to its "normal state" [29]. Perara [29] also reviews the field of physical ageing extensively. Further work is needed, but it is evident that physical ageing can be an important phenomenon.

When coatings are baked industrially, there are further complications involved. Oven temperatures can vary not only the air temperature in the oven as a whole, but also within the oven. The rate of heating of a coating can depend on the substrate thickness. For example, the temperature of the coating on the sheet metal roof of a car increases faster than the temperature of the coating on joints, where the metal thickness is greater. To achieve the desired properties, some minimum time at a temperature is required, but overbaking can lead to excessive cross-linking. There is a *cure window* for any baked coating; within this range of time and temperature, satisfactory properties are obtained. As discussed in Section 11.3, high-solids acrylic melamine coatings have narrower cure windows than conventional solids coatings had. The effects of some of the variables in thermal history have been modeled [30].

4.3.1. Fracture Mechanics

When exposed to stress, some coatings crack, leading to drastic film failure. Weathered clear coats on automobiles, fabrication of precoated metal, grain cracking of some wood furniture finishes, and cracking of exterior house paint are examples. All of these are examples of failure by fracture mechanics. For a variety of reasons, stresses can accumulate in films; if the stresses exceed the tensile strength of the films, failures will result. The main sources of stress in coatings are thermal expansion mismatches, humidity stresses due to mismatches in swelling between the coating and the substrate, increased cross-linking such as by exterior exposure, and densification due to physical ageing.

The failure of clear coats on automobiles has been studied. Such failures are encountered especially after weathering. When coatings are exposed to UV radiation and high humidity, cross-link density increases, which leads to shrinkage of the film, increasing stress. Fracture mechanics of weathered automobile coatings has been discussed in an excellent paper [31]. With UV absorbers, the protection is least at the surface, leading to higher cross-linking at film surfaces and in turn to surface cracks. To study the stresses required to grow cracks in weathered automobile coatings, cracks of known size are made in the base coat and clear coat on steel. Then they are extended in a tensile tester and the strain is determined at which cracks in the clear coat are observed. The driving force, G, can be calculated with the equation where E_f is the modulus divided by $(1 - \nu_f)^3$ (ν is Poisson's ratio, typically taken to be near 0.35), Z is a geometry constant (3.95 for surface cracking), σ is the stress applied, and h is the thickness of the clear coat.

$$G = \frac{Z\sigma^2 h}{E_f}$$

When the driving force exceeds the fracture energy ($G \geq G_c$), crack propagation ensues. Note that fracture energy depends on film thickness and on the stress squared.

In the same study coatings on strips cut from weathered panels were pulled in tension in a mechanical testing machine at 20 mm min^{-1} and the strain at which cracks appeared was noted. Uncertainty in results was large; testing 8 to 10 samples reduced uncertainty to $\pm 25\%$. The following equation was used to calculate G_c:

$$G_c = \frac{\varepsilon^2 h E_f \pi g(\alpha, \beta)}{2}$$

where ε is the strain at cracking and $g(\alpha, \beta)$ is a constant relating to the mismatch between the coating and the underlying layer. For a coating on steel $g(\alpha, \beta) = 0.78$, and for a clear coat on a base coat it equals 1.26. In coatings that cracked on exposure, failures almost always occurred in the clear coat layer. If adhesion between the clear coat and base coat was poor, failure resulted in delamination.

Further understanding of changes in G_c was gained by study of films of the separate base and clear coatings [32]. The effects of temperature change and exposure to different levels of relative humidity were reported. Overbaking was shown to reduce G_c. Three MF–acrylic clear coats showed that the G_c varied considerably with formulation; an epoxy–acid clear coat showed the lowest G_c. Cracks can also propagate to the surface between the top coat and the lower interface, which may then lead to delamination. (See Section 6.2 for a discussion of fracture mechanics and adhesion.)

4.4. ABRASION AND MAR RESISTANCE

Abrasion is the wearing away of a surface, whereas *marring* is a disturbance of a surface that alters its appearance. Both phenomena are included in the field of *tribology*, the science of surfaces in sliding contact. Terminology is not standardized, and terms such as *scratching*, *buffing*, *gouging*, and *wearing* are used with meanings that sometimes overlap *abrasion* and *marring*.

4.4.1. Abrasion Resistance

One might suppose that hard materials are less likely than soft materials to fail by abrasion. In some cases, this assumption is true, but in many other cases, softer materials are more abrasion resistant; for example, rubber tires resist abrasion far better than steel tires. Evans studied the mechanical properties of a series of floor coatings with known actual wear life [33]. He determined tensile-at-break, elongation-at-break, and work-to-break. His data are given in Table 4.2; the coatings are listed in order of increasing wear life. One might suppose that higher tensile strength would give higher abrasion resistance; the data show the reverse. (It should not be assumed from these limited data that abrasion resistance is always inversely related to tensile strength.) Elongation-at-break values gave

TABLE 4.2. Mechanical Properties of Floor Coatings

Floor Coating	Tensile Strength (psi)	Elongation-at-Break (%)	Work-to-Break (in.-lb/in^3)	Taber[a] (rev/mil)
Hard epoxy	9000	8	380	48×10^3
Medium epoxy	4700	19	600	33×10^3
Soft epoxy	1100	95	800	23×10^3
Urethane elastomer	280	480	2000	36×10^3

[a] See Section 4.6.3.4 for a discussion of these results.

the proper rank order, but Evans concluded that work-to-break values best represented the relative wear lives. Intuitively, it seems reasonable that abrasion resistance would be related to work-to-break. Work-to-break values vary with the rate of application of stress and should be determined at a rate comparable to that encountered in use.

In studies on another series of coatings, Evans and Fogel determined that work-to-break did not always correlate with abrasion resistance determined by loss of gloss in a ball mill abrasion tester when the stress–strain tests were carried out at ambient temperatures [34]. They reasoned that the strain rate of their instrument was too low relative to the stress application in the test. Using a time–temperature superposition relationship, they calculated that the tests at an accessible strain rate should be carried out at $-10^{\circ}\mathrm{C}$ in order to compensate for the instrumentally inaccessible high rate of stress application at ambient temperature. The resulting work-to-break values did correlate with abrasion resistance for urethane films with a T_g equal to or greater than $-10^{\circ}\mathrm{C}$.

In studies of erosive wear of clear coats for automobiles, it has been shown that wear resistance increases as energy-to-break of films increases [35]. Erosion rate is also affected by the substrate; for example, clear coats applied directly to steel showed significantly less durability than when applied over primer and base coats. Wear tends to increase as the angle of application of stress decreases.

Urethane coatings generally exhibit superior abrasion resistance combined with solvent resistance. This combination of properties may result from the presence of intersegment hydrogen bonds in addition to the covalent bonds. At low levels of stress, hydrogen bonds act like cross-links, reducing swelling on exposure to solvent. At higher levels of stress, the hydrogen bonds can dissociate, permitting the molecules to extend without rupturing covalent bonds. When the stress is released, the molecules relax and new hydrogen bonds form. Urethanes are used as wear layers for flooring, as well as top coats in aerospace applications, where this combination of properties is desirable.

Factors in addition to work-to-break are involved in abrasion resistance. The coefficient of friction of the coating can be an important variable. For example, abrasion of the coating on the exterior of beer cans during shipment can be minimized by incorporating a small amount of incompatible wax or fluorosurfactant in the coating. When the two coated surfaces rub against each other, the incompatible additive reduces surface tension and the coefficient of friction, so that transmission of shear force from one surface to the other is minimized and abrasion is reduced.

Another variable is surface contact area. Incorporation of a small amount of a small particle size SiO_2 pigment in a thin silicone coating applied to plastic lens eyeglasses reduces abrasion, adding to the effect of the low surface tension of the silicone surface. The pigment particles reduce contact area, permitting the glasses to slide more easily over a surface. Another example of the same principle is the incorporation of a small amount of coarse SiO_2 inert pigment in wall paints to reduce *burnishing*. If a wall paint without such a pigment is frequently rubbed, as around a light switch, it abrades to a smoother glossier surface: that is, it burnishes. The coarse inert pigment reduces burnishing by reducing contact area.

An approach that has been used for many years in resin-bonded pigment print colors on textiles is to incorporate rubber latex in the print paste. The latex particles are not soluble in the resin and end up as individual particles in the resin, along with the pigment particles. The abrasion resistance is markedly improved by the latex addition. Similar work is now being done to improve the abrasion resistance of continuous coatings. Presumably, the relatively soft rubber particles act to dissipate stresses on the film, minimizing the chance of a stress concentration leading to film rupture. Glass microspheres have been shown to increase abrasion resistance of epoxy coatings by damping the energy released by impacts on the surface [36]. Lee reviewed abrasion resistance as one type of wear in a broad approach to fracture and surface energetics of polymer wear [37].

4.4.2. Mar Resistance

Mar resistance is related to abrasion resistance, but there is an important difference. Abrasion may go deeply into the coating, whereas marring is usually a near-surface phenomenon; mars less than 0.5 μm deep can degrade appearance. Marring is a major problem with automobile coatings, particularly those with a clear coat as the final top coat (Section 30.1.2). In going through automatic car washes, the surfaces of some clear coats are visibly marred and may lose gloss due to marring [38,39]. Mar resistance is also a critical requirement in coatings for floors and for transparent plastics: for example, on polycarbonate glazing or eyeglasses. Physically, marring is a complex phenomenon; while mars may be very shallow, the physical properties deep in the coating film can influence mar resistance.

The physics of marring is complex. Different authors use different terms to describe the phenomena involved. Various models have been proposed to describe what happens to a viscoelastic material when a hard object is drawn over its surface. One such model classifies the response of the material as elastic, plastic, or fracture. Since the elastic response recovers essentially instantaneously, only plastic deformation and fracture lead to marring. Qualitatively, mars caused by plastic deformation have shoulders, whereas those caused by fracture do not. Although simplistic, this model has the advantage that the three responses can be measured quantitatively by scanning probe microscopy [40] or with a nano-indenter [41]. Most coatings exhibit a mixture of responses. Different coatings vary widely in their responses, and the same coating may respond quite differently as the force or rate of marring stress changes. A further complication is that mars in some coatings can heal slowly by reflow (creep).

Efforts are underway to relate mar resistance to the chemical structure of coatings, but relatively few systematic studies have been published. In general, MF cross-linked acrylic clear coats are more resistant than isocyanate cross-linked coatings (urethanes) to marring, but MF cross-linked coatings have poorer environmental etch resistance. MF cross-linked polycarbamates are an exception, combining etch and mar resistance (Section 11.3.4). Since urethanes generally have superior abrasion resistance, it is surprising that they have inferior mar resistance; possibly, this might be explained by differences between surface and bulk properties. A study of marring of clear coats by a scanning probe microscope indicated that an acrylic polyurethane had a thin layer of deformable plastic material on its surface, whereas an acrylic–MF clear coat had a layer of elastic material [40]. Reference [42] reviews mar test methods and compares them by subjective estimations of performance. Methods include two simulated car wash tests, a crockmeter test originally developed for evaluating abrasion of colored textiles, microindentation hardness tests, scrub resistance tests, a Rota-Hub test, a collate sanding machine, microscratch resistance, a nano-scratch tester, and dynamic mechanical analysis. Reference [43] compares a variety of scratch tests on cross-linked trimethoxypropylsilane-functional clear coats for plastics. New instruments, *nanomechanical analyzers* (nano-indenters), that can characterize near-surface mechanical properties are now available [44,45].

Two strategies are available for the design of coatings with exceptional mar resistance. They can be made hard enough that the marring object does not penetrate far into the surface, or they can be made elastic enough to recover after the marring stress is removed. If the hardness strategy is chosen, the coating must have a minimum hardness. If the T_b (Section 4.2) is above the testing temperature, groove formation is minimized; however, such coatings may fail by fracture. Film flexibility is an important factor influencing fracture resistance. Use of 4-hydroxybutyl acrylate instead of 2-hydroxyethyl acrylate in an acrylic resin cross-linked with MF resin gave improved results, as did use of a polyol-modified hexamethylene diisocyanate isocyanurate instead of isophorone diisocyanate isocyanurate in cross-linking urethane coatings [46]. Further improvement was obtained using silicone-modified acrylic resins. Courter proposes that maximum mar resistance will be obtained with coatings having as high a yield stress as possible without being brittle [47]. In this way, high yield stress minimizes plastic flow, and avoidance of brittleness thereby minimizes fracture. Courter's paper provides a good review of attempts to relate bulk mechanical properties of coatings to their mar resistance, but these studies have not led to a broadly applicable theory of marring. This is understandable, since the mechanical properties near a coating's surface are likely to be quite different from the mechanical properties of the bulk material.

A study of the scratch resistance of 49 different clear top coats subjected to a simulated car wash test has been reported [48]. High correlation between measurements and visual evaluation was obtained. Determination of dynamic mechanical proper ties showed that best performance was associated with high storage modulus at a relaxation time of 1 s and high minimum strain that would cause plastic deformation of the films.

A further problem related to mar resistance is *metal marking*. When a metal edge is rubbed across a coating, a black line is sometimes left on the coating where metal has rubbed onto the surface of the coating. A common test for metal marking resistance is to draw a coin across the surface of a coating to see if a dark streak is left. Coating lore says that a Canadian nickel is the best kind of coin to use. Metal marking usually occurs with relatively hard coatings. The problem can be reduced or eliminated by reducing the surface tension of the coating, so the coefficient of friction is low; then the metal slips over the surface. Additives can be incorporated to increase slip. Modified polysiloxanes have been reported to be particularly effective [49]. Care must be exercised in selecting the particular grade of silicone additive and the amount of the additive used so as to minimize marring, scratching, and metal marking without causing other defects, such as crawling.

4.5. MEASUREMENT OF MECHANICAL PROPERTIES

Most instruments require free films for measurement of mechanical properties. Two major disadvantages to using free films are that (1) the interaction of the film with the substrate can have major effects on some film properties, and (2) free films are sometimes difficult to prepare and handle. Test results are generally more reproducible with thick films than with thin films; however, the results with thick films may not be applicable to thin films. Preparation of thin unsupported films can be difficult. In some cases, it is possible to make a film by drawing down a coating on a release paper with a wire wound bar. Release papers are coated with low surface tension materials to minimize adhesion; but if the surface tension of the release paper is lower than the surface tension of the coating being applied, there is the possibility of crawling; that is, the coating tries to minimize surface free energy by drawing up into a ball. (See Section 23.4 for a discussion of crawling.) One tries to find a release paper with a low enough surface tension so that adhesion is poor, but high enough so that crawling does not occur. A generally more effective method is to apply the coatings to tin-plated steel panels. After curing, one end of the panel is placed in a shallow pool of mercury. Mercury creeps under the coating, forming an amalgam with the tin, and the film comes free of the panel. Mercury vapor is toxic, and care must be taken to minimize the hazard. The safety regulations of some laboratories forbid such use of mercury. After the film is freed from the substrate, a specimen is cut from it. Cutting free films may result in nicks or cracks along the edge of the film. When subjected to stress, cracked films commonly tear easily starting at the imperfection, leading to meaningless results. Handling films with a T_g above room temperature is especially difficult; they tend to be brittle and easily broken.

One must be careful about changes that may occur during storage before testing, such as loss of residual solvent, chemical changes, or physical ageing. Test results will correspondingly change with time. Storage conditions can be critical. Most films absorb some water from the atmosphere. If the T_g is near room temperature, and especially if the film has groups such as urethanes that hydrogen bond strongly with water, the T_g and film properties can be strongly affected by the humidity conditions in storage, since water acts as a plasticizer. Comparisons should be done with samples that have been stored at the same temperature and humidity. In actual use, films encounter a variety of humidity conditions and hence show a variation in properties.

Several types of instruments are available for determining mechanical properties. The Instron Tester is used for tensile (nondynamic) experiments. The free sample is mounted between two jaws of the tester; care must be taken to ensure that the film is in line with the direction of pull. The instrument can be run with a range of rates of jaw separation, but even the highest rates are slow compared to the rates of stress application found in many real situations. This problem can be partially overcome by running the tests at low temperatures. This method has the advantage that stress can be increased until the film fails, making possible determination of tensile strength, tensile modulus, elongation-at-break, and work-to-break. However, one cannot separate the viscous and elastic components of the mechanical properties.

A thermal mechanical analyzer (TMA) is a penetrometer that measures indentation versus time and temperature. An advantage over most tensile instruments is that a TMA includes a furnace and temperature programmer, so that heating, cooling, and isothermal operations are possible. TMAs can be used with films on a substrate. An example of TMA is measuring the *softening point*, which is related to the extent of cure of cross-linking films. Figure 4.8 shows a plot of probe penetration as a function of temperature for an undercured and a well-cured 25 μm acrylic coil coating. The softening points for the two samples are marked on the graph. The softening point is related to, but not identical to, T_g; it is frequently used as an index of flexibility [50].

Various dynamic mechanical analyzers (DMA) are also available [51]. The most versatile are those in which the free sample is subjected to an oscillating strain by attachment under tension to a fixed clamp on one end and a vibrating clamp on the other. Oscillating stresses are imparted to the sample. A range of frequencies can be used, and properties can be determined over a wide range of temperatures. The most sophisticated instruments are set up in line with a computer that analyzes the data and provides storage and loss modulus

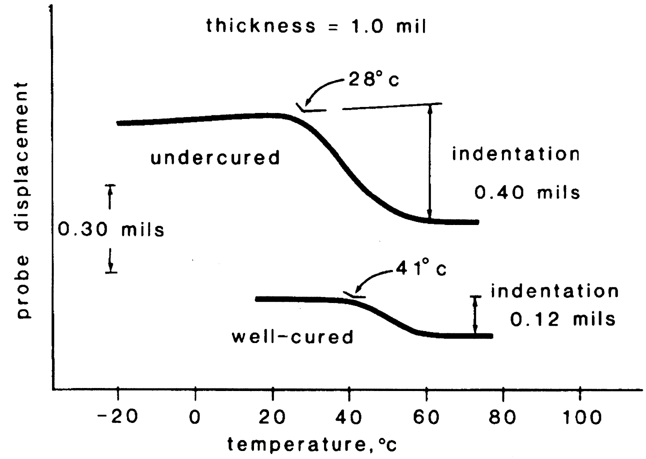


Figure 4.8. TMA plot of probe displacement against temperature for an undercured and a well-cured acrylic coil coating. (From Ref. [5], with permission.)

and tan delta figures and plots as functions of temperature. A schematic diagram is shown in Figure 4.9.

Two types of DMA rheometers are available: controlled stress (CSS) types and controlled shear rate (CSR) types. In CSS rheometers one presets a stress and measures the resulting deformation or shear rate. In CSR rheometers one presets the shear rate and measures the stress. Rheometers that can operate in either mode are also available.

Another type of instrument used for dynamic mechanical analysis is a torsional pendulum. In its simplest form, one end of a film is fastened in jaws, and the lower end is attached to a disk to which weights can be added. The lower weight is twisted, setting up a pendulum motion whose decay can be analyzed to give the dynamic properties. Torsional pendulums have been most widely used not with film but with a fiber braid that is saturated with liquid cross-linking polymers. The instrument has the advantage that it can be used to follow changes in dynamic properties, starting with liquid coatings as reactions occur on the braid. It has the disadvantages that the sample is not a film and that there are large surface areas of fiber–polymer interface that may affect properties. A torsional pendulum apparatus has been modified so that shrinkage can be measured simultaneously with mechanical properties [52]. Since the volume change is largely

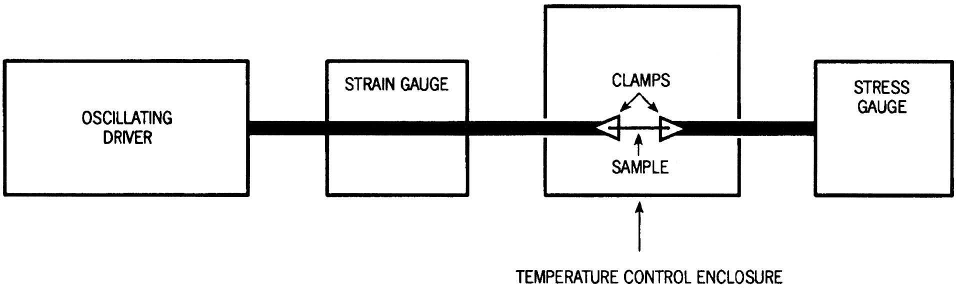


Figure 4.9. Dynamic mechanical analyzer.

proportional to the extent of cure, it can be used as a measure of the progress of cure, while simultaneously measuring changes in mechanical properties.

The range of tensile modulus that can be measured with a torsional pendulum without changing the weight on the pendulum is limited. Furthermore, since the resonance frequency is used as a measure of viscoelastic behavior, modulus results and the measuring frequency are not independent. These difficulties can be overcome by using a DMA instrument with glass or carbon fiber braid support [53].

4.6. TESTS OF COATINGS ON SUBSTRATES

A variety of test methods has been established to characterize properties of coatings. In general, these methods do not permit calculation of the basic mechanical properties, but rather, test some combination of properties of the coating. There are two categories of such tests: One type can be appropriate for prediction of actual performance; the second type is only suitable for quality control. There are very real needs for both types of tests. But too commonly, paint tests, which may be appropriate for quality control, are used to predict performance, even though they are not capable of providing results that permit performance predictions. Three broad classes of coating tests are field exposure tests, laboratory simulation tests, and empirical tests.

4.6.1. Field Exposure Tests

As stated in the introduction to this chapter, the only reliable way of knowing how a coating will perform is to use it and see how it performs. The next best approach is to use the coating in field applications on a smaller scale and under especially stringent conditions that may accelerate possible failure. The more limited the test and the greater the degree of acceleration, the less reliable are the predictions, but carefully designed and analyzed tests of this type can be very useful. There are many examples; we cite a few to illustrate the principles.

Highway marking paints can be tested by painting stripes across the lanes of traffic instead of parallel to the traffic flow. In this way, exposure of the paint to wear is greater, and many paints can be tested and compared on a short length of highway, where they will receive the same amount of traffic wear. Controls with known performance should be tested alongside new coatings. Tests should be done at different times of the year because the effects of hot sun, snow plows, salt application, and so on, must be considered. Tests should be set up on different types of highway materials, such as concrete and asphalt. Floor paints can be evaluated similarly in busy hallways.

Test automobiles painted with new coatings are driven on *torture tracks* with stretches of gravel, through water, under different climate conditions, and so on. Sample packs of canned goods are made; the linings are examined for failure and the contents evaluated for flavor after various lengths of storage.

4.6.2. Laboratory Simulation Tests

Many tests have been developed to simulate use conditions in the laboratory. The value of these tests depends on how well use conditions are simulated and how thorough a validation procedure has been used. An important key to the value of any test for performance prediction is the simultaneous evaluation of standards with known performances that cover the range from poor to excellent performance. It is not enough to use only the extremes of standards; although such information may be a first step for checking the possible applicability of a test, performance prediction requires more than two standard data points. Enough replica tests must be run to decide how many repeat tests must be run to give results within desired confidence limits. Chemists commonly think of standard deviations, but these are only 67% confidence limits; the odds are 33% that the proper value is outside the standard deviation range. (See Ref. [2] for a comprehensive discussion of problems in predicting service life.)

An example of a well-validated test is the laboratory shaker test devised to simulate the abrasion of can coatings when six-packs of beer are shipped by railcar [54]. Six-packs are loaded onto a shaker designed to simulate the pressures, rate of shaking, range of motion, and so on, actually encountered in rail shipments. The test was validated using cans with known field performance. The times to reach different degrees of abrasion failure were established. In unpublished work, in laboratories of several coatings suppliers and can manufacturers, the results were compared with known performance and with the results of standard abrasion tests. It was found that none of the standard laboratory abrasion tests gave satisfactory predictions, but this test gave results that could be used for performance prediction.

The automobile industry uses *gravelometers* to evaluate resistance of coatings to chipping when struck by flying gravel. Pieces of standard gravel or shot are propelled at the coated surface by compressed air under standard conditions, usually at low temperature. The tests have been standardized by comparison to a range of actual results and have been found to give reasonably good predictions of actual performance. A more sophisticated instrument, a precision paint collider, which permits variations in angle and velocity of impact and temperature has been described [55]. It was used in studies of impact failure of various coatings on automotive bumpers made with various plastic polymers. In some cases, cohesive failure occurred in the upper layers of the plastic; in other cases, the coating delaminated from the plastic.

Several laboratory devices are available that approximately reproduce stamping or other forming operations to test the ability of coated metal to withstand fabrication. Individual companies design such tests to match the conditions of their factory's forming operations as closely as possible. Commonly, such simulation tests check only one or a few of the performance requirements, so they must be used along with other tests to predict overall performance. For example, the shaker test for beer cans obviously can give no information on the important ability of the coating to withstand the pasteurization procedure, but separate simulation tests are available for testing pasteurization performance. In most cases, simulation tests are designed for use in performance prediction rather than quality control. Generally, the sample preparation and testing time are too long for checking whether production batches are equal to the standard.

4.6.3. Empirical Tests

A range of empirical tests is used for coatings. In some cases, the results can be used as part of the data to predict performance, particularly when comparing formulations that are very similar to standards with known performance. In most cases, empirical tests are more appropriate for quality control. They are frequently required in product specifications, an appropriate practice when empirical tests are used for quality control. But quality control tests established for one coating should be revalidated if they are to be applied to a new type of coating. Commonly, there is a considerable range of error, and many replicates should be run.

We can only mention a few of the most widely used tests. ASTM annually publishes books describing tests; most of the tests of importance to the coatings field are in Volumes 06.01, 06.02, and 06.03: *Paint—Tests for Formulated Products and Applied Coatings*. The books are published annually, but most of the methods are not changed, although they are supposed to be reviewed every four years. Each method has a number, such as ASTM D-2794-93 (Reapproved 1999). The "93" indicates that the test was approved in 1993. In this particular case, the test was reevaluated and reapproved in 1999. If one finds a reference to a test as D-1876-71 and then refers to a 1997 ASTM book and finds it listed as D-1876-88, it means that the test was last reviewed, and possibly revised, in 1988. In general, one should use the new test method. Sometimes, a method will be designated as D-459a. The "a" indicates that there was a minor rewriting that did not change the basic method. A too common assumption is that because a test method is given an ASTM designation, it can be used not just for quality control, but also to predict performance. This is frequently not the case. However, following ASTM procedures does provide the best chance of obtaining comparable test results. Some ASTM methods include precision statements, usually based on repeatability and reproducibility studies involving different laboratories. The precision statements should not be ignored; many people believe that the tests are more precise than they proved to be in ASTM round robin tests [56]. In Europe, tests established by the German Institute for Standards (Deutsches Institut für Normung, DIN) are widely used.

A useful reference book is the *Paint and Coating Testing Manual: Gardner–Sward Handbook* [57]. It provides descriptions of a wide range of test methods and summaries of each major class of properties, as well as background information and comparisons of the utility of various tests. Hill provides a brief informative, discussion of the more important tests in his monograph on mechanical properties [51].

4.6.3.1. Hardness Measuring the hardness of a viscoelastic material is not as straightforward as it might appear. Units of hardness, force per unit area (Nm^{-2}), are the same as those of modulus. When interpreting hardness and modulus data, it is important to know how the force was applied (tensile, shear, bending, or compressive?), the rate of application of stress, and the temperature. Since the area changes during deformation, it is also important to know what the area was before, during, and after deformation. As reviewed by Guevin, three types of empirical hardness tests are used for coatings: indentation, scratch, and pendulum tests [58].

One indentation test is run with a Tukon Indentation Tester (ASTM D-1474-98). An indenter with a diamond-shaped tip is pressed into the film with a fixed weight for a fixed time. The indenter is raised, and the indentation left in the film is measured with a calibrated microscope. The results are expressed in Knoop Hardness Numbers (KHN), which are related to the weight divided by the area of the indentation. Results are affected by film thickness; thin films on hard substrates give higher values than do thicker films of the same coating. Meaningful results are obtained only with high T_g films. Intermediate-T_g materials may have partial recovery of the indentation in the time needed to move the sample under the microscope and make the measurement. Low T_g films give considerable response variation, and the indenter may leave no indentation at all on a rubbery material. A careless tester may conclude that a rubbery material is very hard, even though it is obviously soft. The Tukon method is most appropriate for baked coatings, since they are more likely to have a T_g above the testing temperature.

A widely used scratch test is the pencil hardness test (ASTM D-3363-00). Pencils with hardnesses varying from 6B (softest) to 9H (hardest) are available. The "lead"—actually graphite and clay—in the pencil is not sharpened as for writing, but is squared off by rubbing perpendicularly on abrasive paper. For the test, the pencil is held at a 45° angle to the panel and pushed forward with a pressure just below that which will break the lead. Hardness is reported as the grade of pencil that does not cause any marring of the surface. Experienced testers can reproduce results to ±1 hardness grade. Probably, the test reflects some combination of modulus, tensile strength, and adhesion.

A pendulum test, particularly used in the United States, is the Sward rocker (ASTM 2134-93). The rocker is a circular device made up of two rings joined with a glass level gauge and is weighted off center. The circumference of the rings rests on the panel. The rocker is rolled to a marked angle and released. The number of rocks (swings) required to dampen the motion down to a smaller fixed angle is determined. The rocker is calibrated to give 50 rocks (a hardness reading of 100) on polished plate glass. Hard coatings give higher readings (but less than 100) than soft coatings. Dampening is caused by rolling friction as well as by mechanical loss. The results depend on film thickness and surface smoothness. The Sward rocker is probably most useful for following the increase of hardness of a coated panel during drying of an ambient cure coating. It has only limited validity for comparing the hardness of different coatings.

In Europe, Koenig and Persoz pendulums are used. In these tests, a pendulum makes contact with a coated panel through two steel balls. As the pendulum swings back and forth through a small angle, movement of the balls requires some deformation of the coating near the surface. Test results are reported as the time (in seconds) for the swing to be dampened from a higher to a lower angle (from the perpendicular)—from 6 to 3° in the case of the Koenig pendulum and from 12 to 4° in the Persoz test. Usually, harder coatings give longer times. However, soft, rubbery coatings may also give longer times. Based on the reasonable assumption that the main contribution to dampening the pendulum is absorption of mechanical energy by the film, these apparently conflicting results can be explained in terms of the loss modulus. As shown in Figure 4.7, loss modulus values are low in both the regions below and well above T_g and are highest in the transition region. Low loss modulus could account for longer dampening times for both soft, rubbery films, with T_g values below ambient temperature, and hard films, with T_g values well above ambient temperature. This hypothesis predicts that dampening times for coatings in the transition region at ambient temperature may be very sensitive to temperature, since loss modulus goes through a maximum in this region.

4.6.3.2. Formability and Flexibility One flexibility test is a *mandrel bend test*, in which a coated panel is bent around a rod or cone (the mandrel). The panel is bent with the coated side away from the mandrel. Any crack in the coating on the bend is reported as a failure. In the cylindrical mandrel test, a series of different mandrels is used, and the smallest diameter that permits a bend without failure is reported as the mandrel flexibility. In a *conical mandrel test*, one end of the panel is clamped, and a lever is used to bend the panel over a cone. The distance from the small end of the cone to the end of a crack is reported. This distance, which is proportional to the radius of curvature of the mandrel at that point, can be used to estimate the elongation-at-break [57]. Thicker films crack more easily than thinner films because the elongation at the same distance along the mandrel is greater. The bent edge should be inspected with a magnifying glass to see hairline cracks, and the panels should also be inspected the next day because cracks sometimes appear later. If adhesion is poor, the film comes loose from the panel. The severity of the test can be increased by testing at low temperature (by putting the panel and tester in a freezer before testing). The severity of the test is also affected by the rate of bending.

Another formability test, widely used for testing coil coatings, is the *T-bend test*. The coated panel is bent back on itself with the coating side out. If there is no crack at the edge, the result is reported as 0T. The zero means there is no additional layer of metal inside the bend. If the coating cracks, the panel is bent back on itself again. Repeated bends back over the original bend are made until the coating does not crack. The radius of curvature gets greater as the number of bends increases. The results are reported as 0T, 1T, 2T, 3T, and so on, counting the number of thicknesses of metal inside the bend. The severity of the test is affected by temperature and rate of bending, and the panels should be reexamined after some time has elapsed.

4.6.3.3. Impact Resistance *Impact tests* evaluate the ability of a coating to withstand extension without cracking when the deformation is applied rapidly [ASTM D-2794-93 (reapproved 1999)]. A weight is dropped down a guide tube onto a hemispherical indenter that rests on a coated panel. An opening opposite the indenter in the base support on which the panel rests permits deformation of the panel. If the coated side is up (i.e., the coating is hit directly by the indenter), the test is called a *direct impact test*. If the back of the panel is up, the test is called a *reverse impact test*. The weight is dropped from greater and greater heights until the coating on the panel cracks. In the United States, the results are reported in in.-lbs (i.e., the number of inches the weight falls times its weight). In the most common apparatus, the maximum is 160 in.-lb. Generally, reverse impact tests, in which the coating is extended, are more severe than direct impact tests in which the coating is compressed. The thickness, mechanical properties, and surface of the substrate affect the results substantially. If the substrate is thick enough, it is not distorted by the impact, and almost any coating will pass. Comparison of results on different substrates is meaningless. Different lots of test panels of the same type can have subtle differences in their surfaces that can affect test results. The test panels should be aged for at least one day before testing and should be inspected immediately after the test and again the next day.

4.6.3.4. Abrasion Resistance In the *Taber Abraser test*, abrasive wheels roll on a panel, creating a circular wear path. The test is continued until the coating is worn through. Results are reported as the number of rotations required to wear through 1 mil (25 μm) of coating. The results often do not correlate with field use tests. For example, in the Taber abrasion results for the four floor coatings described in Table 4.2, the hard epoxy coating had the poorest abrasion resistance in actual field use, but it exhibited the highest rating in the Taber test. Another example in which correlation was poor is the beer can abrasion problem mentioned previously. On the other hand, some authors report that Taber tests correlate with visual observation of abrasion of clear coats on cars by automatic car washes [39], although others disagree. Generally, softer coatings tend to give poorer Taber Abraser results, probably because the abrasion disks rotate at a constant speed and therefore impart more energy to softer coatings. However, very soft coatings may clog the abrasive on the wheel and give spurious results.

Another abrasion test is the *falling sand test*, in which sand falls out of a hopper through a tube onto a coated panel held at a 45° angle to the stream of sand. The result is reported in liters of sand required to wear through a unit thickness of coating. A more sophisticated version of the falling sand test has been reported [35]. A gas blast erosion apparatus has been shown to give reproducible results. When the stream of particles is perpendicular to the surface, the erosion scar produced is circular; the radius of the scar provides an accurate measure of abrasion. The velocity of the particles and the angle of impact can be varied.

Yet another method of determining abrasion uses a ball rotating in a slurry of small abrasive particles to measure abrasive wear of a small area of coating in the upper 30 μm of a film with good reproducibility [35].

4.6.3.5. Solvent Resistance Solvent resistance is not a mechanical property, but it is included here because it is one of the properties that must be balanced with mechanical properties for many applications. It is also appropriate to mention here because resistance to swelling of cross-linked films is related to XLD, which affects many mechanical properties.

The most common test of solvent resistance is the methyl ethyl ketone (MEK) double rub test (ASTM D-4752-98). This test can be done by rubbing a tissue soaked with MEK on the panel, but it is more conveniently done with a felt tip marker pen filled with solvent. The test can be mechanized so that there is one stroke back and forth (one double rub) on the film each second, and a timer can be used as a counter. A soft thermoplastic coating will rub off with very few rubs. In the case of thermosetting coatings, the number of rubs that the coating withstands increases as the degree of reaction increases. The test is sensitive to the development of low cross-link density but insensitive to changes as the cross-link density gets higher. Usually, the test is stopped after 200 double rubs, and therefore, a series of highly cross-linked coatings may all be reported to give 200+ double rub resistance, even though there may be differences in the extent of cross-linking. At higher cross-link densities, DMA or solvent swelling can be used to determine the extent of cross-linking, as discussed in Section 4.2.

Another solvent resistance test is to expose the coating to the solvent for a certain period of time (say, 15 minutes) and then carry out a pencil hardness test on the exposed area. For example, a test for aircraft top coats specifies that the coating shall not lose more than two pencil hardness units after exposure to hydraulic fluid for 15 minutes.

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5

Exterior Durability

Exterior durability of coatings refers to their resistance to change during outdoor exposure; such changes include changes of modulus, loss of strength, embrittlement, discoloration, loss of adhesion, chalking, loss of gloss, and environmental etching. Thus, both aesthetic and functional properties are involved. The terms *outdoor durability* and *weatherability* are also used. Corrosion protection by coatings is discussed in Chapter 7.

The most common chemical processes leading to degradation of coatings are photoinitiated oxidation and hydrolysis resulting from exposure to sunlight, air, and water. These processes are interrelated, including enhanced photoxidative degradation in high humidity and enhanced hydrolytic degradation during photoexposure. Furthermore, both processes are accelerated by higher temperatures. Hydrolytic degradation may be enhanced by exposure to acid, as from acid rain. Other atmospheric degradants include ozone and oxides of nitrogen and sulfur. Changes in temperature and humidity may result in cracking, which arises from the expansion and contraction of coatings or substrates. Rates at which these processes occur vary, depending on exposure site(s), time of year, coating composition, and substrate.

5.1. PHOTOINITIATED OXIDATIVE DEGRADATION

Coatings formulated for exterior durability should exclude or minimize resin components that are readily oxidized and that absorb UV radiation at wavelengths longer than 290 nm. Photoinitiated oxidation of polymers by a chain reaction is outlined in Scheme 5.1. Absorption of UV by a polymer (P) or other coating component produces highly energetic photoexcited states (P*) that undergo bond cleavage to yield free radicals (P•). Free radicals undergo a chain reaction with O_2 (autoxidation), leading to polymer

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Organic Coatings: Science and Technology, Third Edition, by Zeno W. Wicks, Jr., Frank N. Jones,
S. Peter Pappas, and Douglas A. Wicks

degradation. Hydroperoxides (POOH) and peroxides (POOP) are unstable products of photoinitiated oxidation; they dissociate with sunlight and moderate heat to yield alkoxy (PO·) and hydroxy (HO·) radicals, so the degradation reactions are autocatalytic. These radicals are highly reactive toward hydrogen abstraction and yield polymer radicals (P·), which enter into the propagation stage of polymer degradation. Tertiary alkoxy radicals dissociate into ketones and a lower-molecular-weight polymer radical (P′·), resulting in scission of the polymer. As shown in Scheme 5.1, chain propagation leading to oxidative degradation proceeds by hydrogen abstraction from the polymer autocatalytically.

To achieve good exterior durability, functional groups in a coating that are vulnerable to hydrogen abstraction should be avoided or minimized. A general ordering of common $\underline{\text{CH}}$ groups having decreasing vulnerability to free radical abstraction is the following (the groups at the bottom of the list are least susceptible to oxidative degradation):

Scheme 5.1

Initiation:

$$\text{Polymer (P)} \xrightarrow{\text{Sunlight}} \text{P}^* \tag{5.1}$$

$$\text{P}^* \longrightarrow \text{free radicals (P}\cdot\text{)} \tag{5.2}$$

Propagation:

$$\text{P}\cdot + \text{O}_2 \longrightarrow \text{POO}\cdot \tag{5.3}$$

$$\text{POO}\cdot + \text{Polymer (P—H)} \longrightarrow \text{POOH} + \text{P}\cdot \tag{5.4}$$

Chain termination:

$$2\text{POO}\cdot \longrightarrow \text{POOP} + \text{O}_2$$

$$2\text{P}\cdot \longrightarrow \text{P—P or disproportionation products}$$

$$\text{POO}\cdot + \text{P}\cdot \longrightarrow \text{POOP or disproportionation products}$$

$$2\text{POO}\cdot \longrightarrow \text{ketones (aldehydes)} + \text{alcohols}$$

Autocatalysis:

$$\text{POOH(P)} \xrightarrow{\text{Sunlight}} \text{PO}\cdot + \cdot\text{OH}(\cdot\text{OP})$$

$$\text{PO}\cdot\ (\cdot\text{OH}) + \text{polymer (P—H)} \longrightarrow \text{POH (H}_2\text{O)} + \text{P}\cdot$$

Polymer scission:

$$\text{PO}\cdot \longrightarrow \text{ketones} + \text{P}\cdot$$

amines: $-\underline{CH_2}-NR_2 \cong$ diallyl: $-CH{=}CH-\underline{CH_2}-CH{=}CH-$

$\cong$ allyl ether: $-CH{=}CH-\underline{CH_2}-O- >$

ethers, alcohols: $-\underline{CH_2}-O-R(H) \cong$ urethanes: $-\underline{CH_2}-NH-CO-OR \cong$

allyl: $CH{=}CH-\underline{CH_2}- \cong$ benzyl: $Ph-\underline{CH_2}- >$

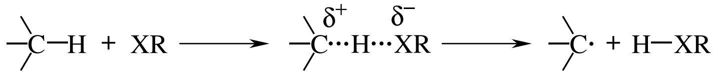
esters: $-\underline{CH_2}-CO-O-\underline{CH_2}- \cong$ tertiary alkyl: $R_3\underline{CH} >$

secondary alkyl: $-\underline{CH_2}- >$ primary alkyl: $\underline{CH_3} \gg$

methylsiloxanes: $-Si(\underline{CH_3})_2-O-$

The order is based on available bond dissociation energies and well-established activating effects of heteroatoms and aryl/vinyl groups; neighboring groups and steric hindrance as well as statistical effects should also be considered. For example, poly(vinylidene fluoride), $-\!\!\left(CH_2-CF_2\right)\!\!-_n$, is known to weather substantially better than other polymers having CH_2 groups, which probably reflects the neighboring F groups as well as the statistical reduction of CH_2 groups. Linolenic esters having 1,4,7-triene groups are more readily oxidized than linoleic esters having 1,4-diene groups, which may be attributed to a neighboring group effect of the third ene group in linolenates as well as to the statistical effect of two highly activated CH_2 groups between double bonds in linolenates compared to one in linoleates. In general, hydrogen abstraction from tertiary alkyl groups is disfavored statistically and is expected to be particularly sensitive to steric hindrance effects.

Enhancement of hydrogen abstraction by electron-donating N and O groups and retardation by strongly electron-withdrawing F groups can be attributed to polar contributions to the transition state for hydrogen abstraction. Since most hydrogen abstracting agents are electronegative (e.g., peroxy or alkoxy radicals), the transition state will be stabilized by partial negative charge on the abstracting agent and, correspondingly, partial positive charge on the C from which the hydrogen is abstracted, as shown, where RX represents the hydrogen abstracting agent. Accordingly, the energy of the transition state will be lowered by electron-donating groups, which stabilize the partial positive charge and raised by electron-withdrawing groups, which destabilize the partial positive charge.

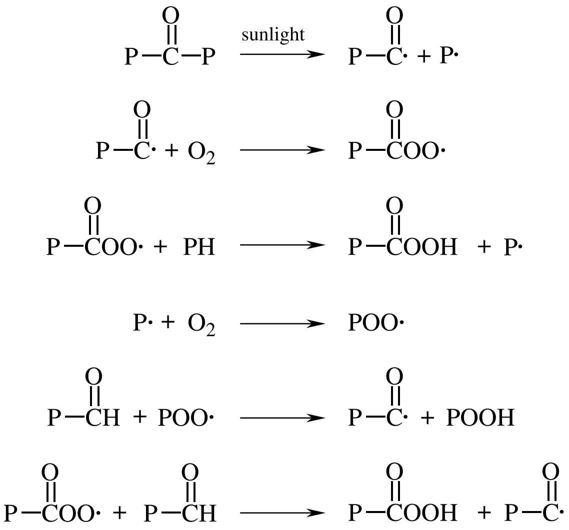


$$\rangle C-H + XR \longrightarrow \rangle \overset{\delta^+}{C}\cdots H\cdots \overset{\delta^-}{XR} \longrightarrow \rangle C\cdot + H-XR$$

None of these functional groups absorbs sunlight directly. In the absence of absorbing aromatic groups, absorption of sunlight occurs primarily by inadvertently present peroxide and ketone groups, both of which absorb ultraviolet (UV) above 290 nm. Essentially, all resins used in coatings contain some hydroperoxides, as do most organic substances. Peroxides, ketones, and aldehydes are also formed in photoinitiated oxidation. (Scheme 5.1) Photolysis of peroxides and ketones is shown in Schemes 5.1 and 5.2, respectively. As shown in Scheme 5.2, photoxidation of aldehydes and ketones yields peracids, which are strong organic oxidants. Peracids may play a significant role in oxidative degradation.

Methyl-substituted silicones and silicone-modified resins exhibit high photoxidation stability, generally in proportion to the silicone content. The excellent exterior durability

Scheme 5.2 *Oxidation of aldehydes and ketones (peracid formation).*



$$\begin{aligned}
\mathrm{P{-}\overset{O}{\overset{\|}{C}}{-}P} &\xrightarrow{\text{sunlight}} \mathrm{P{-}\overset{O}{\overset{\|}{C}}\cdot + P\cdot} \\
\mathrm{P{-}\overset{O}{\overset{\|}{C}}\cdot + O_2} &\longrightarrow \mathrm{P{-}\overset{O}{\overset{\|}{C}}OO\cdot} \\
\mathrm{P{-}\overset{O}{\overset{\|}{C}}OO\cdot + PH} &\longrightarrow \mathrm{P{-}\overset{O}{\overset{\|}{C}}OOH + P\cdot} \\
\mathrm{P\cdot + O_2} &\longrightarrow \mathrm{POO\cdot} \\
\mathrm{P{-}\overset{O}{\overset{\|}{C}}H + POO\cdot} &\longrightarrow \mathrm{P{-}\overset{O}{\overset{\|}{C}}\cdot + POOH} \\
\mathrm{P{-}\overset{O}{\overset{\|}{C}}OO\cdot + P{-}\overset{O}{\overset{\|}{C}}H} &\longrightarrow \mathrm{P{-}\overset{O}{\overset{\|}{C}}OOH + P{-}\overset{O}{\overset{\|}{C}}\cdot}
\end{aligned}$$

of fluorinated resins may be attributed, at least in part, to the absence (or reduced level) of C—H groups.

Aromatic groups with directly attached heteroatoms, as found in aromatic urethanes (Ar—NH—CO—OR) and bisphenol A (BPA) epoxies (Ar—O—R), absorb UV above 290 nm and undergo direct photocleavage to yield free radicals that can participate in oxidative degradation. BPA epoxies also have readily abstractable hydrogens positioned on carbon directly attached to ether and alcohol oxygen. Accordingly, BPA epoxies are expected to be susceptible to oxidative degradation, as evidenced by studies on model compounds [1].

Coatings made using aromatic isocyanates yellow badly after only short exposures to UV radiation. Coatings based on BPA epoxies generally chalk rapidly on exposure outdoors. Since ketones absorb UV, they should be avoided. When acrylic resins are polymerized in ketone solvents such as methyl amyl ketone, ketone groups can be incorporated in the resin by chain transfer [2]; to avoid introduction of ketone groups, it is preferable to use polymerization solvents such as esters or toluene.

Highly chlorinated resins such as vinyl chloride copolymers, vinylidene chloride copolymers, and chlorinated rubber degrade by autocatalytic dehydrochlorination on exposure to either heat or UV. They must be formulated with stabilizers, as discussed in Section 5.3.

5.2. PHOTOSTABILIZATION

A major step toward formulation of a coating with exterior durability is to start with binders that resist photoxidation and hydrolysis. Substantial further improvement can often be achieved by use of photostabilizers. Defenses against photoinitiated oxidative degradation include UV absorbers to reduce UV absorption by the polymer (Scheme 5.1, Eq. 5.1), excited state quenchers to compete with bond cleavage of P* (Scheme 5.1, Eq. 5.2), and antioxidants to reduce oxidative degradation (Scheme 5.1, Eqs. 5.3 and 5.4). Review articles and books on photostabilization and thermal stabilization of coatings, including degradative pathways, are available [3].

Scheme 5.3

UV absorber (A):

$$A \xrightarrow{\text{sunlight}} A^*$$

$$A^* \longrightarrow A + \text{heat}$$

$$\text{Overall: radiation} \longrightarrow \text{heat}$$

Excited state quencher (Q):

$$P \xrightarrow{\text{sunlight}} P^*$$

$$P^* + Q \longrightarrow P + Q^*$$

$$Q^* \longrightarrow Q + \text{heat}$$

$$\text{Overall: radiation} \longrightarrow \text{heat}$$

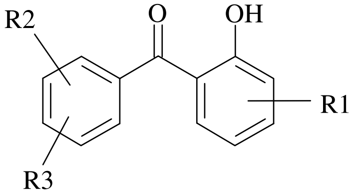
5.2.1. UV Absorbers and Excited State Quenchers

Important characteristics of UV stabilizers—both absorbers (A) and quenchers (Q)—are photostability and chemical and physical permanence. Photostability requires that the photoexcited stabilizer (A^* or Q^*) can return to the ground state by converting the UV energy into thermal energy, as shown in Scheme 5.3. This process generally occurs by reversible intramolecular hydrogen transfer or *E–Z* (*cis–trans*) isomerization of double bonds.

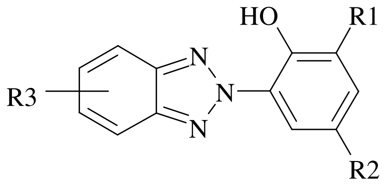
An important feature of excited state quenchers is their effective quenching volume, within which quenching of photoexcited polymers occurs efficiently. Effective quenching volume depends on the mechanism of energy transfer. These considerations have been discussed and related to the prospects for stabilizing aromatic polymers [4]. Stabilization by UV absorbers requires strong absorption in the wavelength region in which the polymer and/or trace impurities also absorb. Stabilization by quenchers require strong absorption in the wavelength region in which the excited state polymer and/or impurities emit radiation. Stabilizers, which function as UV absorbers in some coatings, may perform as excited state quenchers in other coatings. The most effective stabilizers probably function by both roles.

One cannot eliminate UV absorption by the resin by adding a UV absorber, which can only reduce absorption by the binder to slow the rate of photodegradation reactions. Since absorption increases as the path length increases and incident radiation is attenuated in the lower layers by absorption in the upper layers, UV absorbers, as well as quenchers, are most effective in protecting the lower parts of a film or substrate (e.g., a base coat, wood, or plastic under a clear top coat containing an absorber) and least effective in protecting the layer at the air interface. It follows that the thickness of a clear top coat, which contains a UV absorber/quencher, can be an important variable affecting the protection of base coats or plastics under them, since thicker films transmit less radiation. A critical consideration in the design and selection of UV absorbers/quenchers is their absorption spectra. In general terms, one would like to have very high absorption of UV radiation, from 290 to 380 nm. To avoid color effects by an absorber or quencher, ideally, there would be no absorption above 380 nm.

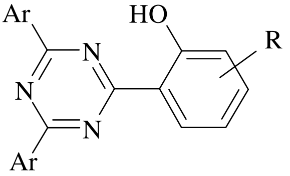
Substituted 2-hydroxybenzophenones, 2-(2-hydroxyphenyl)-2*H*-benztriazoles, 2-(2-hydroxyphenyl)-4,6-phenyl-1,3,5-triazines, benzylidenemalonates, and oxalanilides are classes of UV stabilizers. Specific members of these classes may act as UV absorbers, as excited state quenchers, or as both, but they are frequently called *UV absorbers* (UVA) in the coatings literature.



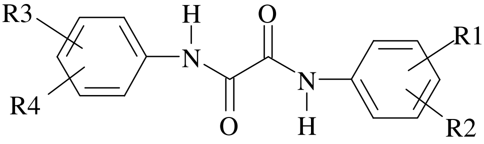
Benzophenones



Benzotriazoles

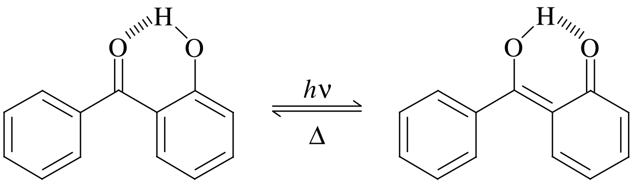


s-Triazines



Oxalanilides

These UV stabilizers convert UV energy into heat by intramolecular hydrogen transfer or *cis–trans* isomerization. For example, UV absorption or excited state quenching by a 2-hydroxyphenyl-substituted stabilizer yields a photoexcited state that converts excess electronic energy into chemical energy by undergoing intramolecular hydrogen transfer to yield an unstable intermediate. The unstable intermediate spontaneously undergoes reverse hydrogen transfer to regenerate the UV stabilizer with conversion of the chemical energy into heat. The process is illustrated with 2-hydroxybenzophenone.



The UV stabilizer must be soluble in the coating film. (Pigments that serve as UV absorbers, discussed in Section 5.2.4, are insoluble.) Several grades of the various stabilizers are available with different substituents on the aromatic rings that provide for solubility in different polymer systems. Commonly, the stabilizer is added to the top coat of a multicoat system. However, especially in baking systems, migration may result in the stabilizer being distributed through the whole coating, reducing the concentration in the top coat. This effect has been demonstrated by analyzing sections through a film of clear coat–base coat automotive finishes [5]. In one combination of coatings, in which UV stabilizer was added only to the clear coat, the content through the whole film, both clear coat and base coat, was essentially uniform. In a second case, with a different type of base coat, a major fraction of the stabilizer stayed in the clear coat. In coatings for plastics, it has been shown that stabilizers can migrate into the plastic [6].

A critical requirement of a UV stabilizer is permanence. Loss of stabilizer can result by two mechanisms. There can be physical loss by vaporization, leaching, or migration and/or there can be chemical loss by deterioration of absorbance by photochemical reactions of the stabilizer. If a UV stabilizer has even a small vapor pressure, it slowly volatilizes from the surface over the long term period for which durability is desired. Analysis of one UV stabilizer as a function of depth into the film initially and after one year exterior exposure [on a Florida black box (Section 5.6.1)] showed significant losses, particularly near the surface of the film [5]. Most hydroxyphenyltriazines have very low vapor pressures and show the best photo-permanence, followed by benzotriazoles, benzophenones, and oxalanilides. Longer term physical permanence may be achieved by using oligomeric photostabilizers. Polymer-bound stabilizers can also be used assuring physical permanence.

UV stabilizers can degrade chemically and lose effectiveness. The degradation presumably proceeds via free radical intermediates, and therefore degradation proceeds most rapidly in binders that are most readily photodegraded by a free radical mechanism. (The complex factors involved in permanence are discussed extensively in Ref. [7].)

5.2.2. Antioxidants

Antioxidants may be classified into two groups: preventive and chain-breaking antioxidants. *Preventive antioxidants* include peroxide decomposers, which reduce hydroperoxides to alcohols and become oxidized into harmless products. Examples of peroxide decomposers are sulfides and phosphites that are initially oxidized to sulfoxides and phosphates, respectively, as shown in Eqs. 5.5 and 5.6 for dilauryl thiodipropionate (LTDP) and triphenylphosphite. Further reactions may occur.

$$\mathrm{POOH} + \mathrm{S(CH_2CH_2CO{-}OC_{12}H_{25}} \longrightarrow \mathrm{POH} + \mathrm{O{=}S(CH_2CH_2CO{-}OC_{12}H_{25})_2} \quad (5.5)$$

$$\mathrm{POOH} + \mathrm{(PhO)_3P} \longrightarrow \mathrm{POH} + \mathrm{(PhO)_3P{=}O} \quad (5.6)$$

Metal complexing agents are a second type of preventive antioxidant. They tie up transition metal ions that may be present as contaminants and that catalyze the undesired conversion of hydroperoxides into peroxy and alkoxy radicals by redox reactions, as exemplified in Scheme 5.4. The resulting peroxy and alkoxy radicals are undesirable because they promote oxidative degradation, as shown in Scheme 5.1. For oxidative cure of drying oils and alkyds (Section 14.2.2), transition metal ions are deliberately added as catalysts (driers) to accelerate autoxidation. Thus, the reactions in Scheme 5.4 are involved in both oxidative cross-linking and oxidative degradation. Accordingly, drier concentrations should be minimized to reduce subsequent degradation during exterior exposure.

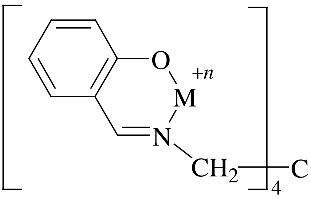
Scheme 5.4

$$\mathrm{POOH} + \mathrm{Co^{2+}} \longrightarrow \mathrm{POO\cdot} + \mathrm{H^+} + \mathrm{Co^{3+}}$$

$$\mathrm{POOH} + \mathrm{Co^{3+}} \longrightarrow \mathrm{PO\cdot} + \mathrm{HO^-} + \mathrm{Co^{2+}}$$

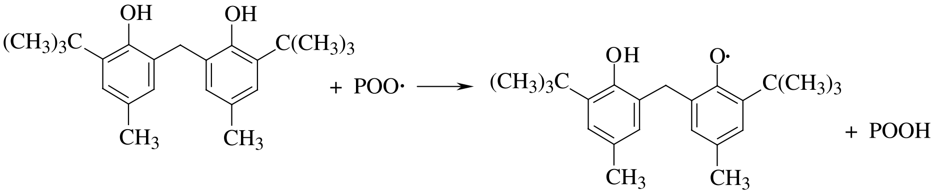
$$\text{Overall: } \mathrm{2POOH} \longrightarrow \mathrm{POO\cdot} + \mathrm{PO\cdot} + \mathrm{H_2O}$$

The tetrafunctional bidentate imine derived from *o*-hydroxybenzaldehyde (salicylaldehyde) and tetraaminomethylmethane is reported to complex a large number of transition metal ions effectively, including Co, Cu, Fe, Mn, and Ni (represented by M^{n+} in complex **1**) [8].



(**1**)

Chain-breaking antioxidants function by interfering directly with chain propagation steps of autoxidation, shown in Scheme 5.1. An example is a hindered phenol, 2,2′-methylenebis(4-methyl-6-*tert*-butylphenol), which reacts with peroxy radicals in competition with hydrogen abstraction from a polymer (PH) to yield a resonance-stabilized, less reactive phenoxy radical:

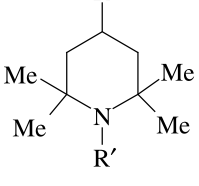


(5.7)

Note that hydroperoxides are generated in Eq. 5.7; this is a basis for synergistic stabilization of polymers by a combination of peroxide decomposers and chain-breaking phenolic antioxidants. Synergistic stabilization means that the combination of stabilizers is more effective than the additive effect of each stabilizer by itself.

5.2.3. Hindered Amine Light Stabilizers

Hindered amine light stabilizers (HALS) are amines with two methyl groups on each of two alpha carbons; most are derivatives of 2,2,6,6-tetramethylpiperidine, as shown in general formula **2**. They are reported to function both as chain-breaking antioxidants [9] and transition metal complexing agents [10]. The former function appears to be most important. Note that the 2,2,6,6-methyl groups prevent oxidation of the ring carbons attached to the nitrogen.



(R′ = H, alkyl, alkanoyl, alkoxy)

(**2**)

Scheme 5.5

$$R_2N{-}R' + O_2 \xrightarrow{UV} R_2NO\cdot + \text{other products}$$

$$R_2NO\cdot + P\cdot \longrightarrow R_2NOH + R_2NOP + P(\text{minus H}) \tag{5.8}$$

$$R_2NOH(P) + POO\cdot \longrightarrow R_2NO\cdot + POOH(P) \tag{5.9}$$

HALS derivatives undergo photoxidative conversion into nitroxyl radicals ($R_2NO\cdot$) that react with carbon-centered radicals by disproportionation and combination to yield corresponding hydroxylamines and ethers, respectively, as shown in Eq. 5.8 in Scheme 5.5. The hydroxylamines and ethers, in turn, react with peroxy radicals to regenerate nitroxyl radicals, shown in Eq. 5.9 in Scheme 5.5. In this manner, HALS derivatives interfere with propagation steps involving both carbon-centered and peroxy radicals in autoxidation (Scheme 5.1). In contrast to nitroxyl radicals, hindered phenols do not react with carbon-centered radicals. The chain breaking antioxidant activity of hindered phenols is limited to reaction with peroxy radicals, and oxygen is required as a costabilizer.

To be effective, HALS derivatives must undergo rapid photoxidation to form nitroxyl free radicals on exterior exposure of the coating. In a photoexposed film, only a small fraction (about 1%) is present as the nitroxyl radical, the major storage components being the corresponding hydroxylamine (R_2NOH) and ethers (R_2NOP). Continued stabilization requires the presence of the nitroxyl radical, and its disappearance is followed shortly by rapid polymer degradation. Probably, the ultimate demise of HALS occurs, at least in part, by oxidation of the nitroxyl radical, accompanied by opening of the piperidine ring. Transition metal ions and peracids are potential oxidants for this process.

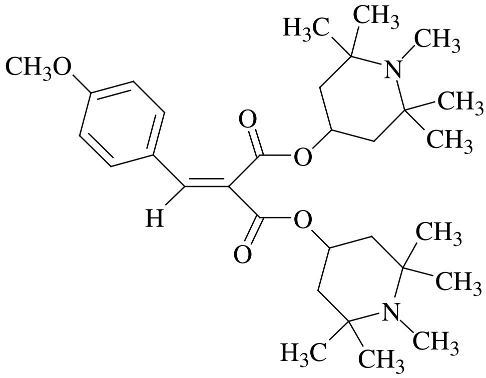
A variety of HALS compounds is available. The R in general formula **2** is often a diester group that joins two piperidine rings; this increases the molecular weight, decreasing volatility. The first commercial HALS compounds, still used to a degree, had $R' = H$. Later versions with $R' =$ alkyl exhibit better long-term stability. Both of these types are basic and interfere with acid catalyzed cross-linking reactions, such as those involving melamine–formaldehyde resins. Alkanoyl HALS compounds with $R' = C({=}O)R'$ are not basic, but their initial reaction to form nitroxyl free radicals is slower (Section 5.6.2) [3(c)]. More recently, hydroxylamine ethers ($R' = OR''$) have gained wide acceptance. The octyl ether provides a HALS compound with low basicity that converts rapidly to nitroxyl free radicals [11]. HALS compounds, especially with $R' = H$, can accelerate degradation of polycarbonate plastics, possibly by base catalyzed hydrolysis.

Combinations of UV absorbers and HALS compounds can act synergistically [3(c), 12]. The UV absorber reduces the rate of generation of radicals, whereas the HALS compound reduces the rate of oxidative degradation by the radicals. A further factor is that UV absorbers are inefficient at protecting the outer surface of a film; in contrast, HALS compounds can effectively scavenge free radicals at the surface. Analysis of films after exterior exposure shows that significant amounts of HALS derivatives remain after two years black box Florida exterior exposure [5] (Section 5.6.1).

For automobile use, a base coat and a clear coat are applied over a primed TPO (polypropylene–EPDM rubber blend). For example, an acrylic–MF base coat and an acrylic polyurethane clear coat could be applied. A UV absorber and HALS compound are included in the clear coat to assure exterior durability. However, in contrast to the same coating applied over steel, it has been found that the UVA and HALS can migrate through the coatings and into a TPO plastic resulting in poorer durability than over steel. To minimize this problem, the use of UVAs and HALS with hydroxyl groups that will react with the isocyanate in the clear coat to bind the stabilizers to the polymer chains has been studied. With the stabilizers bonded, retention of stabilizers in the clear coat is much higher and durability is improved [13]. An extensive study of the use of similar reactive UVAs and HALSs using an acrylic MF base coat and a 2K urethane clear coat also showed marked improvement in performance as compared to unreactive UVAs and HALSs [14].

Wood discolors rapidly on outdoor exposure to UV, as well as visible light, and more slowly indoors. A major reason for the effect is the reactions of lignin in the wood on exposure to the radiation. A two coat system has been recommended to protect wood against discoloration. The first coat contained the nitroxyl derivative of 4-hydroxy-2,2,6,6-tetramethylpiperidine to trap radicals formed by the radiation. Although as noted above, in most cases it is desirable to put the HALS in the top coat, in this case it was most important to put it in a coat in direct contact with the lignin-containing wood. In the second coat a mixed bis, tris, and tetra-*para*-substituted-tris-resorcinol-triazine was used as the UV absorber to screen the radiation [15].

The *N*-2,2,6,6-pentamethylhydroxypiperidinyl diester of 4-methoxyphenylmethylene-malonic acid combines the UV absorber function of a benzylidene malonic ester and the antioxidant properties of HALS derivatives [16]. Furthermore, on exposure of films, this HALS derivative grafts onto the polymer chains, eliminating volatility and migration losses. It reacts with MF cross-linked acrylic and 2K urethane acrylic coatings when exposed to radiation, hence preventing loss by volatilization or leaching. It also absorbs UV radiation and is used with UV stabilizer, *o*-hydroxyphenyl-*s*-triazine, to give excellent stabilization over long periods of time [17]. The use of three types of UV stabilizers with this HALS compound has shown that photostability diminishes more rapidly in the order *o*-hydroxyphenyltriazenes > *o*-hydroxybenzotriazoles > oxanilides [17].



5.2.4. Pigmentation Effects

Many pigments absorb UV radiation. The strongest UV absorber known is fine particle-size carbon black. Many carbon blacks have structures with multiple aromatic rings and in some cases, phenol groups on the pigment surface. Such black pigments are both UV absorbers and antioxidants. Enhanced exterior durability is obtained with carbon black pigmented coatings. When Henry Ford said, "The customer can have any color car he wants, as long as it is black," he was not just being crotchety. Black was by far the most durable paint available at the time.

Other pigments absorb UV radiation to varying degrees. For example, 50-μm coatings pigmented with fine particle size, transparent iron oxide pigments absorb virtually all radiation below about 420 nm [18]. This strong absorption is particularly useful in stains for use over wood, since the pigmented transparent coating protects the wood from photodegradation.

Nano-zinc zirconium silicate has been patented for use as a UV absorber in automotive clear coats. Because of the small particle size, it does not affect the transparency of the clear coat. It has the advantage that it in insoluble and nonvolatile [19].

Rutile TiO_2 white pigment absorbs UV strongly. Absorption is a function not only of wavelength and concentration, but also of the particle size of the pigment [20]. The optimum particle size for absorption of UV by rutile TiO_2 increases from 0.05 μm for 300 nm radiation to 0.12 μm for 400 nm radiation. This size is smaller than the optimum particle size of 0.19 μm for hiding (Section 19.2.3). Rutile TiO_2 with an average particle size of 0.23 μm still absorbs UV strongly. Anatase TiO_2 also absorbs UV strongly, although not as strongly as rutile TiO_2 in the near UV. Thus, TiO_2, especially rutile TiO_2, functions as a UV absorber in coatings. However, TiO_2 can accelerate photodegradation of films on exterior exposure, causing *chalking* of coatings: that is, degradation of the organic binder and exposure of unbound pigment particles on the film surface that rub off easily, like chalk on a blackboard. Degradation of the binder is enhanced by interaction of photoexcited TiO_2 with oxygen and water to yield oxidants, as shown in Scheme 5.6 [21]. Photoexcitation of TiO_2 results in promoting a low energy valence band electron into the higher energy conduction band, creating a separated electron (e)/hole (p) pair, signified by $TiO_2^*(e/p)$ in Scheme 5.6. Electron capture by O_2 (reduction) and hole capture by H_2O (oxidation) result in regeneration of ground-state TiO_2 and lead to hydroperoxy and hydroxy radicals that can participate in oxidative degradation, as shown in Scheme 5.1. Anatase TiO_2 is more active in promoting oxidative degradation than rutile TiO_2, so much so that anatase is generally not used in outdoor coatings except in rare cases where chalking is desired.

The photoactivity of TiO_2 pigments is reduced by coating the pigment particles with a thin layer of silica and/or alumina (Section 20.1.1) to form a barrier layer against the redox reactions. Treated rutile pigments are available that accelerate chalking to very minor extents, and these grades are used in exterior coatings. A laboratory test has been developed to compare the photoreactivity of various grades of TiO_2 [22]. Various stabilizing additives, including HALS, have also been reported [23].

Scheme 5.6

$$
\begin{aligned}
\mathrm{TiO_2 + light} &\longrightarrow \mathrm{TiO_2^*(e/p)} \\
\mathrm{TiO_2^*(e/p) + O_2} &\longrightarrow \mathrm{TiO_2(p) + O_2\cdot^-} \\
\mathrm{TiO_2(p) + H_2O} &\longrightarrow \mathrm{TiO_2 + H^+ + HO\cdot} \\
\mathrm{H^+ + O_2\cdot^-} &\longrightarrow \mathrm{HOO\cdot} \\
\mathrm{2HOO\cdot} &\longrightarrow \mathrm{H_2O_2 + O_2} \\
\mathrm{TiO_2^*(e/p) + H_2O_2} &\longrightarrow \mathrm{TiO_2 + 2HO\cdot}
\end{aligned}
$$

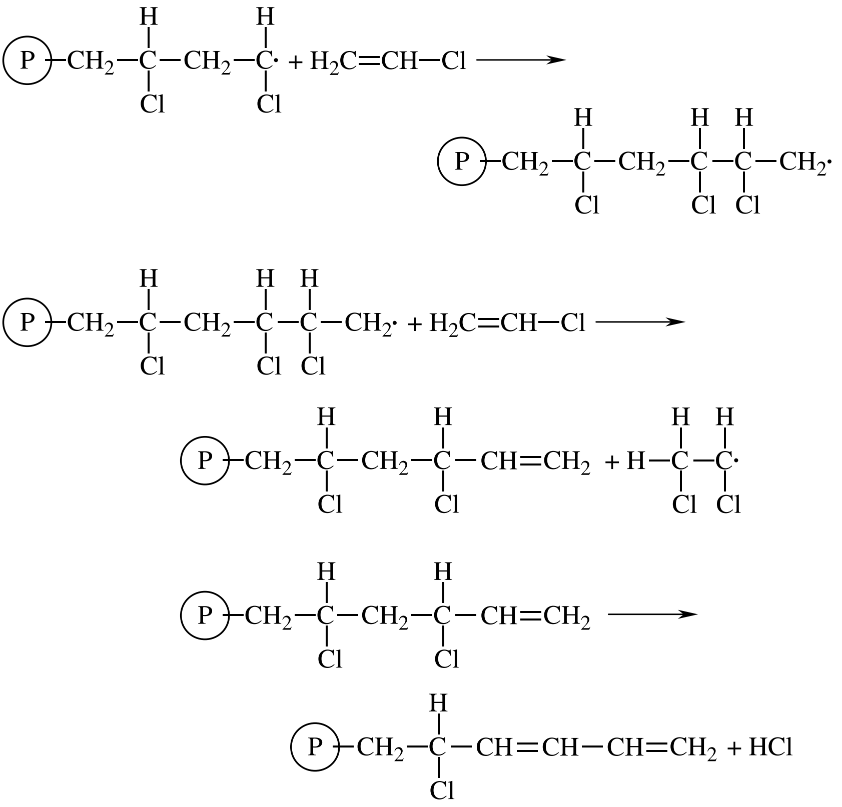
Chalking of exterior house paints eventually leads to complete erosion of the film. Chalking also leads to reduction in gloss, since the film becomes rougher. However, loss of gloss does not necessarily correlate with ease of chalking [24]. It was shown that initial gloss loss in some TiO_2 pigmented coatings resulted from film shrinkage, which in some cases was greater with more resistant grades of TiO_2. In paints containing both TiO_2 and color pigments, chalking results in color changes as a result of the gloss loss; the higher surface reflectance of the low gloss films gives an appearance of weaker colors.

Formulating coatings for exterior use can be complicated by pigment–binder interactions. In some cases, a pigment shows excellent color retention after exterior exposure when formulated with one class of resins, but poor durability when formulated with another class. For example, thioindigo maroon had excellent color retention when used in nitrocellulose lacquers, but poor color stability when used in acrylic lacquers. Although one can use experience in other systems as an initial basis for selecting pigments for use with a new class of resins, field tests are required to assure that each combination of pigments and resins is suitable.

5.3. DEGRADATION OF CHLORINATED RESINS

Highly chlorinated resins undergo dehydrochlorination on exposure to either heat or UV. The reactions are autocatalytic; with poly(vinyl chloride) the ultimate products are

Scheme 5.7



$$\text{\textcircled{P}}-CH_2-\underset{\text{Cl}}{\overset{\text{H}}{\text{C}}}-CH_2-\underset{\text{Cl}}{\overset{\text{H}}{\text{C}}}\cdot + H_2C{=}CH-Cl \longrightarrow \text{\textcircled{P}}-CH_2-\underset{\text{Cl}}{\overset{\text{H}}{\text{C}}}-CH_2-\underset{\text{Cl}}{\overset{\text{H}}{\text{C}}}-\underset{\text{Cl}}{\overset{\text{H}}{\text{C}}}-CH_2\cdot \qquad (5.10)$$

$$\text{\textcircled{P}}-CH_2-\underset{\text{Cl}}{\overset{\text{H}}{\text{C}}}-CH_2-\underset{\text{Cl}}{\overset{\text{H}}{\text{C}}}-\underset{\text{Cl}}{\overset{\text{H}}{\text{C}}}-CH_2\cdot + H_2C{=}CH-Cl \longrightarrow \text{\textcircled{P}}-CH_2-\underset{\text{Cl}}{\overset{\text{H}}{\text{C}}}-CH_2-\underset{\text{Cl}}{\overset{\text{H}}{\text{C}}}-CH{=}CH_2 + H-\underset{\text{Cl}}{\overset{\text{H}}{\text{C}}}-\underset{\text{Cl}}{\overset{\text{H}}{\text{C}}}\cdot \qquad (5.11)$$

$$\text{\textcircled{P}}-CH_2-\underset{\text{Cl}}{\overset{\text{H}}{\text{C}}}-CH_2-\underset{\text{Cl}}{\overset{\text{H}}{\text{C}}}-CH{=}CH_2 \longrightarrow \text{\textcircled{P}}-CH_2-\underset{\text{Cl}}{\overset{\text{H}}{\text{C}}}-CH{=}CH-CH{=}CH_2 + HCl$$

conjugated polyenes. As the number of conjugated double bonds in series increases, the polymer progressively discolors, finally becoming black. The resulting highly unsaturated polymer undergoes autoxidation, resulting in cross-linking and embrittlement.

The mechanism of degradation of poly(vinyl chloride) has been studied extensively. Dehydrochlorination is promoted when chlorine is situated on a tertiary carbon or on an allylic carbon. It has been proposed that at least one major weak point results from addition of a vinyl chloride monomer in a head-to-head fashion, as in Eq. 5.10 in Scheme 5.7, to the growing polymer chain, followed by chain transfer of Cl to monomer as in Eq. 5.11 [25]. The resulting allylic chloride is highly susceptible to dehydrochlorination, which generates a new allylic chloride with two conjugated double bonds (Eq. 5.12). Progressive dehydrochlorination is favored because the growing number of conjugated double bonds increases the lability of allylic chlorides down the chain.

A variety of stabilizing agents are used. Since dehydrochlorination is catalyzed by hydrogen chloride, HCl traps such as epoxy compounds and basic pigments are useful. Diels–Alder dienophiles can act as stabilizers; the Diels–Alder addition breaks up the chain of conjugated double bonds. Dibutyltin diesters are effective stabilizers. It is proposed that the activated chlorine atoms are interchanged with ester groups of the tin compounds to form the more stable ester-substituted polymer molecules. Dibutyltin maleate is a particularly effective stabilizer, since it acts as both an ester interchange compound and a dienophile. Barium, cadmium, and strontium soaps act as stabilizers. Choice of stabilizer combinations can be system specific, especially depending on whether stabilization is needed against heat, UV, or both. In the case of UV stabilization, UV absorbers can further enhance stability.

5.4. HYDROLYTIC DEGRADATION

A general ordering of functional groups subject to hydrolysis is esters $>$ carbonates $>$ ureas $>$ urethanes $\gg$ ethers, with esters being the most vulnerable and ethers the least. However, activated ethers, such as in etherified melamine–formaldehyde (MF) cross-linkers (Chapter 11), and etherified resole phenolics (Section 13.6), as well as their cross-linked products with hydroxy-functional resins, are more reactive than ureas and urethanes. The tendency of each type of group to hydrolyze can be reduced by steric hindrance: for example, by placement of alkyl groups in the vicinity of the susceptible groups such as esters (Section 10.1.1). The alkyl groups may also reduce hydrolysis by decreasing the solubility of water, hence reducing rates of hydrolysis. Studies have shown that the lower the water solubility of the diacid or diol used to make a polyester, the greater the resistance to hydrolysis [26]. Rates of hydrolysis are also influenced by neighboring groups. For example, phthalate half esters, in which the groups are ortho, are more readily hydrolyzed under acidic conditions (often encountered during exterior exposure) than are isophthalate half esters, in which the groups are meta (Section 10.1.2). Hydrolysis of polyesters results in backbone degradation. On the other hand, the backbones of (meth)acrylic resins are completely resistant to hydrolysis, since the linkages are carbon–carbon bonds. Acrylate, and particularly methacrylate, ester side groups are very resistant to hydrolysis, owing to the steric effects of the acrylic backbone. Carbonate esters are more stable to hydrolysis than are carboxylic esters.

Hydrolysis of MF cross-linked hydroxy-functional resins is enhanced by residual acid catalysts (generally, sulfonic acids) used to catalyze cross-linking (Section 11.3.1). Curing temperatures can be reduced by increasing the concentration of sulfonic acid in the coating, but the sulfonic acid remaining in the cured film enhances susceptibility to hydrolysis. An apparently ideal solution would be to use transient, or fugitive, acid catalysts, which either leave the film or become neutralized after cure. Degradation of acrylic–MF coatings at 50°C and different humidity levels was studied with infrared spectroscopy (FTIR) and atomic force microscopy (AFM). Formation of —NH_2 and —COOH groups was observed, and material was lost. It is interesting that the degradation was not uniform; pits in the surface form, deepen, and grow during exposure [27].

Base coat–clear coat finishes for automobiles are subject to *environmental etching*. In warm, moist climates with acidic rain or dew, such as Jacksonville, Florida, small, unsightly spots appear in the clear coat surface, sometimes within days. The spots are uneven shallow depressions in the clear coat surface. Presumably, they result from hydrolytic erosion of resin in the area of a droplet of water containing a significant acid concentration. While testing by exposure of panels for 14 weeks in Jacksonville has been widely used to evaluate coatings, it has been shown that the variations in rain, dew, sunshine, and acidity there cause considerable variability in results year to year [28]. An artificial weathering test is recommended. The laboratory test was continuous exposure to UV with repeated cycles of application of spraying panels with a dilute solution of a mixture of sulfuric, nitric, and hydrochloric acids to simulate acid dew, a dry period of 9 hours at 35°C and 30% RH, another dry period at 60°C and 5% RH, and a 4-hour rain period spraying with demineralized water.

Several factors are involved in differences in resistance to environmental etching [29,30]. Since urethane linkages are more resistant to acid hydrolysis than are the activated ether cross-links obtained with MF cross-linked hydroxy-functional resins, generally, urethane–polyol clear coats are less susceptible to environmental etching than many MF–polyol clear coats. When MF resins are used to cross-link carbamate-functional resins (Section 8.2.2), good resistance to environmental etching can be combined with mar resistance. Temperature and T_g are also important, as is surface tension of the clear coat. A variety of approaches have been undertaken to minimize the problem (see Section 30.1.2 for further discussion).

Acrylic–urethane coatings are reported to be stabilized more effectively by HALS than are acrylic–melamine coatings [31]. This may reflect, at least in part, the tendency of acrylic–melamines to degrade by hydrolysis; HALS derivatives do not stabilize against hydrolysis. Both urethane and melamine coatings undergo oxidative degradation. CH groups adjacent to urethane nitrogen groups are expected to be activated toward H-abstraction by free radicals, as are CH groups adjacent to nitrogen and ether oxygen groups in melamines. However, evidence has been presented that hydroperoxide levels are significantly lower in melamine than in urethane cross-linked coatings, indicative of lower free radical formation rates. The results have been attributed to the ability of melamines to decompose hydroperoxides [32] but may also be explained by lower susceptibility to oxidation of CH groups on melamine.

Hydrolytic degradation of acrylic–urethane [31] as well as acrylic–melamine [33] coatings are reported to be accelerated by UV exposure. This may result from the increase of hydrophilic groups, such as hydroperoxides, alcohols, ketones, and carboxylic acids, resulting from photoxidation, which increases the solubility of water in the coating. Photoxidation may also occur at specific sites to generate groups that are more susceptible to hydrolysis. Photodegradation of acrylic–melamine coatings is also reported to be accelerated in high humidity [33]. This result has been attributed to conversion of formaldehyde (from hydrolysis) into performic acid, a strong oxidant.

Silicone coatings, which are highly resistant to photodegradation, are subject to hydrolysis at cross-linked sites, where silicon is attached to three oxygens [34,35]. Apparently, the electronegative oxygens facilitate nucleophilic attack at Si by water (Section 16.1.2). The reaction is reversible, so the cross-links can hydrolyze and re-form. If a silicone-modified acrylic or polyester coating is exposed to water over long periods or is used in a climate with very high humidity, the coating can get softer. It is common to include some MF resin as a supplemental cross-linker in the formulation. Apparently, the MF cross-links with the acrylic or polyester are more hydrolytically stable than the bonds between the silicone resin and the polyester or acrylic.

5.5. OTHER MODES OF FAILURE ON EXTERIOR EXPOSURE

Although exposure to UV and the hydrolytic effects of rainfall and humidity are major causes of exterior failure of coatings, many other phenomena can occur.

Automotive finishes can undergo microcracking when there is a rapid change of temperature: for example, when a car is driven out of a heated garage on a very cold winter day. The stress built up by the differential of coefficients of expansion of coating and steel as the temperature drops rapidly can lead to shrinkage in excess of the elongation-at-break of the coating.

When paint is applied to wood, it must be able to withstand the elongation that results from the uneven expansion of wood grain when it absorbs moisture; otherwise, *grain cracking*, cracking parallel to the grain, occurs. This failure mode can occur with interior coatings; however, it is more likely to happen with exterior coatings, particularly with alkyds or drying oils that embrittle with exterior exposure. As a result of their greater exterior durability and extensibility, acrylic latex paint films seldom fail this way.

Another problem of exterior, oil-based house paints on wood siding is blistering. Blistering results from the accumulation of water in the wood beneath the paint layer. The vapor pressure of the water increases with heating by the sun, and blisters form to relieve the pressure. Since latex paints have higher moisture vapor permeability than that of oil-based paints, the water vapor can pass through a latex paint film, relieving the pressure before blisters grow. However, the high moisture vapor permeability of latex paint films can lead to failures of other types. For example, if calcium carbonate fillers are used in an exterior latex paint, *frosting* can occur. Water and carbon dioxide permeate into the film, dissolving calcium carbonate by forming soluble calcium bicarbonate, a solution of which can diffuse out of the film. At the surface of the film, the equilibrium changes direction, and the calcium bicarbonate is converted back to a deposit of calcium carbonate.

Dirt retention can be a difficult problem with latex house paints. Latex paints must be designed to coalesce at relatively low application temperatures. At warmer temperatures, soot and dirt particles that land on the paint surface may stick tenaciously and not be washed off by rain. This problem is minimized with low gloss paints because the high pigment content increases the viscosity of the paint film surface. The problem is particularly severe in areas where soft coal is burned. As would be expected, dirt pickup is less for paints formulated with higher T_g polymers [36]. It was also shown that the more hydrophobic styrene–acrylic latex paints picked up less dirt than do acrylic latex paints having the same T_g. Surface tension is also a factor; for example, 2-ethylhexyl acrylate (EHA) as a co-monomer reduces dirt retention [37]. Cross-linking of functional latexes also reduces dirt pickup.

Growth of fungi (mold and mildew) can lead to blotchy, dark deposits on the surface of coatings. Retardation of mildew growth is discussed in Section 32.1.

Often, one needs to be a detective to determine the origin of a paint failure. For example, there were suddenly numerous reports of ugly dirt spots on houses in Bismarck, North Dakota. It turned out that the flight pattern of airplanes taking off from the Bismarck airport had been changed. Oily droplets from plane emissions were landing on the paint, softening its surface to make it a good adhesive for dirt. The wide range of things that can happen to coatings outdoors makes the problem of predicting performance from the results of any simplified test conditions difficult.

5.6. TESTING FOR EXTERIOR DURABILITY

Unfortunately, no test is available that reliably predicts the exterior durability of all coatings. The best way to determine whether a coating will be durable for some length of time in a particular environment is to apply the coating to the product and use the coated product in that environment to determine its lifetime. Even this is difficult, due to the wide variety of environments and variability in coatings and application conditions. The limitations of accelerated tests, the need for data based on actual field experience, and methods of building a database are described in the introduction to Chapter 4 and more extensively in Ref. [38]. Bauer [39] recommends use of reliability theory using statistical distribution functions of material, process, and exposure parameters for predicting exterior durability of automotive coatings. Valuable data can be obtained by analysis of customer complaints; they are especially useful for defining performance standards. By analyzing field experience and customer complaint data over many years, coatings and automobile manufacturers have accumulated an increasingly useful data bank. The information can be used to test hypotheses relating structure to performance. Established structure–performance relationships are useful starting points for designing new coatings. The data can also be used to evaluate laboratory tests. Similar databases are accumulated by some manufacturers and users of maintenance paints, marine coatings, and coil coatings for exterior siding.

5.6.1. Accelerated Outdoor Testing

Accelerated test methods are desirable to permit prediction of performance in shorter times than possible by actual field use. Reference [40] provides an analysis of various test methods. The most reliable accelerated tests are outdoor fence exposures of coated panels, especially if they are carried out in several locations with quite different environments. Various means of exposure and testing of exposed panels are reviewed in Ref. [41]. Even at one location, there are sometimes substantial variations in conditions that lead to variability of test results [38,39,42]. The most commonly used exposure for architectural paints and industrial coatings is in southern Florida with panels facing south at a 45° angle; automotive coatings are commonly tested at 5° from horizontal. For coil coatings, a major supplier exposes at 90° for sidewall panels and 45° for roofing panels [43]. It is important to maintain records of the weather throughout the exposure period. Modern practice is to use photocells to record the cumulative amount of radiant energy striking a test specimen. Since different colors absorb different amounts of infrared radiation, the maximum temperatures reached by coatings during exposure depends on their color; this difference can affect exposure test results.

Southern Florida has a subtropical climate with high humidity, temperature, and sunshine levels. Arizona has more hours of sunshine per year and a higher average daily high temperature but lower humidity. Martin [44] presents a review of the differences between exposure conditions in Florida and Arizona. Cities in the northeastern states and in northern Florida have higher levels of acid in the atmosphere; the Denver area has a higher UV intensity because of the high altitude and a greater temperature change from day to night. Bauer estimates that for automotive coatings, a lower humidity in Arizona approximately offsets the higher UV intensity and temperature, and that one year of exposure in Florida has a comparable effect to two years in Michigan, where the UV intensity and temperature are lower but the humidity is higher [39]. The most severe conditions are found in humid equatorial locations (e.g., Venezuela).

Test specimens are examined periodically to compare their appearance before and after exposure. Usually, at least part of the coating surface is cleaned for the comparison. Ease of cleaning, change in gloss, change in color, degree of chalking, and any gross film failures are reported. Changes in color are particularly difficult to assess, since change in gloss or chalking changes the color even if there has been no change in the color of the components of the coating. The effects of changes in gloss and chalking on the color of the components can be minimized by cleaning the panels and then coating part of each panel with a thin layer of clear gloss lacquer. The lacquer layer minimizes the effect of differences in surface reflection on the color. Test fence exposures can eliminate some formulations as inadequate after a few months of exposure; however, two to five years may be required to permit one to conclude that resistance to exposure at that location under those conditions is adequate.

Film degradation can be accelerated by using *black box exposure*. Panels are mounted at 5° to the horizontal on black boxes rather than with the backs of the panels open to the air. This method is widely used for testing automotive top coats. A substantial increase in the temperature of the coating when the weather is sunny accelerates degradation. The temperature increase, and therefore the extent of acceleration, can vary substantially from coating to coating, especially with color. A variable that can affect the extent of change due to black box exposure is the relationship between the temperatures and the T_g of the film. Coatings that will seldom be exposed to direct sunlight (indoor architectural paints, auto interior paints) are tested outdoors under glass that absorbs UV similarly to absorbtion by window or auto glass.

Loss of gloss was formerly the primary mode of failure of automotive top coats, but since the adoption of clear coat–base coat finishes, a major mode of failure has become clear coat cracking in combination with delamination between top coats and base coat, primer, or plastic substrate [39]. Application of sufficient film thickness and proper choice of UV stabilizers and HALS compounds can be critical to avoiding delamination.

Results can be obtained in substantially shorter times by using Fresnel reflectors to concentrate sunlight on test panels. High intensity is achieved by reflecting sunlight from moving mirrors that follow the sun to maintain a position perpendicular to the sun's direct beam radiation. Fresnel reflector devices with trade names such as EMMAQUA (Equatorial Mount with Mirrors for Acceleration plus water) FRECKLE, and Sun-10 are operated in the Arizona desert [44]. They enhance the intensity of sunlight on the panel surfaces by a factor of 8 over direct exposure; it is said to accelerate degradation rates 4 to 16 times the rate for nonaccelerated exposure [41]. Panels are cooled by blowing air both over and under the samples. Since rainfall and humidity in the desert are low, the test facilities permit periodic spraying of water on the panel surfaces. In any highly accelerated test, it must be remembered that the rate of volatilization of UV stabilizers depends more on temperature than on radiant energy intensity; stabilizer losses may be smaller during accelerated testing than during long term exposure.

Fresnel reflector weathering devices record actual exposure energies per unit area, expressed in MJ m^{-2}. For comparison, the results can be approximately translated into Arizona or Florida exposure times based on relative solar intensity (i.e., energy per unit time). Comparisons based on intensity of exposure to a 10 nm band of UV around 313 nm give results that correlate most closely with field exposures. In addition, spraying with water at night has been found to give results that more closely correspond to field exposure than spraying only during the daylight hours, as was done in earlier procedures.

5.6.2. Analysis of Chemical and Mechanical Changes

Analysis of chemical changes occurring in coatings that have been subjected to exterior exposure is a powerful tool. Chemical changes become detectable long before the physical changes (gloss loss, cracking, delamination, etc.) that characterize failure become evident. Analysis can permit early detection of impending failure after relatively brief exposure, shortening evaluation time for new coatings. However, to have predictive value, chemical changes must be correlated with actual field experience for each type of coating, and only a few correlations have been reported. In addition to predicting failure, studies of chemical changes can help determine the mechanisms of failure, providing a basis for formulating more resistant coatings. Various approaches are reviewed in Refs. [11] and [40]. Early mechanical changes, measured by scanning electron microscopy (SEM) or by dynamic mechanical analysis (DMA), can also be correlated with chemical changes and with field experience [45].

Coatings, in general, embrittle on exposure, with an increase in T_g making them more subject to cracking; but it has been pointed out that the degree to which stress builds up in films is also an important factor in determining whether a film will crack [46]. If no stress were to build up, even a brittle film would not fail. But other factors are also involved. Flat surfaces will have lower stress buildup than will curved surfaces. Thin clear coats build up less stress than thick coats but offer less protection of base coats, owing to reduced UV absorption. Humidity and thermal changes can result in stress buildup, owing to expansion and contraction as a consequence of temperature and/or humidity increase or decrease, respectively. Repeated cycles of temperature and humidity changes can lead to fatigue. Overbaking can increase stress. (See Section 4.3.1 for a discussion of the effects of fracture mechanics on cracking of weathered clear coats.)

Electron spin resonance spectrometry (ESR) can monitor changes in free radical concentrations within a coating. The rate of disappearance of stable nitroxyl radicals has been correlated with loss of gloss in long-term Florida exposure [12]. In this technique, nitroxyl radical precursors are incorporated into TiO_2 pigmented acrylic–melamine coatings subjected to ambient or accelerated short-term UV exposure. Similarly, the rate of buildup of phenoxy radicals from bisphenol A epoxy resins incorporated into acrylic–melamine coatings exposed to UV radiation in an ESR spectrometer cavity has been correlated with cracking of coating films exposed in a QUV weathering device [47]. The latter technique was used to evaluate UV stabilizers.

Use of ESR spectrometry to monitor the rate of disappearance of nitroxyl radicals in acrylic–melamine coatings allows calculation of photoinitiation rates (PR) of free radical formation, which were found to correlate with rates of gloss loss (GLR): GLR $\propto$ $(PR)^{1/2}$. This proportional relationship of GLR with $(PR)^{1/2}$ is consistent with a free radical process and results from termination by second-order radical–radical reactions [12]. Photoinitiation rates, determined by this method, have also been used to evaluate experimental conditions for the synthesis of acrylic polyols by free radical polymerization, including the effect of initiator, temperature, and solvent on the projected exterior durability of the resulting acrylic–melamine coating [48].

The nitroxyl early detection method has also been used to investigate the synergistic stabilizing effect of a benzotriazole UV stabilizer and a HALS derivative in acrylic–urethane coatings. The UV stabilizer reduces the photoinitiation rate (PR) of free radical formation, whereas the HALS derivative reduces the propagation rate by lowering the concentration of free radicals.

A somewhat more direct application of ESR to studying photostability of coating films is the determination of free radical concentration after UV irradiation of films at a temperature of 140 K, well below T_g [49]. Under these conditions, free radicals are stable. The method is appropriate for evaluation of stabilizers such as HALS compounds by comparing the radical concentrations with and without stabilizer. Useful comparisons can be made in 3 hours [12].

ESR instruments are expensive; an alternative approach is to grind exposed films cryogenically to a fine powder and measure the buildup of hydroperoxides by titration with periodate. A linear relationship between photoxidation rates (PR) and hydroperoxide concentrations in acrylic–urethane and acrylic–MF coatings was reported [48,50]. The relationship GLR $\propto$ $(PR)^{1/2}$, established by ESR as shown previously, was assumed to apply to data obtained by titration.

Fourier transform infrared spectroscopy (FTIR) is another powerful tool for following chemical changes on a surface [42]. Photoacoustic FTIR has also been used and has the advantage that the sample does not have to be removed from the substrate. Furthermore, not only the surface, but also different depths within a film can be analyzed [51].

A study of a variety of exposure tests and analytical tools to give early predictions of gloss retention of seven latex paints with known exterior durability has been reported. The most useful results were obtained with x-ray photoelectron spectroscopy (XPS). XPS was used to analyze the surface of films for titanium, aluminum, and silicon in comparison with polymeric carbon before and after exterior exposure. (The aluminum and silicon are from the surface treatment of the TiO_2 in the paint.) Exposure leads to the degradation of polymer from the film surface, increasing the ratio of the metals to the polymeric carbon. Initially, surfactant bloom to the surface interfered with the analysis; but this disappeared after 2 weeks exposure. It was found that results obtained after 12 weeks Florida exposure (after the surfactant effect was gone) gave good predictions of gloss loss after 96 weeks of Florida exposure [52]. Atomic force microscopy (AFM) has been recommended for studying mechanical and chemical changes in the surface of films over time [53].

A study of changes in clear coats after five years of exterior exposure has led to the suggestion that four nontraditional tests should be added to the usual tests for performance: UVA concentration retention, HALS retention at the film surface and in the film bulk, FTIR analysis of the ratio of (—OH, —NH)/—CH peak areas, and clear coat fracture energy [54].

A variation on accelerating degradation of a binder in TiO_2 pigmented films is to substitute the surface-treated rutile TiO_2 that would be used in a commercial coating with untreated, photoactive anatase TiO_2. Similarly, one can study delamination failures of automotive coatings by exposing panels with no UV stabilizer in the clear coat over various substrates [38]. The results could permit one to decide whether a major effort should be put into improving the resistance of the substrate to photoxidation or aid in predicting the required minimum film thickness of a clear coat containing a UV stabilizer to protect the substrate.

5.6.3. Accelerated Weathering Devices

Many laboratory devices for accelerating degradation are available. See Ref. [55] for descriptions of various devices and their advantages and disadvantages. The various devices expose panels to UV sources with different wavelength distributions. Also, the panels are subjected to cycles of water spray (or high humidity). Although these tests are widely used, results frequently do not correlate with actual exposure results. A general problem with accelerated weathering methods is the difficulty in accelerating the effects of radiation, heat, and moisture uniformly, not to mention the effects of other atmospheric degradants. The predictive value of accelerated weathering with artificial light sources is particularly questionable when a light source includes wavelengths below 290 nm. Variability of performance of the test instruments can also be a problem, especially when comparing results from laboratory to laboratory [42]. Typically, a number of specimens are tested at the same time, and the device geometry must expose them all to the same level of radiation.

An evaluation of accelerated weathering devices available in 1985 for a polyester–urethane coating using photoacoustic–FTIR spectroscopy concluded that none of the conventional devices were suitable, including a carbon arc device with Corex D filters, a xenon arc device with borosilicate inner and outer filters, and a UV device with FS-40 fluorescent bulbs [56]. All artificial light sources resulted in the loss of isophthalate groups in the coating, which was not observed during accelerated weathering in Florida (5° south) or in Arizona (EMMAQUA). These results correlate with the general wisdom that polyesters, presumably with phthalate or isophthalate groups, perform worse than acrylics in accelerated weathering devices relative to their performance in Florida or Arizona exposure. The unnatural weathering that resulted in loss of isophthalate groups was attributed to excessive amounts of short wavelength light (lower than 290 nm) from the artificial light sources.

A comparison of spectra of sunlight (Miami average optimum) and artificial weathering devices that illustrates this disparity is provided in Figure 5.1. As shown, the FS-40 fluorescent bulbs utilized in Atlas UVCON and Q-Panel QUV devices exhibit strong unnatural emission below 300 nm.

Many examples of reversals of results comparing coatings with known exterior durability with laboratory tests have been found. For example, poor results in early evaluations of HALS compounds by QUV testing might have led to their abandonment. Fortunately, remarkable outdoor durability results were obtained, which prompted continued development. Another example is that some automotive base coat–clear coats containing alkanoyl HALS (Section 5.2.3) performed very well in QUV tests but had poor resistance to delamination in the field. It is suspected that this type of HALS compound is quickly activated by short wavelength UV but that sunlight turns it on too

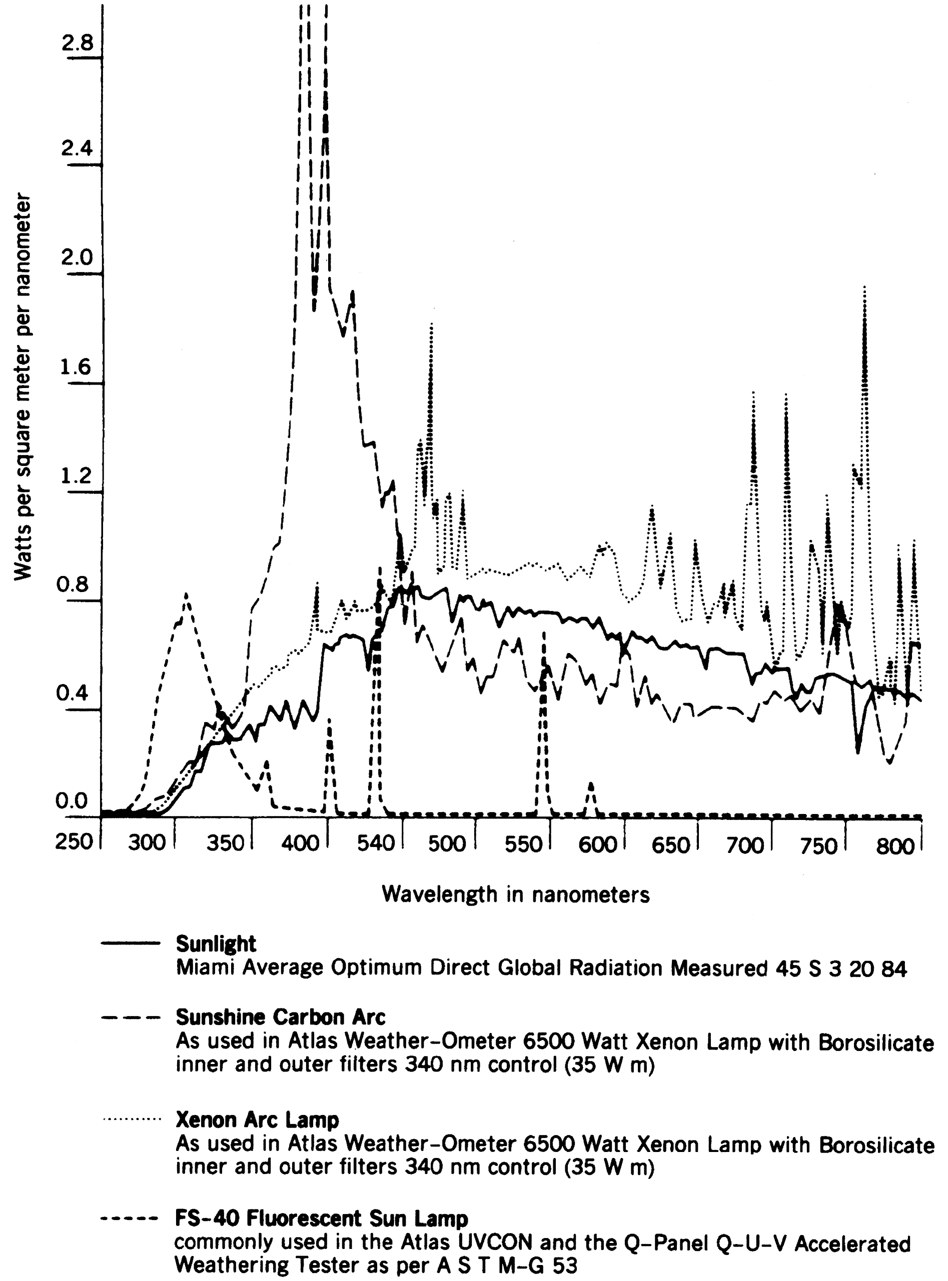


Figure 5.1. *Wavelength distribution of radiation from various sources. (Courtesy of Atlas Electric Devices, Chicago.)*

slowly. In this case, reliance on the QUV test to predict performance had severe economic consequences. Not only are there examples of poorer coatings showing better laboratory test results, and vice versa, but there are also disparities and reversals when comparing various laboratory test methods. Thus, one may optimize a coating formulation for performance in a particular weathering device only to find that it performs poorly in a different weathering device or outdoors. More serious, as might have occurred in the original work on HALS compounds, is the possibility of rejecting a superior material on the basis of accelerated laboratory testing. The argument that laboratory tests are at least useful for eliminating coatings that exhibit clearly inadequate performance is specious, since accumulated knowledge of failure mechanisms is adequate to eliminate such formulations without testing.

More recently, device manufacturers claim considerable improvement over older devices. Filtered xenon-lamp weather test devices that closely match the short UV content of sunlight have become available. In addition, UV-A-340 fluorescent bulbs are available that closely approximate sunlight between 290 and 340 nm. Automotive companies favor xenon-lamp testers.

Although accelerated weathering devices have been improved by closer correspondence of UV emissions with sunlight, it appears unlikely that a completely satisfactory device will be developed because the variations in exterior environments to which coatings are exposed are so great. As with any other highly accelerated test, stabilizer loss by volatilization may well be insignificant during the test period but very important over the long time periods of actual use. This situation serves to emphasize the need to accumulate data banks of real field use results and to correlate these results with structure to develop a basic understanding of the mechanisms of failure.

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6

Adhesion

Adhesion is an essential characteristic of most coatings. Unfortunately, there is inadequate basic scientific understanding of the variables affecting adhesion. As a result, some of the comments in this discussion are based only on reasonable deductions that fit in with accumulated experience.

One difficulty in dealing with adhesion is defining what *adhesion* means. In most cases, a coatings formulator thinks of adhesion in terms of the question: How hard is it to remove the coating? But a physical chemist would think in terms of the work required to separate two interfaces that are adhering. These perspectives can be different considerations; the latter is only one aspect of the former. Removal of a coating requires breaking or cutting through the coating and pushing the coating out of the way, as well as separating the coating from the substrate.

6.1. SURFACE MECHANICAL EFFECTS ON ADHESION

Resistance to separation of coating and substrate can be affected by mechanical interlocking. Consider the schematic representations in Figure 6.1. With a very smooth interface between coating and substrate, as shown in sketch A, the only forces holding the substrate and coating together are the interfacial attractive forces per unit of geometric area. With a rough surface on a microscopic scale, as represented in sketch B, two other factors are important. In some places, there are undercuts in the substrate; to pull the coating off the substrate, one would either have to break the substrate or break the coating to separate them. The situation is analogous to using a dovetail joint to hold two pieces of wood together. Another factor is that the actual contact area between the coating and the rough substrate is substantially larger than the geometric area.

Organic Coatings: Science and Technology, Third Edition, by Zeno W. Wicks, Jr., Frank N. Jones, S. Peter Pappas, and Douglas A. Wicks

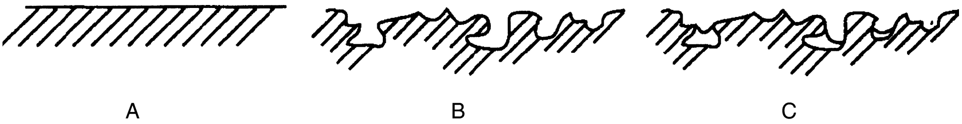


Figure 6.1. Geometries of surface interactions between a coating and a substrate. A, smooth interface between coating and substrate; B, rough surface on a microscopic scale; C, rough surface with incomplete penetration of coating.

Better adhesion can generally be obtained if the surface of a substrate is roughened before coating; however, as can be seen in sketch C, surface roughness can be a disadvantage. If the coating does not completely penetrate into the microscopic pores and crevices in the surface, dovetail effects are not realized, and the actual interfacial contact area can be smaller than the geometric area. Furthermore, when water permeates through the film to the substrate, there will be areas of contact of water with uncovered substrate, which can be a major problem, especially if the coating is to protect steel against corrosion.

The importance of surface roughness is widely recognized, but its effect on coatings has not been subjected to many scientific studies. The scale of the roughness of surfaces can vary from macroscopic to microscopic to submicroscopic. It is important to consider the situation on a microscopic and submicroscopic scale. What factors control the rate of penetration of a liquid into such pores and crevices? The situation is analogous to penetration of a liquid into a capillary on the micro scale, although possibly not on the nano scale. Equation 6.1 shows the variables affecting distance of penetration L (cm) into a capillary of radius r (cm) in time t (s), where γ is surface tension (mN m^{-1}), θ is contact angle, and η is viscosity (Pa•s):

$$L = 2.24\left[\frac{\gamma}{\eta}(r\cos\theta)t\right]^{1/2} \tag{6.1}$$

The rate of penetration, L/t, increases with increasing surface tension of the coating. However, there is an upper limit to this surface tension effect because the rate is strongly affected by contact angle. The rate is fastest when the cosine of the contact angle is 1: that is, when the contact angle is zero. The cosine can be 1 only if the surface tension of the liquid is less than that of the solid substrate. The radius of the capillary is a variable of the substrate, not of the coating.

Accordingly, the variable over which the formulator has greatest control is viscosity (η). The critical viscosity is that of the continuous (external) phase of the coating, not the bulk viscosity of the coating, including the internal phase of pigment and polymer particles, which are too large to participate, as effectively, in penetrating the microscopic and submicroscopic surface irregularities. The lower the viscosity of the external phase, the more rapid the penetration. Since in most cases, the viscosity of the vehicle increases after application; it is important to keep the viscosity low for a long enough time for penetration to approach completion. Since the viscosity of resin solutions increases with molecular weight (MW), one would expect that lower MW resins would provide superior adhesion after cross-linking, everything else being equal. This hypothesis has been confirmed in the case of epoxy resin coatings on steel [1]. Another possible advantage of low MW resins is that their molecules may be better able than high MW molecules to penetrate smaller crevices. Coatings with low viscosity external phases, slow evaporating solvents, and relatively slow cross-linking rates have been found, in general, to give better adhesion. In general, baked coatings give better adhesion than do air dry coatings. (The term *air dry* is used widely but is potentially confusing. It generally means that the film is formed at ambient temperature, but does not necessarily mean that oxygen is required for cross-linking.) When a coated article goes into an oven, the temperature increases, the viscosity of the external phase decreases, and penetration into surface irregularities becomes easier. This is only one of several possible explanations for the advantages of baked coatings when adhesion is critical.

6.2. EFFECTS OF INTERNAL STRESS AND FRACTURE MECHANICS

Internal stresses in coatings amount to forces that counteract adhesion; less external force is required to disrupt the adhesive bond. The common statement that internal stresses result from shrinkage is misleading; rather, internal stresses result from the inability of coatings to shrink as they form films on rigid substrates. When solvent evaporates from a thermoplastic coating (lacquer), in the early stages, the polymers can accommodate the resulting voids by relaxation; thus, shrinkage occurs. However, as film formation proceeds, T_g rises and free volume is reduced; it becomes more difficult for the polymer to accommodate the voids from solvent evaporation, so it becomes fixed in unstable conformations, and internal energy (stress) increases. This phenomenon is particularly likely to occur in coatings in which the T_g approaches the film-forming temperature [2]. In some cases, the stresses build up sufficiently that spontaneous delamination occurs [3]. Stresses can result not only from volume contractions, but also from volume expansions, such as swelling of films by exposure to high humidity [3] or water immersion [4].

In thermosetting coatings, cross-linking reactions lead to the formation of covalent bonds that are shorter than the distance between two molecules before they react. When such reactions occur at temperatures near the T_g of the film, stresses result from the inability of the coating to undergo shrinkage. As the rate of cross-linking increases, stresses also tend to increase, since less time is available for polymer relaxation to occur. An extreme example is UV curing of acrylated resins by free radical polymerization that occurs in a fraction of a second at ambient temperatures (Section 29.2). Shrinkage, measured by thermomechanical analysis (TMA), has been shown to lag significantly behind polymerization [5]. The high rates of polymerization, together with the relatively large shrinkage that accompanies polymerization of double bonds, contribute to the generally observed poor adhesion of UV cure acrylated resins to smooth metal surfaces. Heating after UV curing relaxes the cross-link network and often improves adhesion.

Nonuniform curing, particularly in the later stages, as well as film defects or imperfections in the film, can lead to localized stresses that exert adverse effects on adhesion [6]. Localization of stresses at imperfections falls within the discipline of *fracture mechanics*. The effects of fracture on abrasion resistance are considered in Section 4.3.1. The phenomena have been studied most extensively in adhesive bonding of substrates [7], but must also affect adhesion of coatings. If there is a local imperfection in a film, any stress applied to that part of the film could be concentrated at the imperfection. Localized imperfections result in greater stress (force per unit area) and greater probability of forming a crack. Once a crack starts, the stress concentrates at the point of the crack, leading to crack propagation. If the crack propagates to the coating–substrate interface, stress concentration can cause the film to delaminate. (Fractures and stress fractures within metal substrates are important considerations in adhesion and corrosion, but they are beyond the scope of this book.)

Although the principle is widely recognized, identification of causes of imperfections is more difficult. Pigment particles with sharp crystal corners and air bubbles are examples of potential sites for concentration of stresses. On the other hand, incorporation of particles of rubber may lead to dissipation of stresses (Section 4.3.1). Presumably, such stress dissipation would reduce the probability of fracture mechanical adhesive failure.

6.3. RELATIONSHIP BETWEEN WETTING AND ADHESION

Wetting is a major, and perhaps limiting, factor in adhesion. If a coating does not spread spontaneously over a substrate surface so that there is intermolecular contact between the substrate surface and the coating, there cannot be interactions and hence no contribution to adhesion. The relationships between wetting and adhesion were studied extensively by Zisman [8]. A liquid spreads spontaneously on a substrate if the surface tension of the liquid is lower than the surface free energy of the solid. [Surface free energies of solids have the same dimensions as surface tension (Section 24.1).] If the surface tension of a liquid is too high, a drop of the liquid stays as a drop on the surface of the solid—it has a contact angle of 180°. If a liquid has a sufficiently low surface tension, it spreads spontaneously on the substrate and has a contact angle of 0°. At intermediate surface tensions, there are intermediate contact angles. A schematic drawing of a drop of liquid with an intermediate surface tension is shown in Figure 6.2.

The relationship between contact angle θ and the surface free energy of the substrate γ_S, the surface tension of the liquid γ_L, and the interfacial tension between the solid and the liquid γ_{SL} for a planar surface is given as

$$\cos\theta = \frac{\gamma_S - \gamma_{SL}}{\gamma_L} \qquad (6.2)$$

Maximum adhesion requires a contact angle of 0°. Experimental determination of contact angles of complex systems such as coatings, especially on rough substrates with heterogeneous compositions, is difficult [9]. In general, it is sufficient to conceptualize the

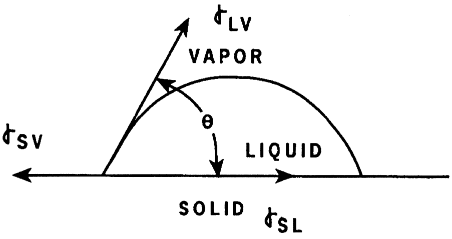


Figure 6.2. *Contact angle.*

relationships by saying that adhesion requires that the liquid have a lower surface tension than the surface free energy of the substrate to be coated. From a practical standpoint, it is useful to do cruder but easier experiments. One can apply a drop of coating on a substrate, put the sample in an atmosphere saturated with the solvents in the coating, and watch the spreading. If the droplet of coating stays as a small ball, spreading is poor and adhesion problems should be expected. If the drop spreads out to a thin, wide circle, the coating meets at least one criterion for good adhesion. It is also useful to carry out a second type of experiment, in which a coating is spread mechanically on a substrate under a solvent saturated atmosphere and then observed. Generally, a liquid that spreads spontaneously in the first experiment will remain spread out in the second experiment. But sometimes, a liquid that spreads on the surface will draw up into droplets, or at least pull away in sections from the substrate when standing, without solvent evaporation.

Consider, for example, the application of *n*-octyl alcohol to a clean steel surface. The surface tension of *n*-octyl alcohol is lower than the surface free energy of steel, and it spreads on steel spontaneously. However, if one spreads out a film of *n*-octyl alcohol on steel, the film draws up to form droplets on the surface of the steel. The low surface tension of the *n*-octyl alcohol results from the linear hydrocarbon chain; however, after spreading on the polar surface of the steel, the hydroxyl groups of the *n*-octyl alcohol molecules interact with the surface so that a monolayer of oriented *n*-octyl alcohol molecules forms on the surface. This makes a new surface, aliphatic hydrocarbon, which has a low surface tension, lower than the surface tension of *n*-octyl alcohol. The *n*-octyl alcohol above a monolayer *dewets*. The behavior of *n*-octyl alcohol illustrates a principle important in formulating coatings: One must be careful about using additives with single polar groups and long hydrocarbon chains in coatings to be used directly on metals. An example is the poor adhesion to steel that can result from use of dodecylbenzenesulfonic acid as a catalyst (Section 11.3.1.1). Adhesion of latex films can be affected by a layer of surfactant forming at the interface between the coating and the substrate [10].

6.4. ADHESION TO METAL SURFACES

The metal and the surface characteristics of the metal can have major effects on adhesion; Ref. [11] provides a review of metal surface characteristics, cleaning, and treatments. The surface tension of a clean metal surface (usually, metal oxide) is higher than that of any potential coating. However, metal surfaces are frequently contaminated with oil, and such surfaces can have very low surface tensions. Whenever possible, it is desirable to clean the surface of the metal before applying a coating. Sometimes, the metal is wiped with rags wet with solvent. A more effective method is *vapor degreasing*, in which the object is hung from a conveyor that carries it into a tank above a boiling chlorinated solvent. The cold steel surface acts as a condenser, condensing solvent on the surface of the steel, where it dissolves oils. The solution drips off, removing the oil. The solvent is purified by distillation for reuse. Surfactant solutions are also used to clean oil from metals [11]. Care must be exercised in selecting surfactants and in rinsing the surface after cleaning. It is possible for some surfactants to adsorb on the surface, creating a hydrocarbon layer on the surface of the metal.

Steel can be cleaned by abrasive particle blasting such as sandblasting. (See Ref. [11] for a discussion.) The surface of the steel, including rust, is removed, leaving a rough surface. Sandblasting is widely used for steel structures such as bridges and tanks, but it leaves the steel surface too rough for products such as automobiles and appliances. Sandblasting is effective, but there are health hazards to workers from inhalation of silica dust and old paint debris. A variety of alternative blasting techniques are being used or evaluated [12]. These include use of other dry, abrasive materials, such as steel grit or water-soluble abrasives, including sodium bicarbonate and salt, to replace sand; cryogenic cleaning by blasting with dry ice pellets; vacuum blasting using aluminum oxide; and for cleaning softer metals such as aluminum, plastic pellet blasting. Ultrahigh pressure hydroblasting at pressures above 175 mPa (25,000 psi) is very effective in removing oil and surface contaminants such as salt.

Formulations are tested on laboratory panels, but the surfaces of these panels are not the same as those of the product to which the coating will be applied. Furthermore, commercial test panels vary: for example, the side of the panel next to the wrapping of a package of panels was shown to have a different surface analysis than that of inner panels from the same package [13]. Washing the panels with warm water and rinsing with acetone before coating generally improved adhesion. When possible, laboratory tests should also be carried out on the ultimate substrate, or at least on sample pieces of metal to be used in production, simulating, as closely as possible, factory cleaning and treating procedures.

6.4.1. Surface Preparation

When good adhesion, corrosion protection, and a relatively smooth surface are required, it is common to treat the surface of the metal chemically. The treatments for steel are called *conversion coatings* or *chemical pretreatments*. A variety of phosphate-based conversion coatings are used. One such coating involves spray or immersion application of a phosphoric acid–based "iron phosphate" solution. This method provides a mild etch of the steel surface and precipitation of a ferrous–ferric phosphate monolayer. Adhesion of coatings is markedly increased; however, corrosion protection is enhanced only slightly. More enhancement is often possible by using zinc phosphate conversion coating. The steel object is immersed in a bath of zinc acid phosphate solution and a coprecipitate of zinc and ferric phosphates is formed on the steel surface, as shown in Scheme 6.1. Both adhesion and corrosion protection are enhanced.

The coprecipitate forms a mesh of crystals that adheres tightly to the surface, increasing the surface area on a microscopic scale. Depending on the zinc concentration in the treatment bath, different crystals can be deposited. At relatively high zinc concentrations, the crystals are predominantly hydrated zinc phosphate, $Zn_3(PO_4)_2 \cdot 4H_2O$, called hopeite. Under zinc-starved conditions, the crystals have been identified as phosphophyllite, $Zn_2Fe(PO_4)_2 \cdot 4H_2O$ [14]. The performance of the conversion coating is affected by the

Scheme 6.1

$$\begin{aligned}
HPO_4^{2-} &\rightleftharpoons H^+ + PO_4^{3-} \\
2H^+ + Fe &\longrightarrow Fe^{2+} + H_2 \\
Fe^{2+} + [Ox] &\longrightarrow Fe^{3+} \\
3Zn^{2+} + 2PO_4^{3-} &\longrightarrow Zn_3(PO_4)_2 \downarrow \\
Fe^{3+} + PO_4^{3-} &\longrightarrow FePO_4 \downarrow
\end{aligned}$$

uniformity and degree of surface treatment. Zinc phosphate coatings are generally applied in the range 1.5 to 4.5 $g\,m^{-2}$. A variety of other phosphate coatings are also used. (See Ref. [11] and Sections 7.3.1.1, 27.1, 27.2, and 30.1.1 for further discussions of conversion coating.)

The reactions shown in Scheme 6.1 are straightforward. Achieving the high rates of reaction required to permit minimum dwell times for treatment is more difficult. Proprietary formulations reduce times to the order of minutes or seconds. Treatment quality is dependent on time, temperature, and pH; these and other variables must be closely controlled to assure that the desired type and dimensions of crystals are formed. The treated surface must be rinsed thoroughly to remove any soluble salts, since these salts could lead to blister formation when water vapor permeates through a coating film applied over the soluble salts; rinsing also removes loosely adhering crystals. It has been common for the last rinse to contain a low concentration of chromic acid to protect against corrosion. Due to the toxic risks of hexavalent chromium, replacements for the chromate rinse are being sought. Over zinc phosphate, a rinse of 0.5% methyltrimethoxysilane with sufficient H_2ZrF_6 to give a pH of about 4 is reported to give better performance than a chromic acid rinse [15]. However, over iron phosphate, the silane–H_2ZrF_6 rinse gave a poorer performance then did a chromic acid rinse.

The mechanism of action of a phosphate crystal layer is not fully understood. One factor is that the coating penetrates into the crystal mesh, providing a mechanical attachment to the crystals attached to the surface. The interfacial area for interaction is greater than for a relatively smooth steel surface. It is also possible that hydrogen-bond interactions between these crystals and the resin molecules are stronger (i.e., less readily displaced by water) than those between the steel surface and the resin molecules.

The surface of aluminum is a thin, dense, coherent layer of aluminum oxide. For many applications, no treatment other than cleaning is required. However, for applications in which there might be exposure to salt, surface treatment is necessary. Most treatments for aluminum have been chromate treatments. An example of one such treatment is an acid bath containing chromate, fluorides, and a ferricyanide salt as an accelerator. The resulting coating is said to have the following composition: $6Cr(OH)_3 \cdot H_2CrO_4 \cdot 4Al_2O_3 \cdot 8H_2O$. (See Ref. [11] for further discussion.) In the past several years, many chrome- and cyanide-free proprietary aluminum conversion coatings have been developed that demonstrate a performance equivalent to that of chrome coatings.

To provide greater protection against corrosion, steel coated with zinc is widely used in construction and automobiles. Several types of zinc-coated steel are used; the best known is galvanized steel. There can be large variations in adhesion, depending on the condition of the zinc layer of the galvanized steel. If zinc-coated steel has been exposed to rain or high humidity before coating, there may have been some degree of surface oxidation, leading to formation of a combination of ZnO, $Zn(OH)_2$, and $ZnCO_3$; all of these are basic and somewhat soluble in water. Therefore, it is important to use saponification resistant resins in primers for galvanized steel. Resins such as alkyds, which tend to saponify, are likely to give poor adhesion in service. Zinc surfaces on automobile bodies are treated with zinc, manganese, or nickel phosphate conversion coatings before cationic electrodeposition of primer [16]. The effectiveness of phosphate coatings is affected by the presence of small amounts of other metals in the zinc coating [17]. The coating of galvanized steel is reviewed in Ref. [17].

Stainless steel, because of its smoothness and lack of oxide and hydroxide groups on the surface, is difficult to adhere to. In some cases, roughening the surface provides a basis for anchoring; in others, pretreatment with an electrochemically produced flash of chromium/chromium oxide is required [18].

Plasma treatment is a new approach being investigated for cleaning and treating the surface of cold-rolled steel [19]. Initially, the steel is cleaned by plasma discharge, and then trimethylsilane is introduced into the plasma chamber, leading to polymerization of a thin layer of polymer bonded to the surface. Laboratory tests indicated superior adhesion of electrodeposition coatings (Chapter 27) to the surface compared to a conventionally pretreated galvanized steel substrate. If the process can be scaled up successfully for production, substantial benefits can be foreseen. Cold-rolled steel is less expensive and more readily recycled than electrogalvanized steel, and the waste disposal problems associated with electrogalvanizing and phosphating would be eliminated.

Another approach being investigated is use of bis(trialkoxysilyl)alkanes to react with the surface of steel (Section 6.4.3).

6.4.2. Coating–Substrate Interaction

The surface of clean steel is not iron; rather, hydrated iron oxides are present as a monolayer on the iron. The layer is not a layer of rust particles but a monolayer of hydrated oxide [20]. The surface is rarely, if ever, uniform on the molecular level. Adhesion to this surface is promoted by developing hydrogen bonds between groups on the resin molecules and the oxide and hydroxide groups on the surface of the steel. (In the case of phosphate conversion–coated steel, there is the further possible hydrogen bond interaction with the phosphate groups.) Some authors prefer to interpret the interactions in terms of association between soft acids and soft bases [21].

It follows that adhesion is promoted by using resins having multiple hydrogen-bond donating and accepting groups, such as carboxylic acid (strongly hydrogen-donating), amine (strongly hydrogen-accepting), hydroxyl, urethane, amide (the latter three being both hydrogen-donating and hydrogen-accepting), and phosphate (hydrogen-donating and hydrogen-accepting). One might assume that a large number of such substituents on a molecule would be desirable. However, it is known from adsorption studies that if there are large numbers of polar groups, at equilibrium the adsorbed layer can be very thin. The principle can be illustrated by considering a polymer molecule with an aliphatic backbone chain with polar groups on every other carbon atom. At equilibrium, adsorption of adjacent polar groups is favored sterically, resulting in a thin adsorbed layer with the polar groups on the steel surface and only hydrocarbon groups exposed to the rest of the coating. The interactions between the rest of the coating and the hydrocarbon groups would be expected to be weak, resulting in a weak boundary layer and poor cohesion. If a smaller number of hydrogen-bond-donating groups are scattered along a resin chain, adsorption of resin molecules may occur with loops and tails sticking up from the surface so that some of the polar groups are adsorbed on the surface and some are on the loops and tails, where they can interact with the rest of the coating. On those parts of the resin molecule in the loops and tails, there can be groups to hydrogen-bond with molecules in the coating, as well as functional groups, which can react with a cross-linker in the coating.

BPA epoxy resins (Sections 13.1.1 and 15.8) and their derivatives commonly provide excellent adhesion to steel. These resins have hydroxyl and ether groups along the chain, which can provide interactions with both the steel surface and other molecules in the coating. The cross-linkers employed with these resins often introduce additional hydrogen-bonding groups, such as amines. It may also be important that the backbone consists of alternating flexible 1,3-glyceryl ether and rigid bisphenol A groups. It seems logical that such a combination could provide the flexibility necessary to permit multiple adsorption of hydroxyl groups on the surface of the steel, along with the rigidity to prevent adsorption of all of the hydroxyl groups. The remaining hydroxyl groups can participate in cross-linking reactions or can hydrogen bond with the rest of the coating. The effects of variations in epoxy resin composition on adhesion are discussed in Refs. [1] and [22].

In general, the results of many studies of adsorption of polymer molecules on metal surfaces are consistent with the picture given above. However, many of these studies involve adsorption from dilute solutions. Observations are made over relatively long time intervals, permitting equilibrium conditions to develop. With polydisperse MW adsorbents, low MW species are adsorbed first, but at equilibrium, they are displaced by higher MW molecules with larger numbers of polar groups. What really happens when a coating is applied? The resin is in a relatively concentrated solution, and the solvent evaporates in a relatively short time. There may not be time for equilibrium to be established. Depending on the coating, those groups that happened to be near the surface when the film was applied might remain there and could lead to poor adhesion, even if the same resins could provide good adhesion given the opportunity for appropriate orientation and equilibration to occur. Such a scenario is compatible with improved adhesion using slow evaporating solvents, which can also permit more complete penetration into surface crevices. Perhaps another reason that baking coatings commonly leads to improved adhesion is greater opportunity for orientation of molecules at the substrate–coating interface at the higher temperature. There is need for further research on interactions and orientation at the interface of coatings and substrates.

Surface analysis can be useful in understanding factors affecting adhesion. The surfaces of uncoated steels have been studied by Auger analysis; organic compounds have been detected on the surface of some cold-rolled steels. These organic compounds apparently become embedded in the surface of the steel during coil annealing. If this happens, it becomes difficult to obtain high quality phosphate conversion treatments on the steel [23]. Such steels more commonly lead to adhesion failures and to inferior corrosion protection by coatings.

X-ray photoelectron spectroscopy (XPS) can be used to study the surface of steel from which a coating has been removed as well as the underside of the coating. This technique can be particularly powerful for showing where failure occurred: that is, whether failure was between the steel and the coating or between the main body of the coating and a monolayer (or a very thin layer) of material on the surface of the steel. Other valuable analytical procedures for thin surface layers are attenuated total reflectance (ATR) and FTIR. Such techniques have been most useful for diagnosing problems; further use of these and other analytical techniques for understanding the mechanisms of adhesion can be anticipated.

Although strong interaction between coating and steel is critical for achieving good adhesion, it is also important to develop interactions that cannot be displaced easily by water. A reason that the presence of multiple groups on resin molecules, such as hydroxyl groups on epoxy resins, may be desirable is that some may remain bonded to the steel while others are reversibly displaced by water. This phenomenon has been termed *cooperative adhesion* [24]. It has been found empirically that amine groups on the cross-linked resin molecules promote corrosion protection. Explanations for the effect are controversial; one hypothesis is that the amine groups interact strongly with the steel surface and are not as easily displaced by water from the surface as are hydroxyl groups. Phosphate groups are another substituent group that has been found to impart improved adhesion in the presence of water (i.e., wet adhesion). For example, the use of epoxy phosphates in epoxy coatings has been shown to improve both adhesion and wet adhesion [22] (Section 13.5). Phosphate functional (meth)acrylate esters as comonomers have been shown to improve wet adhesion of acrylic latex and solventborne acrylic coatings [25].

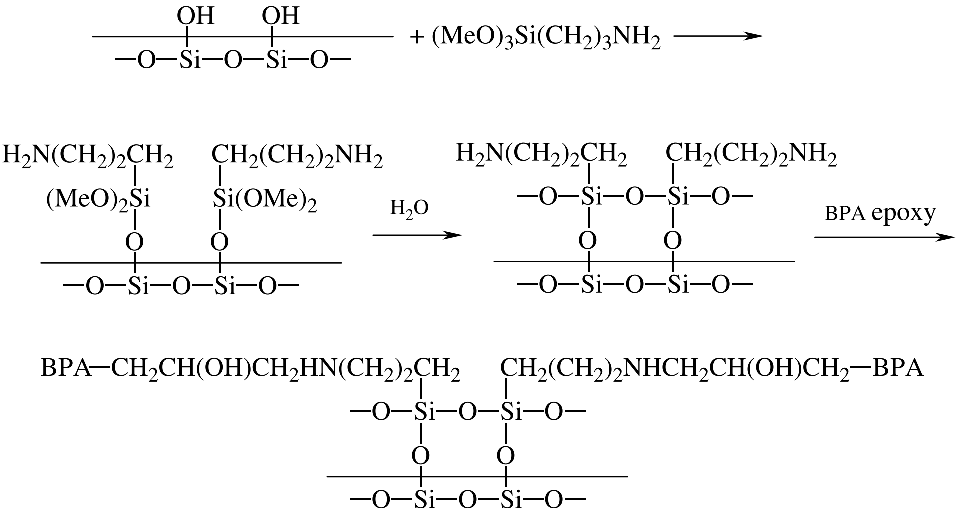
6.4.3. Covalent Bonding to Glass and Metal Substrates

Stronger interactions with the substrate surface should be possible by forming covalent bonds compared to the more readily displaced hydrogen-bonds. One such approach is the use of reactive silanes, which are very effective in enhancing adhesion of coatings to glass [26] (Section 16.2). A variety of reactive silanes is available; they all have a trialkoxysilyl group attached to a hydrocarbon chain, the other end of which has a functional group such as amine, mercaptan, epoxy, or vinyl. The alkoxysilyl group can react with hydroxyl groups on the surface of glass and with other alkoxysilyl groups after hydrolysis, so the surface of the glass becomes covalently bonded to a series of hydrocarbon tails substituted with reactive groups that can cross-link with the coating being applied.

In formulating an epoxy–amine coating for glass, one could add 3-aminopropyltrimethoxysilane to the amine package of the two package coating. After application, the trimethoxysilyl group can react with silanol groups on the surface of the glass to generate siloxane bonds, as shown in the first step of Scheme 6.2. The trimethoxysilyl groups can also react with water to produce silanol groups, which can in turn react with remaining silyl methoxy groups to generate polysiloxane groups at the glass surface; see the second step in Scheme 6.2. The terminal amine groups can react with epoxy groups in the resin so that the coating is multiply bonded to the surface of the glass, as shown in the third step in Scheme 6.2.

When water vapor penetrates through the coating to the glass interface, hydrolysis of some of the interfacial Si—O bonds occurs. However, with multiple interfacial bonds,

Scheme 6.2



some of the bonds remain intact and prevent the coating from delaminating. Furthermore, hydrolysis is reversible, so the hydrolyzed bonds can re-form. Before the advent of reactive silanes, it was difficult to formulate coatings that maintained adhesion to glass after exposure to a humid atmosphere.

Reactive silanes have also been added to coatings with the objective of improving adhesion to steel and other metal surfaces [26]. There is a growing body of indirect evidence of improvement. In theory, the trialkoxysilyl group could react with hydroxyl groups attached to iron, although direct evidence for this theory is in short supply. In the past, reactive silanes were not widely adopted as additives to improve the adhesion of coatings to steel, although their use is said to be increasing. Perhaps the lack of widespread use results from the lower stability of the bonds formed with iron than of those formed with glass and other metals, such as aluminum [27]. In the case of amino silanes, the amine group may be preferentially adsorbed on iron. An extensive review of the journal and patent literature is available [28].

Many investigations of the use of bis(trialkoxysilyl)alkanes for the treatment of metals have been reported [29]. For example [29], clean steel is rinsed with water and then the wet steel is dipped into an aqueous solution of bis(trimethoxysilyl)ethane (BTSE). BTSE hydrolyzes in the water and then adsorbs on the surface of the steel, reacting with hydroxyl groups and cross-linking with other BTSE molecules. The multiple covalent attachments form a coating that is stable when immersed in water. The surface can then be treated with a reactive silane that reacts with silanol groups and also provides a reactive group to react with a coating binder. Many variables affect the treatment; they are currently being investigated in the laboratory, and commercial use is projected. Laboratory tests indicate excellent adhesion in the presence of water and good corrosion protection.

Another approach to achieving chemical bonding to steel is the use of resins containing groups that can form coordination complexes with ferric compounds. For example, one can make resins with acetoacetic ester substituents (Section 17.6). Such esters are highly enolized and can coordinate with metal ions, including ferric salts. Preliminary reports indicate improvement in adhesion and corrosion protection [30]. Because of the potential hydrolysis of acetoacetic esters, evaluation over relatively long time intervals will be required to assess their commercial utility.

6.5. ADHESION TO PLASTICS AND TO COATINGS

In contrast to clean steel and other metals, commonly, there is a problem wetting the surface of plastic substrates with a coating. Wetting of many plastics is difficult, owing to their low surface free energies, and can be further reduced by the presence of mold release agents on molded plastic parts. Mold release agents should be avoided if at all possible. If essential, release agents should be selected that are relatively easily removed from the molded part, and care should be exercised to remove all traces. Even after cleaning, the surface free energies of some plastics are lower than the surface tensions of many coatings, resulting in a contact angle $>0^\circ$. The contact angle between coating and substrate should be 0° to permit spreading. Determination of contact angle is experimentally difficult, especially due to surface roughness and inhomogeneity [9].

Attainment of satisfactory adhesion to polyolefins, which generally have low surface free energy, usually requires treatment of the surface to increase its surface free energy. This can be done by oxidation of the surface to generate polar groups such as hydroxyl, carboxylic acid, and ketone groups. The presence of these groups not only increases surface free energy so that wetting is possible with a wider range of coating materials, but also provides hydrogen-bond acceptor and donor groups for interaction with complementary groups on coating resin molecules. A variety of processes can be used to treat the surface [31,32]. The surfaces of films, flat sheets, and cylindrical objects can be oxidized by flame treatment with gas burners using air/gas ratios such that the flames are oxidizing. Oxidation can also be accomplished by subjecting the surface to a corona discharge atmosphere; the ions and free radicals generated in the air by the electron emission serve to oxidize the surface of the plastic.

Adhesion to untreated polyolefins can be assisted by applying a thin *tie coat* of a low solids solution of a chlorinated polyolefin or chlorinated rubber. Ryntz has reviewed the various approaches and provided the results of various types of surface analysis [31]. (See Section 31.2.2 and Ref. [33] for further discussion of surface treatments.)

Both theoretical and experimental studies show that the molecules at the surface of a polymer are more mobile than those in the bulk material [34]. One theoretical study indicated that the layer of mobile molecule segments is about 2 nm in thickness [35]. Because polymer surfaces are dynamic, they adjust to the environment; polar groups will, with time, move away from a polymer–air interface and toward a polymer–water interface. Thus, the polar groups placed on the surface by oxidation treatments can be expected to move to the interior within hours or days after treatment [34].

Although adhesion between coatings and plastic substrates can be enhanced by hydrogen-bond interactions, still further enhancement can be obtained if the temperature is above the T_g of the plastic substrate. At temperatures above T_g, there is adequate free volume to permit resin molecules from the coating to move into the surface of the plastic, and vice versa. Presumably, penetration can be deeper than the thin layer of mobile molecule segments at the surface. When the solvent evaporates, the intermingled molecules increase adhesion. This interaction can be enhanced by having the structure of the coating resin be sufficiently similar to the structure of the plastic that the resin molecules are somewhat soluble in the plastic substrate. In some cases, promotion of adhesion by heating the plastic substrate above its T_g is not feasible because the plastic substrate may undergo heat distortion.

Solvents in the coating that are soluble in the plastic can enhance adhesion. The solvent swells the plastic, lowering its T_g, and facilitating penetration of coating resin molecules into the surface of the plastic. The solvents should evaporate slowly to permit time for penetration to occur. Fast evaporating solvents such as acetone can cause *crazing* of the surface of high T_g thermoplastics such as polystyrene and poly(methyl methacrylate). Crazing is the development of large numbers of minute surface cracks. (See Section 31.2.2 for a further discussion of crazing and coatings for plastics.)

Adhesion to other coatings, commonly called *intercoat adhesion*, is another example of adhesion to plastics. The same principles apply. The surface tension of the coating being applied must be lower than the surface free energy of the substrate coating to permit wetting. The presence of polar groups in both coatings permits hydrogen bonding; in the case of thermosetting coatings, covalent bonding enhances intercoat adhesion. It has been found empirically that the presence of relatively small amounts of amine groups on resins commonly gives coatings with superior intercoat adhesion. Such comonomers as 2-(*N*,*N*-dimethylamino)ethyl methacrylate and 2-aziridinylethyl methacrylate have been used to make acrylic resins with enhanced intercoat adhesion.

Curing temperatures above T_g increase the probability of satisfactory adhesion. Compatible resins in the substrate coating and top coat also increase the probability of satisfactory adhesion. Using solvents in the coating that can swell the substrate coating is a commonly used technique for enhancing intercoat adhesion. Coatings with lower cross-link density are more swollen by solvents and, in general, are easier to adhere to than are coatings with high cross-link density. Sometimes, one can undercure the primer, thus having a lower cross-link density when the top coat is applied. Cure of the primer is completed when the top coat is cured.

Adhesion to high gloss coatings is difficult to achieve because of their surface smoothness. Gloss coatings that have undergone excessive cross-linking on ageing are particularly difficult surfaces on which to apply an adherent coating. Sanding to increase surface roughness may be necessary to achieve intercoat adhesion. One reason for formulating primers with low gloss is that their rougher surfaces enhance adhesion. When possible, increasing the pigment loading of a primer above critical pigment volume concentration (CPVC) facilitates adhesion of a top coat (Chapter 23). Above CPVC, the dry film contains pores. When a top coat is applied, vehicle from the top coat can penetrate the pores in the primer, providing a mechanical anchor to promote intercoat adhesion. Care must be exercised not to have PVC too much higher than CPVC, or so much vehicle will be drained away from the top coat that the PVC of the top coat will increase, leading to a loss of gloss.

An essential requirement of many industrial coatings is *recoat adhesion*: that is, the ability of a coating to adhere to itself well enough that flawed or damaged objects can be repainted without extensive preparation. This requirement can be difficult to satisfy, especially with highly cross-linked gloss enamels. Additives to overcome film defects during application (Section 24.4) may interfere with recoat adhesion.

6.6. TESTING FOR ADHESION

In view of the complexity of adhesion phenomena, it is not surprising that there is difficulty in devising suitable tests for adhesion. As is so often the case in coatings, the only really conclusive way of telling whether adhesion of a coating is satisfactory is to use the product and see whether the coating adheres over its useful life.

A common method formulators use to evaluate adhesion is to see how easily a penknife can scrape a coating from a substrate. By comparing the resistance of a new coating–substrate combination to combinations with known field performance, the formulator has some basis for performance prediction. While a penknife in the hand of an experienced person can be a valuable tool, it has major disadvantages as a test method. The experience is not easily transferred from one person to another; even the technique for the test is not easily transferred. Also, there is no good way to assign numerical values to the results. Thus, it does not provide a basis for following small changes in adhesion as a result of changes in composition to aid in developing hypotheses to relate composition and adhesion.

Relatively satisfactory test methods for evaluating adhesives have been developed, but few of these methods are applicable to coatings. Many investigators have worked on a variety of methods in attempts to devise meaningful tests for evaluating the adhesion of coatings [36,37]. None of these tests are very satisfactory. For research purposes, the most useful technique is a direct pull test. A rod is fastened perpendicular to the upper surface of the coated sample with an adhesive. The panel is fastened to a support with a perpendicular rod on its back so that the two perpendicular rods are lined up exactly opposite each other. The assembly is put into the jaws of an Instron Tester (Section 4.5), and the tensile force required to pull the coating off the substrate is recorded. Since the procedure is subject to considerable experimental error, multiple determinations must be made. Experienced operators can achieve precisions of $\pm 15\%$. The adhesive must bond the rod to the coating surface more strongly than the coating is bonded to the substrate. It is also essential that the adhesive not penetrate into the coating to perturb the coating–substrate interface. Cyanoacrylate adhesives are generally satisfactory. The rods must be aligned with each other exactly and be perpendicular to the coating. If the rod is at even a slight angle to the surface, stress is concentrated on only part of the substrate–coating interface, and less force is required to break the bond. Sometimes, the weakest component is the substrate—this may be nice for advertising purposes, but it does not provide a measure of the adhesive strength.

Another potential complication is cohesive failure of the coating; again, no information on adhesion is obtained. In reading the literature, one sometimes finds data from tests in which cohesive, adhesive, and mixed cohesive–adhesive failures have occurred. The authors may then discuss the improvement in adhesion from some change that resulted in a greater force to get adhesive failure than that of another sample that failed cohesively. Clearly, such comparisons are invalid. When there is cohesive failure, all that is known is that the adhesive strength is above the measured value (within experimental error).

One must use caution in interpreting the results even when the sample appears to have failed adhesively at the substrate–coating interface. Sometimes, when no coating can be seen on the substrate surface after the test, there is a monolayer (or thin layer) of material from the coating left on the substrate surface. In this event, failure was not at the substrate surface but between the material adsorbed on the surface and the rest of the coating. Surface analysis is useful in determining the locale of failure and the identity of the adsorbed material. Fairly often, there is a combination of adhesive and cohesive failure. A possible explanation of such failures is that there was a fractural failure starting at some imperfection within the film, and the initial crack propagated down to the interface. Tensile values from samples that fail in this way cannot be compared to the tensile values of samples that failed adhesively.

The direct pull test does not evaluate the potentially important differences between the difficulty of breaking through a coating film and of shoving it out of the way, as mentioned at the beginning of the chapter. Despite all the difficulties, direct pull tests are the most useful available. Instruments have been devised for direct pull tests under field conditions. The method is quite widely used for quality control in high performance maintenance and marine coatings. Serious disadvantages for use on actual products are that the test is destructive and the area tested must be repainted. See Ref. [36] for a more detailed discussion of the effect of variables on the test results.

Adhesion can be affected by the angle of application of stress. An instrument called STATRAM II has been devised to combine a normal load and lateral traction to measure friction induced damage [38]. Optical measurements are combined with measurements of total energy consumed during the scraping process. The test has been used to study delamination of coatings when plastic automobile bumpers rub together or scrape against solid objects. In many cases, cohesive failure of the plastic occurred near the surface of thermoplastic olefin (TPO) rather than adhesive failure between the coating and the substrate. The composition of coatings, especially solvents, can affect the structure of the upper layer of the plastic. (See Section 31.2.2 for further discussion of adhesion of coatings to plastics.)

Acoustic testing is of increasing interest. When a film cracks, it emits acoustical energy. A coating is applied to a film, placed in a tensile tester, and a transducer is attached to the surface; then as the jaws of the tensile tester are separated, the vibrations of noise are recorded. This permits evaluation of the stress required to lead to film cracking. The devices are particularly useful in comparing dry films to those previously exposed to moisture testing.

Probably, the most widely used specification test is the *cross hatch adhesion test*. Using a device with 6 or 11 sharp blades, a scratch mark pattern is made across the sample, followed by a second set cut perpendicular to the first. A strip of pressure-sensitive adhesive tape is pressed over the pattern of squares and pulled off. Adhesion is assessed qualitatively on a 5 to 0 scale by comparing to a set of photographs, ranging from trace removal along the incisions to removal of most of the area. The test is subject to many sources of error, one being the rate at which the cuts are made. If the cuts are made slowly, they are likely to be even. However, if the cuts are made rapidly, it is possible that there will be cracks proceeding out from the sides of the cuts, due to more brittle behavior of coatings at higher rates of application of stress. Other important variables are the adhesive tape; the pressure with which it is applied; the angle and rate at which the tape is pulled off the surface; bending, if any, of the substrate during the test; and the surface of the coating to which the tape is applied. Some additives that appear to improve adhesion may actually only improve the test results by decreasing adhesion of the tape to the coating. The test may be useful for distinguishing between samples having poor adhesion and those having fairly good adhesion, but it is not very useful in distinguishing among higher levels of adhesion. See Ref. [36] for a more detailed discussion of the variables affecting the test.

Wet adhesion is a critical property for interior linings on tin cans. A paper provides evidence that electrochemical impedance spectroscopy (EIS) is a useful way to study wet adhesion of the coatings [39]. (See Sections 7.3.2 and 7.5, which deal with corrosion, for further discussion of factors affecting adhesion and testing for adhesion in the presence of water.)

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7

Corrosion Protection by Coatings

Corrosion is a process by which materials, especially metals, are worn away by electrochemical and chemical actions. The estimated annual economic cost of corrosion in the United States was $296 billion in 1995, so the incentive to improve corrosion protection technology is enormous [1]. In this chapter we discuss the principles of corrosion and the protective role of organic coatings; specific types of coatings for corrosion control are covered in Chapters 27, 30, and 33.

7.1. CORROSION OF UNCOATED STEEL

The major economic losses are from the electrochemical corrosion of steel, which is the main focus of this chapter. Aluminum is also important, especially in aircraft and military vehicles. Protection of various other metals has been reviewed [2]. Before we consider the role of coatings, it is important to understand the corrosion of uncoated steel.

In the corrosion of metals, electrochemical and chemical reactions are involved. An electrochemical (galvanic) element is formed when two pieces of different metals are connected with a conductive wire and partly immersed in an electrolyte, generally water containing some dissolved salts. An electrochemical reaction begins spontaneously with the oxidation of metal atoms and dissolution of ions at the anodic parts of the corrosion elements. Metals may be arranged in an electromotive series such that the most noble (least easily oxidized) metal forms the cathode. However, because polarization processes may change the character of a metal (e.g., by formation of thin layers of corrosion products or by the adsorption of gases such as hydrogen), the practical electromotive series differs somewhat from the theoretical one. The metals considered herein, in decreasing order of ease of oxidation, theoretically, are magnesium, aluminum, zinc, iron, tin, and copper.

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There are many kinds of steel, which corrode at different rates, depending on their composition and on the presence of mechanical stresses; all are alloys of iron and carbon with other metals. The composition of the surface varies from location to location; as a result, some areas are anodic relative to other areas that are cathodic. Stresses and the morphological structure of the metal surface can also be factors for setting up anode–cathode pairs. Cold-rolled steel has more internal stresses than hot-rolled steel and is generally more susceptible to corrosion, but cold-rolled steel is widely used because it is stronger. Internal stresses can also be created during fabrication or by the impact of a piece of gravel on an auto body, for example.

Steel adsorbs on its surface a thin layer of water, which dissolves traces of soluble salt, thus providing the electrolyte for electrochemical reactions. In the absence of oxygen, ferrous ions are the primary anodic corrosion products of steel. At cathodes, hydrogen is formed, which stops further dissolution of iron by cathodic polarization, except when the pH of the electrolyte is low.

$$\text{Anode:} \quad Fe \longrightarrow Fe^{2+} + 2e^-$$

$$\text{Cathode:} \quad 2H^+ + 2e^- \longrightarrow H_2$$

However, in the presence of oxygen, depolarization of the cathode takes place, hydroxyl anions are formed at the cathodes, and dissolution of iron continues:

$$O_2 + H_2O + 4e^- \longrightarrow 4OH^-$$

$$2Fe + O_2 + 2H_2O \longrightarrow 2Fe^{2+} + 4OH^-$$

The rate of corrosion of steel depends on the concentration of oxygen dissolved in the water at the steel surface, as shown in Figure 7.1. At low concentrations, the rate increases with increasing dissolved oxygen concentration. At high concentrations, the rate declines because of *passivation* (Section 7.2.1). The equilibrium concentration of oxygen in water exposed to the atmosphere at 25°C is about 6 mL L^{-1}.

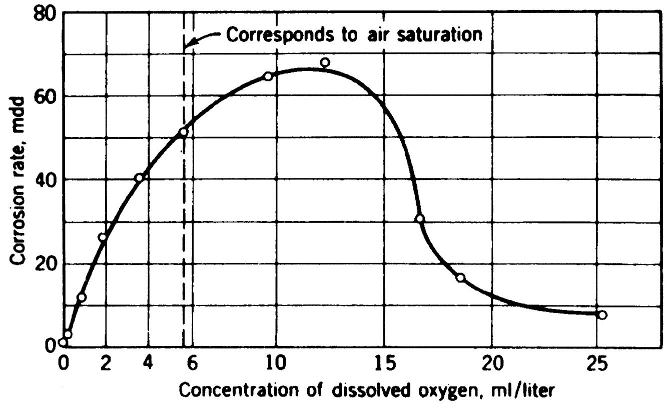

Figure 7.1. Effect of oxygen concentration on corrosion of mild steel in slowly moving distilled water, 48-hour test, 25°C. (From Ref. [3], with permission.)

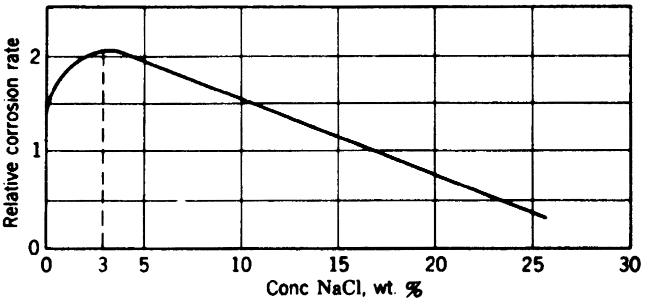

Figure 7.2. *Effect of sodium chloride on corrosion of iron in aerated solutions at room temperature (composite of data from several investigators). (From Ref. [3], with permission.)*

Corrosion can occur at a significant rate only if there is a complete electrical circuit. The rate of corrosion depends on the conductivity of the water at the steel surface. Dissolved salts increase conductivity, which is one reason that the presence of salts increases the rate of corrosion of steel. Effects of salts on corrosion rates are complex; the reader is referred to Ref. [1], or other general texts on corrosion, for detailed discussions. The relationship between NaCl concentration and corrosion rate is shown in Figure 7.2. The dashed vertical line in the figure indicates the salt concentration in seawater. At higher salt contents, the rate of corrosion decreases since the solubility of oxygen decreases as the NaCl concentration increases.

The rate of corrosion also depends on pH, as shown in Figure 7.3. Since iron dissolves in strong acid even without electrochemical action, it is not surprising that corrosion is most rapid at a low pH. Corrosion rate is nearly independent of pH between about 4 and 10. In this pH region, the initial corrosion causes a layer of ferrous hydroxide to precipitate near the anode. Subsequently, the rate is controlled by the rate of oxygen diffusion through the layer. Underneath, the surface of the iron is in contact with an alkaline solution

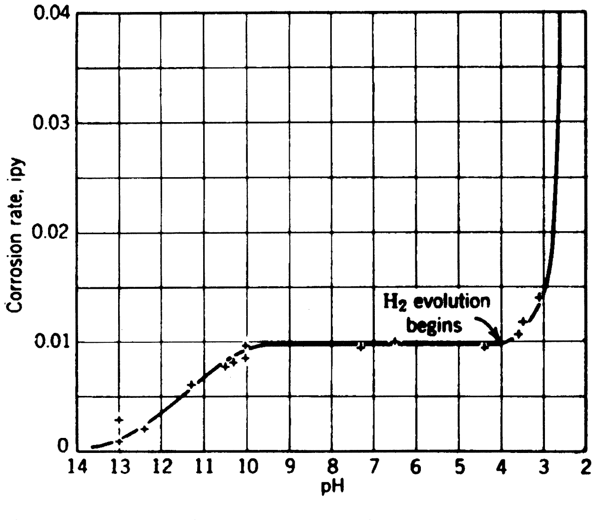

Figure 7.3. *Effect of pH on corrosion of iron in aerated soft water at room temperature. (From Ref. [3], with permission.)*

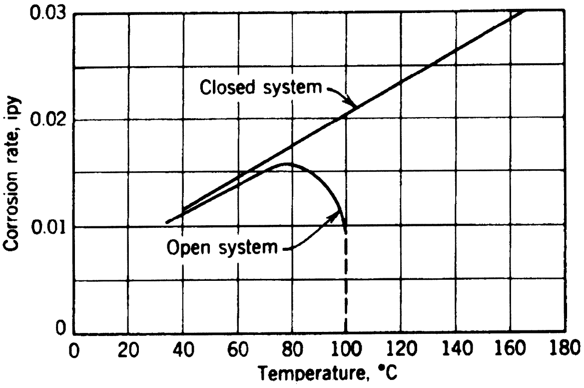

Figure 7.4. Effect of temperature on corrosion of iron in water containing dissolved oxygen. (From Ref. [3], with permission.)

with a pH of about 9.5. When the environmental pH is above 10, the increasing alkalinity raises the pH at the iron surface. The corrosion rate then decreases because of passivation (Section 7.2.1).

Corrosion rate also depends on temperature, as shown in Figure 7.4. The reactions proceed more rapidly at higher temperatures, as indicated by the increase in corrosion rate in a closed system. However, the solubility of oxygen in water decreases as temperature increases, so in an open system, where the oxygen can escape, the rate of corrosion goes through a maximum at some intermediate temperature. The temperature at which the corrosion rate maximizes is system dependent.

7.2. CORROSION PROTECTION OF METALS

In this section we deal with strategies for controlling electrochemical corrosion without the use of organic coatings, which serve to introduce principles for corrosion protection using organic coatings (Sections 7.3 and 7.4). One can suppress the anodic reaction, as discussed in Section 7.2.1; one can suppress the cathodic reaction, as discussed in Section 7.2.2; and one can prevent water, oxygen, and corrosion stimulants from contacting the surface, as discussed in Section 7.2.3.

7.2.1. Passivation: Anodic Protection

As shown in Figure 7.1, increasing oxygen concentration up to about 12 mL L^{-1} increases the corrosion rate because it acts to depolarize the cathode. At higher concentrations, more oxygen reaches the surface than is reduced by the cathodic reaction; beyond that concentration, corrosion is retarded. The mechanism of retardation has not been fully elucidated. According to one theory, if the oxygen concentration near the anode is high enough, ferrous ions are oxidized to ferric ions soon after they are formed at the anodic surfaces. Since ferric hydroxide is less soluble in water than ferrous hydroxide, a barrier of hydrated ferric oxide forms over the anodic areas. Suppression of corrosion by retarding the anodic reaction is called *passivation*. The iron is said to be *passivated*.

The critical oxygen concentration for passivation depends on conditions. It increases with dissolved salt concentration and with temperature, and it decreases with increases in pH and velocity of water flow over the surface. At about pH 10, the critical oxygen concentration reaches the value for air-saturated water (6 mL L^{-1}) and is still lower at higher pHs. As a result, iron is passivated against corrosion by the oxygen in air at sufficiently high pH values. It is impractical to control corrosion by oxygen passivation below about pH 10, since the concentrations needed are in excess of those dissolved in water in equilibrium with air. However, a variety of oxidizing agents can act as passivators. Chromate, nitrite, molybate, plumbate, and tungstate salts are examples. As with oxygen, a critical concentration of these oxidizing agents is needed to achieve passivation, and lower concentrations may promote corrosion by cathodic depolarization. The reactions with chromate salts have been studied most extensively. Partially hydrated mixed ferric and chromic oxides are deposited on the surface, where they presumably act as a barrier to halt the anodic reaction.

Certain nonoxidizing salts, such as alkali metal salts of boric, carbonic, phosphoric, and benzoic acids, also act as passivating agents. Their passivating action may result from their basicity. By increasing pH, they may reduce the critical oxygen concentration for passivation below the level reached in equilibrium with air. Alternatively, it has been suggested that the anions of these salts may combine with ferrous or ferric ions to precipitate complex salts of low solubility to form a barrier coating at the anode. Possibly, both mechanisms operate to some extent.

A fairly new approach to passivation is applying a film of electrically conductive polymer to a steel surface to protect it from corrosion. Polyphenyleneamine, commonly called polyaniline, is available commercially under the trade names Zypan [4] (E. I. DuPont de Nemours & Co.), Versicon (Allied Signal Co.), and Panda (Monsanto Co.). It is said to be effective by leading to the formation of a tight, very thin, metal oxide passivating layer on the surface of the metal. The polymer powders are insoluble in all solvents, non-fusible, and difficult to disperse because of high surface tension. Dispersions are available in a variety of vehicles. Reviews of the effects of conducting polymer coatings on metals are available [5,6]. Electropolymerization and deposition of polyaniline from a phosphate buffer solution onto stainless steel increases the corrosion resistance of the steel [7]. Steel coated with polythiophene by electropolymerization also provides corrosion protection [8]. Another review of conducting polymer coatings emphasizes protection of aluminum with poly[2,5-bis(*N*-methyl-*N*-propylamino)phenylenevinylene] [9].

Aluminum is higher than iron in the electromotive series and is more easily oxidized. Yet aluminum generally corrodes more slowly than steel. A freshly exposed surface of aluminum oxidizes quickly to form a dense, coherent layer of aluminum oxide. In other words, aluminum is passivated by oxygen at concentrations in equilibrium with air. On the other hand, aluminum corrodes more rapidly than iron under either highly acidic or highly basic conditions. Also, salt affects the corrosion of aluminum even more than it affects the corrosion of iron; aluminum corrodes rapidly in the presence of sea water.

7.2.2. Cathodic Protection

If steel is connected to the positive pole of a battery or a direct current source while the negative pole is connected to a carbon electrode, and both electrodes are immersed in salt water, the steel does not corrode. The impressed electrical potential makes the entire steel surface cathodic relative to the carbon anode. The result is electrolysis of water rather than corrosion of steel. This is an example of cathodic protection.

A related method is to connect the steel electrically to a piece of metal higher in the electromotive series than iron: for example, magnesium, aluminum, or zinc. When a block of one of these metals is connected to steel and immersed in an electrolyte, the metal is the only anode in the circuit, and all corrosion takes place at that anode. The metal is called a *sacrificial anode*. This method is often used to protect pipelines and steel hulls of ships. The sacrificial anode is gradually used up and must be replaced periodically. Zinc and magnesium are generally the preferred sacrificial metals. Aluminum is often ineffective because a barrier layer of aluminum oxide forms on its surface (Section 7.2.1). However, aluminum is appropriate for marine applications, since it corrodes readily in salt water.

Another method of cathodic protection is coating steel with zinc to make galvanized steel. The steel is protected in two ways: Zinc functions as a sacrificial anode and also acts as a barrier preventing water and oxygen from reaching the steel surface. Since zinc is easily oxidized, it is passivated by oxygen at concentrations below 6 $\mathrm{mL\,L^{-1}}$. If the surface of a galvanized sheet is damaged and bare steel and zinc are exposed, the zinc corrodes but not the steel. After exposure to the atmosphere, the surface of the zinc becomes coated with a mixture of zinc hydroxide and zinc carbonate. Both are somewhat soluble in water and strongly basic.

7.2.3. Barrier Protection and Inhibition

For steel to corrode, oxygen and water must be in direct molecular contact with the surface of the steel. Barriers that can prevent oxygen and water from reaching the surface prevent corrosion. The zinc layer on galvanized steel acts as a barrier. It may even be considered that a layer of irreversibly adsorbed small molecules can act as a barrier. It is often incorrectly assumed that the tin coating on steel in tin cans acts electrochemically, similarly to zinc in galvanized steel. Tin is lower than iron in the electromotive series, so the iron is the anode and the tin is the cathode. Before a can is opened, the tin coating is intact and acts as a barrier so that no water or oxygen reaches the steel. After a can has been opened, the cut bare edges expose both steel and tin to water and oxygen, and the steel corrodes relatively rapidly.

Many organic compounds are corrosion inhibitors for steel. Most are polar substances that tend to adsorb on high energy surfaces [10]. Amines are particularly widely used. Clean steel wrapped in paper impregnated with a volatile amine or the amine salt of a weak acid is protected against corrosion. Amines are also used in boiler water to minimize corrosion. The reason for their effectiveness is not clear. They may act as inhibitors because they are bases and neutralize acids. It may be that amines are strongly adsorbed on the surface of the steel by hydrogen bonding or salt formation, with acidic sites on the surface of the steel. This adsorbed layer then may act as a barrier to prevent oxygen and water from reaching the surface of the steel. However, this mechanism works only in the presence of an aqueous medium containing the inhibitor.

7.3. CORROSION PROTECTION BY INTACT COATINGS

Organic coatings can be effective barriers to protect steel when it is anticipated that the coating can be applied to cover essentially all of the substrate surface and when the layer remains intact in service. However, when it is anticipated that there will not be complete coverage of the substrate or that the layer will be ruptured in service, alternative strategies using coatings that can suppress electrochemical reactions involved in corrosion may be preferable; they are discussed in Section 7.4. It is seldom effective to try to use both strategies in the same coating layers—one must choose one or the other.

7.3.1. Critical Factors

Until about 1950, coatings were generally believed to protect steel by acting as a barrier to keep water and oxygen away from the steel surface. Then it was found by Mayne [11] that the permeability of paint films was so high that the concentration of water and oxygen coming through the films would be higher than the rate of consumption of water and oxygen in the corrosion of uncoated steel. Mayne concluded that barrier action could not explain the effectiveness of coatings and proposed that the electrical conductivity of coating layers is the variable that controls the degree of corrosion protection. Presumably, coatings with high conductivity would give poorer protection than would coatings of lower conductivity. It was confirmed experimentally that coatings having very high conductivity afforded poor corrosion protection. However, in comparisons of layers with relatively low conductivity, little correlation between conductivity and protection has been found. It may be that high conductivity layers fail because they also have high water permeability; some investigators believe that the conductivity of all coatings is at least a factor in corrosion protection [12,13].

Current understanding of protection of steel against corrosion by intact films is based to a significant degree on the work of Funke [14–17]. He found that an important factor not given sufficient emphasis in earlier work was adhesion of a coating to steel in the presence of water. Funke proposed that water permeating through an intact film could displace areas of the coating from steel. In such cases, the film shows poor *wet adhesion*. Water and oxygen dissolved in the water would then be in direct contact with the steel surface; hence, corrosion would start. As corrosion proceeds, ferrous and hydroxide ions are generated, leading to formation of an osmotic cell under the coating film. Osmotic pressure can provide a force to remove more coating from the substrate. Osmotic pressure can be expected to range between 2500 and 3000 kPa, whereas the resistance of organic coatings to deformational forces is lower, ranging from 6 to 40 kPa [14]. Thus, blisters form and expand, exposing more unprotected steel surface. It has also been proposed that blisters can grow by a nonosmotic mechanism [18]. The suggestion has been made that water absorbed by a coating induces in-plane compressive stress within the coating and extends the interfacial bonds elastically between the coating and the steel substrate [19]. At a point of weak adhesion between the coating and the substrate, the stress can lead to disbondment. It has been demonstrated that the rate of growth of blisters is dependent on the modulus of the coating layer; at a sufficiently high modulus, blister growth is minimized [20].

In either osmotic or nonosmotic mechanisms, the key to maintaining corrosion protection by a coating is sufficient adhesion to resist displacement forces. Both mechanisms predict that if the coating covers the entire surface of the steel on a microscopic as well as a macroscopic scale, and if perfect wet adhesion could be achieved at all areas of the interface, the coating would protect steel against corrosion indefinitely. It is difficult to achieve both of these requirements in applying coatings, so a high level of wet adhesion is important but is not the only factor affecting corrosion protection by coatings. For example, owing to nano- or micro-roughness of the metal surface, not all of its cavities may be filled by binder molecules, for steric reasons. These unprotected cavities, although small, are large enough to allow a local accumulation of water molecules that provides a medium for the action of corrosion cells [21]. Accordingly, Funke found that in addition to wet adhesion, low water and oxygen permeability help increase corrosion protection [16]. In any case, if wet adhesion is poor, corrosion protection is also poor. However, if the adhesion is fairly good, a low rate of water and oxygen permeation may delay loss of adhesion long enough so that there is adequate corrosion protection for many practical conditions.

7.3.2. Adhesion for Corrosion Protection

Chapter 6 deals broadly with adhesion, but wet adhesion, which is especially critical to corrosion protection, is reviewed here. Good dry adhesion must be taken as a given for achieving corrosion protection. If there is no coating left on the substrate, it cannot protect the steel. It has not been so obvious, however, that good wet adhesion is required. Good wet adhesion means that the adsorbed layer of the coating will not desorb when water permeates through the film.

The first step to obtaining good wet adhesion is to clean the steel surface before painting, especially to remove any oils and salts. Application of phosphate conversion coatings gives further advantages (Section 6.4.1). Various types of steel and coated steel may require different cleaning and treatment methods [22]. In most cases, after the phosphate coating is applied, the treated metal is rinsed with chromic acid solution as a “sealing coat.” Waste disposal problems are severe, especially considering the chromic acid wash step. Soluble chromium(VI) compounds have been shown to be carcinogenic and are being replaced as rapidly as possible. Toxic hazards are also associated with soluble nickel compounds.

It is reported that addition of polyethyleneimine to a Ca–Zn phosphating treatment bath gives a satisfactory conversion treatment without a chromate rinse [23]. It has been shown that a dilute solution of trimethoxymethylsilane, with enough H_2ZrF_6 to bring the pH down to about 4, gave even better performance than a chromate rinse as a sealing treatment for phosphated steel [24]. Treatment with a zinc–manganese phosphate solution containing silicotungstates, followed by a hexafluorozirconic acid rinse, has also been disclosed [25]. A nickel and chromium(VI) free treatment system for steel and galvanized steel is carried out by washing with an alkaline cleaner, rinsing, treating with hexafluorozirconic acid, rinsing, and then sealing with a solution of epoxy phosphate [26].

For many applications, aluminum does not have to be treated for corrosion control, due to the coherent aluminum oxide surface of the aluminum. But if exposure to salt is to be expected, the surface must be treated before applying a coating. Chromate surface treatments have been the standard in the industry, but with the concern about carcinogenicity of chromium(VI), alternative chromium(VI) free treatments have been developed, including chromium(III) sulfate plus potassium hexafluorozirconate [27]; an aqueous solution of potassium manganate, potassium fluoride, potassium hydroxide, sodium hydrosulfite, and ortho-phosphoric acid [28]; vanadium tetrafluoroborate (among similar compounds) [29], and chromium(III) sulfate plus potassium hexafluorozirconate [30]. Treatment of aluminum alloys with a waterborne solution of a mixture of bis(trimethoxypropylsilyl)amine and triacetoxysilane is another approach. The treated surface is said to provide corrosion protection equal to that of chromate coatings when coated with powder coatings [31].

DC cathodic polymerization of trimethylsilane in a closed system is used to plasma coat the surface of aluminum-coated aluminum alloys. The coated surface provides corrosion protection and good adhesion for epoxy primers [32]. Surface treatment of aluminum with combinations of tetraethoxysilane and 3-glycidyloxypropyltrimethoxysilane showed that treatments with a high ratio of 3-glycidyloxypropyltrimethoxysilane and a low ratio of water to alkoxy groups gave superior corrosion protection [33]. A patent application for the treatment of cadmium and zinc-nickel coated steel with basic chromium(III) sulfate and potassium hexafluorozirconate and potassium hexafluorosilicate has been disclosed [34].

Bis(trialkoxysilyl)alkanes are being investigated to treat the surface of steel. Clean steel is treated with an aqueous solution of bis(triethoxysilyl)ethane (BTSE). BTSE is hypothesized to react with water and hydroxyl groups on the steel to give a water-resistant anchor on the steel. This hypothesis is supported by a large body of indirect evidence, although direct evidence is in short supply. After drying, the treated metal can be coated and baked. For some types of coatings it is desirable to react the BTSE treated steel with a reactive silane that reacts with silanol groups of the BTSE and provides a functional group to react with a coating binder [35]. A mixture of bis(trimethoxysilylpropyl)amine and vinyltriacetoxysilane has been reported to provide corrosion protection equal to chromate primers on aluminum, galvanized steel, stainless steel, steel, and cobalt/chromium alloy [36,37]. A combination of BTSE and a ureidotriethoxysilane to treat steel, galvanized steel, zinc, and aluminum has also been disclosed [38]. It is reported that galvanized steel treated with zirconium nitrate followed by aminoethylaminopropyltrimethoxysilane and a polyester primer gives a performance equal to that of commercial chromate primed metal [39]. A review of potential uses of silane treatments for steel, galvanized steel, and aluminum is available [40].

An investigation of the effect of treatment of the surface of galvanized steel with rare earth nitrates has been published [41]. Lanthanum nitrate was particularly effective. The results are based on electrochemical testing of samples without organic coatings. Tests with organic coatings will be required before the utility of the treatment can be determined.

After cleaning and treating, a surface should not be touched and should be coated as soon as possible. Finger prints leave oil and salt on the surface. After exposure to high humidity, fine blisters can form, disclosing the identity of the miscreant by the finger prints. A rusty handprint was once observed on a ship after only one ocean and lake passage [10]. It is critical to avoid having any salt on the metal surface when the coating is applied near the ocean.

It is also critical to achieve as complete penetration as possible into the micropores and irregularities in the surface of the steel to prevent pockets that could fill with water and oxygen (Section 7.3.1). An important factor for achieving penetration is that the viscosity of the liquid coatings external phase be as low as possible and remain low long enough to permit complete penetration (Section 6.1). It is desirable to use slow evaporating solvents, slow cross-linking coatings, and when possible, baking primers. Macromolecules may be large compared to the size of small crevices, so lower molecular weight components may give better protection.

Wet adhesion requires that the coating be adsorbed strongly on the surface of the steel and not be desorbed by water that permeates through the coating. Empirically, it is found that wet adhesion is enhanced by having several adsorbing groups scattered along the resin chain, with parts of the resin backbone being flexible enough to permit relatively easy orientation and other parts rigid enough to assure that there are loops and tails sticking up from the surface for interaction with the rest of the coating. Thus, wet adhesion will be better if the coating has a T_g lower then the temperature at which corrosion protection is needed, since desorption will be minimized. However, as discussed in Section 7.3.3, a higher T_g is preferable for reducing oxygen and water permeability. Another reason that baking primers commonly provide superior corrosion protection is that at the higher temperature, there may be greater opportunity for orientation of resin molecules at the steel interface. Amine groups are particularly effective polar substituents for promoting wet adhesion. Perhaps water is less likely to displace amines than to displace other groups from the surface. Phosphate groups also promote wet adhesion. For example, epoxy phosphates have been used to enhance the adhesion of epoxy coatings on steel [42]. Phosphate-functional (meth)acrylic esters as comonomers increase the wet adhesion of solventborne and latex coatings [43].

Saponification resistance is another important factor in wet adhesion [44,45]. Corrosion generates hydroxide ions at the cathode, raising the pH levels as high as 14. Ester groups in the backbone of a binder can be saponified, degrading the polymer near the interface and reducing wet adhesion. Epoxy–phenolic primers are an example of high bake primers that are completely resistant to hydrolysis. In some epoxy–amine primers, there are no hydrolyzable groups. Amine-terminated polyamides, which are used widely in air dry primers to react with epoxy resins, have amide groups in the backbone that can hydrolyze. However, amides are more resistant than esters to base-catalyzed hydrolysis. Alkyd resins are used when only moderate corrosion protection is required and low cost is important. The superior corrosion protection of epoxy ester primers is often attributed to greater resistance to saponification of epoxy esters.

Water-soluble components that may stay in barrier primer layers should be avoided because they can lead to blister formation. For example, zinc oxide is generally an undesirable pigment to use in primers. Its surface interacts with water and carbon dioxide to form zinc hydroxide and zinc carbonate, which are somewhat soluble in water and can lead to osmotic blistering. Insoluble pigments with water-soluble contaminants should also be avoided. Passivating pigments, discussed in Section 7.4.2, cannot function unless they are somewhat soluble in water; their presence in coating layers therefore leads to blistering. Funke showed that hydrophilic solvents, which become immiscible in the drying film as other solvents evaporate, can be retained as a separate phase and lead to blister formation [14].

7.3.3. Factors Affecting Oxygen and Water Permeability

Many factors affect the permeability of coating layers to water and oxygen [46]. Water and oxygen can permeate, to some extent at least, through any amorphous polymer film, even though the film has no imperfections such as cracks or pores. Small molecules travel through the film by jumping from free volume hole to free volume hole. The free volume increases as the temperature increases above T_g. Therefore, normally, one wants to design coatings with a T_g above the temperature at which corrosion protection is desired. Since cross-linking reactions become slow as the increasing T_g of the cross-linking polymer approaches the temperature at which the reaction occurs and become very slow at $T < T_g$, air dry coatings cannot have T_g values much above ambient temperatures. Furthermore, since wet adhesion is improved by having a lower T_g (Section 7.3.2), compromises may be necessary. Permeability is also affected by the solubility of oxygen and water in a film. The variation in water solubility can be large. The permeability of oxygen and water through coating layers is reviewed in Ref. [47].

Oxygen dissolves to only a small degree in any of the resins used in coatings, but there are many other factors that affect permeability of films to oxygen, related primarily to free volume. Hydrophilic polymers show less permeability to O_2 than do hydrophobic polymers because hydrogen bonding reduces free volume availability. Lateral side chains increase free volume and increase permeability. The higher T_g values that can be reached with baked coatings may be another factor in their generally superior corrosion protection. In general, higher cross-link density leads to lower permeability. Both T_g and cross-link density affect other coating properties, so that some compromise between T_g and cross-link density and performance must be accepted.

Permeability of coatings to water is affected by the same factors that affect permeability to oxygen, but there are additional factors as well. Water is more soluble than oxygen in many coatings, and a higher solubility increases permeability. Water can act as a plasticizer for coatings such as epoxy–amines and polyurethanes; the swelling caused by water increases internal stress that can lead to delamination [48]. Internal stress increases when a coating is cycled through wet and dry stages.

Salt groups on a polymer increase the solubility of water in coatings. This makes it difficult to formulate high performance air dry, water-reducible coatings that are solubilized in water by amine salts of carboxylic acids. Although to a lesser degree than salts, resins made with polyethylene oxide backbones are likely to give higher water permeabilities. On the other hand, water has low solubility in halogenated polymers; hence vinyl chloride and vinylidene chloride copolymers and chlorinated rubber are commonly used in formulating top coats for corrosion resistance. Fluorinated polymers have low permeabilities and good wetting properties; hydroxy-functional poly(vinylidene fluoride) cross-linked with polyisocyanates is reported to give good corrosion protection even as a single coat [49]. Although silicones give low surface tension and are used as water repellants, films of silicone resins are highly permeable to water.

Pigmentation can have significant effects on water and oxygen permeability. Oxygen and water molecules cannot pass through pigment particles; therefore, permeability decreases as pigment volume concentration (PVC) increases. However, if the PVC exceeds the critical pigment volume concentration (CPVC), there are voids in the film and the passage of water and oxygen through the film is facilitated. (PVC and CPVC are discussed in Chapter 22.) Some pigments have high-polarity surfaces that adsorb water, and in cases in which water can displace polymer adsorbed on such surfaces, water permeability can be expected to increase with increasing pigment content. As explained in Section 7.3.2, pigments should be insoluble and as free as possible of water-soluble impurities. In theory, the use of hydrophilic pigment dispersants should be avoided, or at least minimized.

Pigments with platelet shaped particles can reduce permeability rates as much as fivefold when they are aligned parallel to the coating surface [15,50]. Since oxygen and water vapor cannot pass through the pigment particles, the presence of aligned platelets can reduce the rate of vapor permeation through a coating. The alignment is critical to the action of the platelets; if they are not aligned, permeability may be increased, especially if the film thickness is small relative to the size of the platelets. A factor favoring alignment is shrinkage during solvent evaporation. (See Section 30.1.2 for a discussion of additional factors.) Mica, talc, micaceous iron oxide, glass flakes, and metal flakes are examples of such pigments. Aluminum flake is widely used; stainless steel and nickel platelets, although more expensive, have greater resistance to extremes of pH. When appearance permits, use of leafing aluminum pigment in the top coat is particularly effective (Section 20.2.5). Leafing aluminum is surface treated, so its surface free energy is very low. As a result, the platelets come to the surface during film formation, creating an almost continuous barrier. In formulating coatings with leafing aluminum, it is necessary to avoid resins and solvents that displace the surface treatment from the flakes.

A Monte Carlo simulation model of the effect of several variables on diffusion through pigmented coatings has been devised [51]. The model indicates, as would be expected, that finely dispersed, lamellar pigment particles at a concentration near, but below, CPVC give the best barrier performance.

There are advantages to applying multiple layers of coatings. The primer can be designed for optimal wet adhesion and penetration into the substrate surface without particular concern about other properties. Intermediate and top coat(s) can provide for minimum permeability and other required properties. The primer film does not need to be thick as long as the top coat is providing barrier properties; the lower limit is probably controlled by the need to assure coverage of the entire surface. Funke has reported good results with a 0.2-μm primer thickness [17] or a 10-nm layer of a wet adhesion promoting polymer. Another advantage of applying multiple coats is the decrease in probability that any area of the substrate will escape being coated.

Film thickness affects the time necessary for permeation through coatings. Thicker films are expected to delay the arrival of water and oxygen at the interface but are not expected to affect the equilibrium condition. Were this the only factor, the corrosion protection afforded by intact films would be expected to be essentially independent of film thickness. However, film thickness affects the mechanical performance of films. For example, erosion losses would take longer to expose bare metal as film thickness increases. On the other hand, the probability of cracking on bending increases as film thickness increases, so there may be some optimum film thickness for the maintenance of an intact film. However, in certain air dry, heavy duty maintenance coatings, there is a film thickness, dependent on the coating, that provides a more than proportional increase in corrosion protection relative to thinner films. Commonly, this film thickness is as much as 400 μm or more. Funke suggests that below certain coating thicknesses, there may be microscopic defects extending down through the film to the substrate [52]. The film may look intact, but there may be microscopic defects that are large compared to the free volume holes through which permeation in fully intact films occurs. A potential source of such defects is cracks resulting from shrinkage of films as the last solvent is lost from a coating, particularly when T_g of the solvent-free system is around ambient temperature. Funke suggests that if the layer is thick enough, such defects may not reach the substrate, hence substantially reducing passage of water and oxygen. This hypothesis is consistent with the general observation that greater protection is achieved by applying more coats to reach the same film thickness. In line with this proposal, the use of barrier platelet pigments permits a reduction in the required film thickness without loss of protection. The platelets may minimize the probability of defects propagating through the film to the substrate. Such defects are less likely to occur in baked films, and this may be another factor in the generally superior corrosion protection afforded by baked films, even though thinner film thicknesses are used.

7.4. CORROSION PROTECTION BY NONINTACT FILMS

There are situations in which it is not possible to assure full coverage of the entire metal surface as required for barrier coatings. Furthermore, coatings that were intact initially may be damaged during their service lives, even those designed to minimize the probability of mechanical failure. In such cases it is generally desirable to design coatings to suppress electrochemical reactions rather than primarily for their barrier properties.

7.4.1. Minimizing Growth of Imperfections: Cathodic Delamination

If there are gouges through the film down to bare metal, water and oxygen reach the metal and corrosion starts. If the wet adhesion of the primer to the metal is not adequate, water creeps under the coating, and the coating comes loose from the metal over a wider and wider area. Poor hydrolytic stability can be expected to exacerbate the situation. This mode of failure is called *cathodic delamination*. Control of cathodic delamination requires wet adhesion and saponification resistance. It has also been shown that blisters are likely to develop under a film near the location of a gouge [10,15].

When wet adhesion varies on a local scale, *filiform corrosion* can occur [53]. It is characterized by development of thin threads of corrosion wandering randomly under the film, but never crossing another track. Formation of these threads often starts from the edge of a scratch. At the head of the thread, oxygen permeates through the film, and cathodic delamination occurs. The head grows following the path of poorest wet adhesion. Behind the head, oxygen is consumed by oxidation of ferrous ions and ferric hydroxide precipitates, passivating the area, explaining why threads never cross. Since the ion concentration decreases, osmotic pressure drops, and the thread collapses, but it leaves a discernible rust track. Filiform corrosion can be difficult to see through pigmented films.

7.4.2. Primers with Passivating Pigments

Passivating pigments promote formation of a barrier layer over anodic areas, passivating the surface (Section 7.2.1). To be effective, such pigments must have minimum solubility. However, if the solubility is too high, the pigment would leach out of the coating film too rapidly, limiting the time that it is available to inhibit corrosion. For the pigment to be effective, the binder must permit diffusion of water to dissolve the pigment. Therefore, the use of passivating pigments may lead to blistering after exposure to humid conditions. Such pigments are most useful in applications in which the need to protect the steel substrate after film rupture has occurred outweighs the desirability of minimizing the probability of blistering. They are also useful when it is not possible to remove all surface contamination (blistering will probably occur anyway) or when it is not possible to achieve complete coverage of the steel by the coating.

Red lead pigment, Pb_3O_4 containing 2 to 15% PbO, has been used in oil primers as a passivating pigment since the mid-nineteenth century. Red lead in oil primers were used for air dry application over rusty, oily steel. The mechanisms of action are not fully understood. They presumably include oxidation of ferrous ions to ferric ions followed by co-precipitation of mixed iron–lead salts or oxides. The somewhat soluble PbO raises the pH and neutralizes any fatty acids formed over time by hydrolysis of the drying oil. Toxic hazards of red lead have resulted in widespread prohibition of its use.

The utility of chromate pigments for passivation of steel and aluminum is well established. Various mechanisms have been proposed to explain their effectiveness [10]. All the proposed mechanisms require that the chromate ions be in aqueous solution. Like all passivators, chromate ions accelerate corrosion at low concentrations. The critical minimum concentration for passivation at 25°C is approximately 10^{-3} mol CrO_4^{2-} L^{-1}. The critical concentration increases with increasing temperature and increasing NaCl concentration.

Sodium dichromate is an effective passivating agent but would be a poor passivating pigment, owing to its high solubility in water (3.3 mol $CrO_4^{2-}L^{-1}$). It would be rapidly leached out of a film and would probably cause massive blistering. At the other extreme, lead chromate (chrome yellow) is so insoluble (5×10^{-7} mol $CrO_4^{2-}L^{-1}$) that it has no electrochemical action.

"Zinc chromates" have been widely used as passivating pigments. The terminology is poor, since zinc chromate itself is too insoluble and could promote corrosion, rather than passivate. Zinc yellow pigment is [$K_2CrO_4 \cdot 3ZnCrO_4 \cdot Zn(OH)_2 \cdot 2H_2O$]. [Alternative ways of giving the same composition are $Zn_4K_2Cr_4O_{20}H_6$ and ($4ZnO \cdot K_2O \cdot 4CrO_3 \cdot 3H_2O$).] It has an appropriate solubility (1.1×10^{-2} mol CrO_4^{2-} L^{-1} at 25°C) and has been widely used in primers. Zinc tetroxychromate [$ZnCrO_4 \cdot 4Zn(OH)_2$, also written as $Zn_5CrO_{12}H_8$] has a solubility lower than desirable (2×10^{-4} mol CrO_4^{2-} L^{-1}), but is used in *wash primers*. Phosphoric acid is added to wash primers before application; it may be that this changes the solubility so that the chromate ion concentration is raised to an appropriate level. Strontium chromate ($SrCrO_4$) has an appropriate solubility in water (5×10^{-3} mol CrO_4^{2-} L^{-1}) and is often used in primers, especially latex paint primers, in which the more soluble zinc yellow can cause problems of package stability.

It has been established that zinc chromates, and presumably other soluble chromates, are carcinogenic to humans. They must be handled with appropriate caution. In some countries, their use has been prohibited, and prohibition worldwide is probable in the future. Enormous efforts have been undertaken to develop less hazardous passivating pigments [54]. However, it is difficult to conclude from the available literature and supplier technical bulletins how these pigments compare with each other and with zinc yellow. In some cases, a formulation that has been optimized for one pigment is compared to a formulation containing another pigment that may not be the optimum formulation for that pigment. (A common example is the substitution of one pigment for another on an equal weight basis rather than formulating to the same ratio of PVC to CPVC; the results could be very misleading, since primer performance is quite sensitive to the PVC/CPVC ratio.) Much of the published data is based on comparing corrosion resistance in salt fog chamber tests (or other laboratory tests) rather than on actual field experience. A problem with accelerated tests is that an important factor in the performance of a pigment is the rate at which it is leached from a film. As discussed in Section 7.5, there is no laboratory test available that provides reliable predictions of field performance.

Basic zinc and zinc–calcium molybdates are said to act as passivating agents in the presence of oxygen, apparently leading to precipitation of a ferric molybdic oxide barrier layer on the anodic areas. Barium metaborate is the salt of a strong base and a weak acid. It may act by increasing the pH, thus lowering the critical concentration of oxygen required for passivation. To reduce its solubility in water, the pigment grade is coated with silicon dioxide. Even then, the solubility may be too high for use in long-term exposure conditions. Zinc phosphate, $Zn_3(PO_4)_2 \cdot 2H_2O$, has been used in corrosion protective primers and may act by forming barrier precipitates on the anodic areas. There is considerable difference of opinion as to its effectiveness. Calcium and barium phosphosilicates and borosilicates are being used increasingly; they may act by increasing pH. Calcium tripolyphosphate has also been recommended [55].

A series of passivating pigments were evaluated in a waterborne epoxy coating [56]. Zinc iron phosphate, zinc aluminum phosphate, zinc molybdenum phosphate, and basic zinc phosphate all performed well in laboratory tests; zinc phosphate was slightly poorer. Field performance remains to be demonstrated. It has been reported that such dual metal phosphate pigments provide passivation superior to that of zinc chromate under acidic conditions but inferior to that of zinc chromate under alkaline conditions [57]. Zinc aluminum phosphate has been shown to be a good corrosion inhibitor for waterborne epoxy–amine coatings [58]. A study of corrosion protection of steel by zinc phosphate, calcium zinc phosphate, zinc ferrite, and calcium-exchanged silica each in a styrene–acrylic latex and a fatty acid modified polyurethane dispersion has been reported. The corrosion resistance was evaluated by a series of tests, including EIS and Prohesion. The polyurethane vehicle gave better resistance than the latex, and the best combination was zinc ferrite with polyurethane; next best was calcium zinc phosphate [59].

These are all inorganic pigments; a wider range of potential oxidizing agents and bases would seem to be available if organic pigments were used. An example of a commercially available organic pigment is the zinc salt of 5-nitroisophthalic acid. It is reported to be as effective as zinc yellow at lower pigment levels. However, since over a long time, any passivating pigment will be lost by leaching, it seems doubtful that an equal lifetime could be achieved at a substantially lower pigment content. The zinc salt of 2-benzothiazoylthiosuccinic acid has been recommended as a passivating agent. A recurrent problem with organic passivators is that many perform extremely well in the early parts of tests but lose effectiveness later.

Sinko reviewed the subject of passivating pigments and concluded that no other practical inorganic can match or surpass the performance of strontium chromate, but that hybrid inorganic–organic pigments can equal or excel its performance [60]. The same author provides manufacturing procedures for inorganic–organic anticorrosion pigments such as $Zn(NCN)_2$/Zn(2-mercaptobenzothiazole) [61] and discloses that the zinc salt of 2,5-dimercapto-1,3,4-trithiazole outperforms strontium chromate in protecting aluminum, and the triisocyanuric acid salt of dicyclohexylamine with strontium doped amorphous silica outperforms chromate on galvanized steel [62].

The morpholine salt of toluylpropionic acid, the zirconium complex of toluylpropionic acid, metal salts of benzothiazoylthiosuccinic acid, and the tridecylammonium salt of benzothiazoylthiosuccinic acid are reported to impart corrosion inhibition and, further, that hindered amine light stabilizers (HALS) and UV absorbers improve corrosion protection [63]. Benzothiazoylthiosuccinic acid and calcium-exchanged silica enhance corrosion resistance of powder coatings; the morpholine salt of toluylpropionic acid improves the corrosion resistance of 2K epoxy–amine primers [63]. Copper can be protected by electropolymerizing 2-mercaptobenzimidazole on the surface [64].

7.4.3. Cathodic Protection by Zinc-Rich Primers

Zinc-rich primers are another approach to protecting steel with nonintact coatings. They were designed initially to provide the protection given by galvanized steel, but have been found to provide excellent protection to steel structures after fabrication [65]. The primers contain high levels of powdered zinc—over 84 wt% is usual. On a volume basis, the zinc content exceeds CPVC, to assure good electrical contact between the zinc particles and with the steel. Furthermore, when the PVC is greater than the CPVC, the film is porous, permitting water to enter, completing the electrical circuit. The CPVC of zinc powder varies, depending primarily on particle shape and particle size distribution; values on the order of 67% have been reported [66]. The zinc serves as a sacrificial anode, and zinc hydroxide is generated in the pores. The structure of the zinc particles can affect performance. Smaller particle size spherical zinc gives better results than larger particle size zinc. Lamellar zinc particles give films with better mechanical properties and satisfactory corrosion protection with a lower weight fraction than with spherical zinc particles [67].

Vehicles for zinc-rich primers must be saponification resistant; alkyds are not appropriate resins for this application. Both organic and inorganic binders are widely used. Among organic binders, epoxies are the most commonly used, and polyurethanes are gaining favor. The principal inorganic vehicles are oligomers derived from tetraethyl orthosilicate by controlled partial hydrolysis with a small amount of water (Section 16.3). Ethyl or isopropyl alcohol is used as the principal solvent, since an alcohol helps maintain package stability. After application, the alcohol evaporates, and water from the air completes the hydrolysis of the oligomer, to yield a film of polysilicic acid partially converted to zinc salts. Cross-linking is affected by relative humidity (RH); properties can be affected adversely if the RH is low at the time of application.

Properly formulated and applied, *zinc-rich primers* are very effective in protecting steel against corrosion. Their useful lifetime is not completely limited by the amount of zinc present, as one might first assume. Initially, the amount of free zinc decreases from the electrochemical reaction; later, loss of zinc metal becomes slow, but the primer continues to protect the steel for some time if the coating remains intact. Possibly, the partially hydrated zinc oxide formed in the initial stages of corrosion of the zinc fills the pores and, together with the remaining zinc, acts as a barrier coating [66,68]. It is also possible that zinc hydroxide raises the pH to the level at which oxygen can passivate the steel.

Zinc is expensive, especially on a volume basis. Early attempts to replace even 10% of the zinc with low-cost inert pigment caused a serious decrease in performance, presumably due to a decrease in metal to metal contact, even though the PVC was above CPVC. A relatively conductive inert pigment, iron phosphide (Fe_2P), has shown promise. In ethyl silicate–based coatings, up to 25% of the zinc can be replaced with Fe_2P [69]; however, with epoxy–polyamide coatings, replacement of part of the Zn with Fe_2P leads to a reduction in protection [70].

Zinc-rich primers are frequently top coated to minimize corrosion of the zinc, to protect against physical damage, and to improve appearance. Formulation and application of top coats require care. If the vehicle of the top coat penetrates the pores in the primer film, conductivity of the primer may be substantially reduced, rendering it ineffective. (See Section 33.1.2 for further discussion.) Zinc-rich primers can be formulated so that the painted objects can be welded.

In response to the need to reduce VOCs, waterborne inorganic zinc-rich primers have been developed. The chemistry of silicate binders is reviewed in Ref. [71]. The binder is a combination of potassium, sodium, and/or lithium silicates with a dispersion of colloidal silica [72]. The ratio of silicate to SiO_2 is critical; if there is insufficient base, phase separation can occur. Commonly, a ratio of 1 to 4 or 5 is appropriate. The ratio can be changed by adding amorphous silica. High humidity impairs drying. High temperature accelerates drying. Carbon dioxide decreases pH and brings the silicate solution nearer the instability region. Anodic inhibition of the metal surface with amines before application reduces problems encountered in drying at high humidity. Hydroxy-functional silicones promote water compatibility, as does addition of methyltrimethoxysilane. It is critical to use zinc dust that has not reacted with CO_2 and water to give a surface of zinc carbonate and zinc hydroxide [73]. Excellent performance on oil and gas production facilities in marine environments has been reported [74]. Organic zinc–rich primers based on water borne epoxy vehicles are also available.

7.5. EVALUATION AND TESTING

There have been many attempts to develop laboratory tests to predict corrosion protection by coatings, and these efforts continue. However, no laboratory test is available that can be used to predict corrosion protection performance of a new coating system. This unfortunate situation is an enormous obstacle to research and development of new coatings, but it must be recognized and accommodated.

Use testing is still the only reliable approach: that is, to apply a coating system and then observe its condition over years of actual use. The major suppliers and end users of coatings for such applications as bridges, ships, chemical plants, and automobiles have collected data correlating the performance of various systems over many years. These data provide a basis for selection of current coatings systems for particular applications. They also provide insight into how new coatings could be formulated to improve chances of success.

Simulated tests are the next most reliable tests for predicting performance. One common approach is to expose laboratory prepared panels on test fences in inland south Florida or on beaches in south Florida or North Carolina. The difficulties in developing tests to simulate corrosion in marine environments are discussed in Ref. [75]. Test conditions must simulate actual use conditions as closely as possible. For example, exposure at higher temperatures may accelerate corrosion reactions; however, oxygen and water permeability can be affected by $T - T_g$. If use temperatures are below T_g but tests are run above T_g, no correlation should be expected.

Variables in the preparation of test panels are frequently underestimated. The steel used is a critical variable [76], as are how the steel is prepared for coating and how the coating is applied. Film thickness, evenness of application, flash off time, baking time and temperature, and many other variables affect performance. Results obtained with carefully prepared and standardized laboratory panels can be quite different than results with actual production products. In view of these problems, it is desirable, when possible, to paint test sections on ships, bridges, chemical storage tanks, and so on, and to observe their condition over the years. The long times required for evaluation are undesirable, but the results can be expected to correlate reasonably with actual use.

Since wet adhesion is so critical to corrosion protection, techniques for studying wet adhesion can be very useful. *Electrochemical impedance spectroscopy* (EIS) is widely used to study coatings on steel. A series of papers discuss the theory, application, interpretation, and limitations of EIS [77]. *Impedance* is the apparent opposition to flow of an alternating electrical current and is the inverse of *apparent capacitance*. When a coating layer begins to delaminate, there is an increase in apparent capacitance. The rate of increase of capacitance is proportional to the area delaminated by wet adhesion loss. High-performance systems show slow rates of increase of capacitance, so tests must be continued for long time periods. EIS is very sensitive for detecting defects but cannot determine whether the defect is characteristic of the coating system or a consequence of poor application. EIS can be very useful in comparing various coating formulations, but because of the wide variation in actual exposure conditions, cannot reliably predict field performance. A review of evaluation of coatings by electrochemical, physicochemical, and physical measurements has been published [78].

The most widely used test method for corrosion resistance is the salt spray (fog) test (ASTM Method B-117-95). Coated steel panels are scribed (cut) through the coating in a standardized fashion, exposing bare steel and hung in a chamber where they are exposed to a mist of 5% salt solution at 100% relative humidity at 35°C. Periodically, the nonscribed areas are examined for blistering, and the scribe is examined to see how far from the scribe mark the coating has been undercut or has lost adhesion. It has been shown repeatedly that there is little, if any, correlation between results from salt spray tests and actual performance of coatings in use [79–82].

Many factors are probably involved in the unreliability of the salt spray test. One major flaw is that the test conditions are constant; no attempt is made to replicate the changes in conditions (warm/cool, wet/dry) that occur during most field exposures. Furthermore, outdoor exposure can have a significant effect on coating properties, and environmental factors such as acid rain vary substantially from location to location. The application of the scribe mark can be an important variable; narrow cuts generally affect corrosion less than broader ones. Also, if the scribe mark is cut rapidly, there may be chattering of cracks out from the main cut, whereas slow cutting may lead to a smooth cut. A passivating pigment with high solubility might be very effective in a laboratory test, but may provide protection for only a limited time under field conditions, owing to the loss of passivating pigment by leaching.

Since with intact films, it is common for the first failure to be blister formation, humidity resistance tests are also widely used (ASTM Method D-2247-94). The unscribed face of a panel is exposed to 100% relative humidity at 38°C while the back of the panel is exposed to room temperature. Thus, water condenses continuously on the coating surface. This humidity test is a more severe test for blistering than the salt fog test because pure water on the film generates higher osmotic pressures with osmotic cells under the film than the salt solution used in the salt fog test. It is common to run the test at 60°C “because it is a more severe test.” The pitfalls of this approach are obvious in view of the previous discussion of the importance of $T - T_g$. Humidity tests do not provide a prediction of the life of corrosion protection, but may provide useful comparisons of wet adhesion. Funke recommends testing for wet adhesion by scribing panels after various exposure times in a humidity chamber, followed immediately by applying pressure sensitive tape across the scribe mark and then pulling the tape off the panel [52]. A peel adhesion test for wet adhesion has been described [83]. Wet adhesion can also be checked after storing panels in water [84].

It is often observed that alternating high and low humidity causes faster blistering than does continuous exposure to high humidity. A possible explanation is that intermediate corrosion products form colloidal membranes, causing polarization and temporary inhibition of corrosion. The membranes are not stable enough to survive drying out and aging. Another factor may be the increase in internal stress that has been reported by cycling through wet and dry periods [48]. A large number of humidity cycling tests have been described, commonly involving repeated immersion in warm water and removal for several hours. In some industries, such tests have become accepted methods of screening coatings, although their predictive value is questionable. Simply correlating them with salt fog tests proves nothing.

A testing regimen called *Prohesion* (a trademark of BP Chemicals) has been reported to correlate better with actual performance than the standard salt spray test [85]. The procedure combines care in selection of substrates that will reflect real products, use of thin films, emphasis on adhesion checks, and a modified salt mist exposure procedure.

Instead of 5% NaCl solution, a solution of 0.4% ammonium sulfate and 0.05% NaCl is used. Scribed panels are sprayed with the mixed salt solution cycling over 24 hours, six 3-hour periods alternating with six 1-hour drying periods using ambient air. During these cycles, water can penetrate through the film to a greater extent than in salt fog chamber testing, in which the humidity is always at 100%; the 5% salt solution minimizes water penetration because of reverse osmotic pressure. In some laboratories, a QUV exposure cycle is included in the cycling regime [86].

Automotive companies have developed a variety of cycling tests, and comparisons have been made with auto company proving ground tests and two-year on-vehicle field results. A study of three tests, the GM Cyclic Corrosion Test 9540-P, Hoogovens' Cyclic Test, the Chrysler Chipping Test, has demonstrated good correlation with on-vehicle performance [87]. The focus of this study was to compare different coated galvanized and cold-rolled steels, not different coatings. The study also demonstrated the lack of correlation with salt spray tests. Other tests that merit consideration are the Society of Automotive Engineers test SAE J-2334 and ASTM D-5894-96, a cyclic corrosion test [88].

Neither salt fog nor humidity tests have good reproducibility. It is common for differences between duplicate panels to be larger than differences between panels with different coatings. Precision can be improved by testing five to eight replicate panels of each coating system. (Commonly, decisions are based on the results from testing two or three panels.) A further problem of evaluating panels for corrosion protection is the difficulty of detecting small blisters and rust areas underneath a pigmented coating film without removing the film. Infrared thermography has been recommended as a nondestructive testing procedure [89]. A great deal of effort has been expended on electrical conductivity tests of paint films and electrochemical tests of coated panels. (See Ref. [90] for an extensive review.)

A variety of cathodic disbonding tests specifically for testing of pipeline coatings has been established by ASTM G-8-96, G-42-96, and G-80-88 (reapproved 1992). In these tests, a hole is made through the coating and the pipe is made the cathode of a cell in water with dissolved salts at a basic pH. Disbonding (loss of adhesion) as a function of time is followed. Although there is considerable variability inherent in such tests and their utility for predicting field performance is doubtful, useful guidance in following progress in modifying wet adhesion may be obtained not only for pipeline coatings, but also more broadly. (For a discussion of research on cathodic delamination, including investigation of the migration of cations through or under coating films, see Ref. [91].)

Appleman has reported the results of an extensive survey of accelerated test methods for anticorrosive coating performance [92]. The need for everyone in the industry to become aware of the current testing situation and to work cooperatively to develop more meaningful methods of testing is emphasized. The lack of laboratory test methods that reliably predict performance puts a premium on collection of databases, permitting analysis of interactions between actual performance and application and formulation variables. It is especially critical to incorporate data on premature failures in the database. Availability of such a database can be a powerful tool for a formulator and may be especially useful in testing the validity of theories about factors controlling corrosion. In time, it may be possible to predict performance better from a knowledge of the underlying theories than from laboratory tests. Many workers feel that this is already true in comparison with salt fog chamber tests.

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8

Acrylic Resins

Acrylic resins are used as the primary binder in a wide variety of industrial coatings. Their major advantages are photostability and resistance to hydrolysis.

8.1. THERMOPLASTIC ACRYLIC RESINS

Thermoplastic acrylic (TPA) polymers have many excellent properties, especially exterior durability, but their use has declined because they require large amounts of solvent to reduce viscosity low enough for application. Lacquers based on TPA polymers were used for automotive top coats from the 1950s to the 1970s. Their high solvent levels make possible brilliant metallic colors since they permit orientation of aluminum flake pigment in the films parallel to the surface (Section 30.1.2). Acrylic lacquers are still used to a degree in refinishing automobiles (Section 33.3) and for other specialized coatings, but as volatile organic compound (VOC) regulations become more restrictive, their use is declining.

Solution thermoplastic acrylic polymers are prepared by chain-growth polymerization (Section 2.2.1). They are copolymers of various (meth)acrylic monomers and, commonly, styrene. For automotive top coats, T_g must be over 70°C. Monomers are selected on the basis of cost and effect on properties: notably, outdoor durability and T_g. Methyl methacrylate (MMA), styrene (S), and *n*-butyl acrylate (BA) are often used. The acrylic copolymers are used with plasticizers. Control of molecular weight (MW) in the synthesis is critical. Film strength increases with MW, although above $\bar{M}_w$ of about 90,000, the change in properties with increasing MW is small. The upper end of MW is limited because solutions of acrylic polymers with $\bar{M}_w$ greater than about 100,000 exhibit *cobwebbing* on spraying; rather than atomizing to small droplets from the orifice of a spray gun,

Organic Coatings: Science and Technology, Third Edition, by Zeno W. Wicks, Jr., Frank N. Jones,
S. Peter Pappas, and Douglas A. Wicks

the lacquer comes out as threads. As the MW increases, the viscosity of solutions increases and the solids that can be spray-applied decreases. Viscosity is particularly affected by the very high MW fractions; therefore, it is critical to minimize this fraction by controlling MW distribution ($\bar{M}_w/\bar{M}_n$) to a narrow range (Section 2.2.1). Commercial TPAs have $\bar{M}_w$ of 80,000 to 90,000 and $\bar{M}_w/\bar{M}_n$ of 2.1 to 2.3. The solids of TPA lacquers at application viscosity are in the range 11 to 13 NVV (nonvolatile volume).

8.2. THERMOSETTING ACRYLIC RESINS

Solids can be increased by using thermosetting acrylic resins (TSA). Since they are designed to react chemically after application, they can have lower MWs. The postreaction leads to a polymer network, which is ideally one interconnected molecule with a very high MW and hence potentially good film properties. The cross-linked film is not soluble in any solvent. The term *thermosetting* implies that the resins cross-link by themselves and require heat to cross-link; however, most TSAs are resins bearing functional groups that are reacted with a different functional polymer or cross-linker, sometimes at ambient temperature.

8.2.1. Hydroxy-Functional Acrylic Resins

Hydroxy-functional acrylic resins are copolymers of non-functional monomers, often MMA, S, and BA, with a hydroxy-functional monomer. They are cross-linked with either melamine–formaldehyde (MF) resins (Chapter 11) or with polyisocyanates (Chapter 12). Solvent-borne hydroxy-functional TSAs for conventional-solids coatings were developed in the 1950s. For conventional (low) solids formulations, their $\bar{M}_n$s are usually 10,000 to 20,000 with $\bar{M}_w/\bar{M}_n$ of 2.3 to 3.3. Thermosetting acrylics are prepared by free radical–initiated chain-growth polymerization under monomer-starved conditions, as described in Section 2.2.1. Polymerization of conventional TSAs is easier to control than that of TPAs, since the effect of MW on application and film properties is not as critical. Due to their lower MW, one can use less expensive aromatic hydrocarbon solvents for the polymerization medium. However, the lower MW of TSA polymers results in more end groups per unit weight. Therefore, the structure of the end groups can have greater effects on performance than in the case of TPA polymers. (Reactions in free radical polymerizations that can lead to various end groups are reviewed in Ref. [1].) Azo initiators are used predominantly, since they cause relatively few side reactions and form end groups with minimal photochemical reactivity. Certain peroxy initiators also meet these requirements, but others leave end groups that reduce exterior durability. Chain transfer to solvent can also result in end groups that reduce exterior durability. For example, terminal groups resulting from chain transfer to a ketone solvent, such as methyl *n*-amyl ketone (MAK), can have a deleterious effect [2].

Hydroxyl groups are often introduced by using a hydroxy-functional comonomer such as 2-hydroxyethyl methacrylate (HEMA). If a lower T_g reactive monomer is desired, 2-hydroxyethyl acrylate (HEA) can be used, but its greater toxic hazard increases handling costs; it is often preferable to reduce T_g by increasing the proportion of low T_g nonreactive monomers such as *n*-butyl acrylate. Commercial grades of HEMA (and HEA) contain appreciable amounts of diester, ethylene glycol dimethacrylate (EGDMA) in the case of HEMA. Separation of the mono- and diesters is not easy since their boiling points are similar. When a relatively small fraction of hydroxy-functional monomer is used, small amounts of diester cause some branching, which does not seem to be harmful. However, larger amounts cause higher molecular weight, broader MW distribution, and even gelation.

2-Hydroxypropyl methacrylate (HPMA) can also be used. It costs less than HEMA and generally has a lower diester content. HPMA is a mixture of isomers in which the secondary alcohol predominates. Since secondary alcohols are less reactive than primary alcohols, TSAs with HPMA substituted for HEMA require higher baking temperatures, longer baking times, or more catalyst to cure to a given cross-link density with MF resins. For example, baking temperatures may have to be increased by 10 to 20°C. Isocyanate cross-linkers also react slower with HPMA-containing TSAs, but there is the accompanying advantage of longer pot life. Use of HPMA in place of HEMA may reduce resistance to photoxidation as a result of the hydrogens on tertiary carbons, which are more easily abstractable. An alternative method for introducing hydroxy functionality is to react a carboxylic acid–functional copolymer made using methacrylic (or acrylic) acid (MAA or AA) with an oxirane such as propylene oxide. Raw material cost is lower with propylene oxide than with HPMA, but exacting process control is required. Another approach to making hydroxy-functional acrylics is to react an AA or MAA copolymer with a glycidyl ester such as glycidyl versatate [3]. Rapid cross-linking hydroxy-functional acrylic resins for use in refinish coatings have also been prepared by reacting glycidyl versatate with methacrylic acid and then copolymerizing this monomer with BA, styrene, and MMA. Rapid cure depends on reacting the methacrylic acid and glycidyl versatate under conditions that maximize formation of primary hydroxy groups [4]. Acrylic resins for high solids coatings can be made by polymerizing BA, BMA, styrene, acrylic acid, and HEMA in the presence of glycidyl versatate. During the polymerization the glycidyl versatate reacts with the carboxylic acid groups, resulting in the formation of another hydroxy group and a long alkyl side chain. The T_g of the resins is lower than conventional acrylics at similar MW and hence permit higher solids coatings. To further increase the solids, the incorporation of the reaction product of TMP with glycidyl versatate as a reactive diluent is recommended. Polyisocyanates are used as cross-linkers [5]. Use of *t*-butyl methacrylate as a comonomer has been recommended. Such resins are reported to give films with better appearance. Refinish clear coats with a VOC content of 3.5 lb/gal have been formulated [6].

An example of a hydroxy-functional TSA is an MMA/S/BA/HEMA/MAA copolymer with a weight ratio of 50 : 15 : 20 : 14 : 1, corresponding to a mole ratio of 54.3 : 15.6 : 16.9 : 11.7 : 1.5. Typical MWs are $\bar{M}_w$ of about 35,000 and $\bar{M}_n$ of about 15,000 ($\bar{M}_w/\bar{M}_n = 2.3$). With the given ratio of comonomers, $\bar{P}_w$ is about 320 and the $\bar{P}_n$ is about 140. For stoichiometric comparisons, one uses the number average, $\bar{M}_n$. This resin has a hydroxyl equivalent weight of slightly over 900, with a number average functionality $\bar{f}_n$ of about 16 hydroxyl groups per polymer molecule. The small amount of carboxylic acid–functional monomer (MAA) is introduced to reduce the probability of pigment flocculation in a liquid coating.

The non-functional monomers (MMA, S, and BA, in this case) are selected on the basis of their effect on T_g, exterior durability, and cost. This monomer combination provides good exterior durability with a relatively high T_g at a moderate cost, as is appropriate for an automotive top coat. This resin also has a relatively high level of hydroxy-functional monomer, appropriate when relatively high cross-link density (XLD) films are desired. For applications requiring more flexible films, such as coil coatings or exterior can coatings, one would use a lower HEMA content. By adjusting the T_g and the functionality, TSAs can be designed for a wide range of end uses. Countless variations can be prepared.

Thermosetting resins and cross-linkers should be selected or designed for use as a system. The appropriate composition of hydroxy-functional TSAs depends on the cross-linker to be used. A TSA resin optimized for a TSA–MF coating would probably not yield optimum properties with a polyisocyanate cross-linker. Depending on the polyisocyanate used with a TSA, the T_g of the final cross-linked films could be higher or lower than would be obtained by cross-linking the same TSA with an MF resin. TSA resins for polyisocyanate cross-linking tend to have lower T_g and lower $\bar{f}_n$ than TSAs for cross-linking with MF resins, in order to compensate for the effect of the intermolecular hydrogen bonding between urethane groups in the cross-linked films (Section 12.4).

During the 1970s, major efforts were launched to make high-solids solution acrylic resins to meet lower VOC emission requirements. It may seem that this problem is simple; why not just reduce $\bar{M}_n$ from 15,000 to 1500? Actually, the problem is complex; as the MW goes down, greater care must be exercised in every aspect of polymerization, coating formulation, and application. In polymerization, the amount of non- or monofunctional resin must be kept to a very low fraction. Due to the larger number of chain ends, the effect of chain transfer to solvents such as ketones, which can introduce photoreactive end groups, is potentially more serious. More care is needed in establishing the stoichiometric ratio of cross-linker, and as noted in Section 25.2.2, the cure window becomes narrower. Controlling film defects during application becomes more difficult as the solids content becomes higher (Chapter 24). It is particularly difficult to avoid sagging of spray applied baking coatings.

An example of a TSA resin has the following composition: S/MMA/BA/HEA; the weight ratio 15 : 15 : 40 : 30; $\bar{M}_w$, 5200; $\bar{P}_w$, 54; $\bar{M}_n$, 2300; $\bar{P}_n$, 20; $\bar{P}_w/\bar{P}_n = 2.7$; equivalent weight, 400; $\bar{f}_n = 5.7$ [7]. It was made for studying MF cross-linking of fairly high solids coatings. The resin was prepared at 65 NVW in methyl amyl ketone (MAK). In comparing this TSA with the conventional TSA described earlier in this chapter, note that $\bar{M}_n$ has been reduced by a factor of 6.5, whereas $\bar{f}_n$ is reduced by only a factor of 2.8. This difference results from the higher content of hydroxy-functional monomer required in the high-solids resin. To attain about the same XLD in the final film, the low MW resin must undergo more reactions. Although not reported, application solids of coatings formulated with this resin would be around 45 NVV. This solids content corresponds to that used in high-solids metallic automotive top coats. However, the solids are still too low to meet EPA regulations for some current end uses, and even stricter regulations are anticipated.

As explained in Section 2.2.1, conventional free radical polymerization inherently limits the extent to which MW of a TSA can be reduced. Satisfactory performance requires that a high fraction of the molecules have at least two hydroxyl groups, but this becomes statistically less probable as the MW is reduced. The problem can be illustrated by comparing the conventional TSA ($\bar{M}_n = 15{,}000$, $\bar{P}_n = 140$) described in Section 8.2 with a hypothetical high-solids TSA having the same monomer ratio with $\bar{M}_n = 1070$ ($\bar{P}_n = 10$), which is about the level needed to formulate with VOCs around 300 gL^{-1}. The conventional resin has an $\bar{f}_n$ of 16 hydroxyl groups. While individual molecules have more or less than 16 hydroxyl groups, statistically the number of molecules with fewer than two hydroxyl groups is very low, and virtually all the molecules are capable of cross-linking. In contrast, the $\bar{f}_n$ of this high-solids TSA would be only about 1.2, and a very large fraction of the molecules could not be cross-linked. Molecules with no hydroxyl groups would either volatilize or remain in the film as plasticizers, to the detriment of film properties. Molecules with one hydroxyl group would terminate cross-linking reactions, leaving *loose ends* in the coating. The theory of elasticity predicts that loose ends seriously diminish the mechanical properties of a network. Experimental experience confirms that loose ends have a substantial effect on initial film properties [8,9]. For example, each percent by weight of monohydroxy oligomer in a TSA may reduce the T_g of the TSA–MF enamel by about 1°C [8].

The problem results from both MW and functional group distribution. Figure 2.2 shows the distribution of molecules of differing degrees of polymerization of a series of resins with $\bar{P}_n = 12$ and $\bar{P}_w/\bar{P}_n = 1.07$, 1.5, and 3.0. The theoretical minimum polydispersity that can be obtained by anionic polymerization is 1.07, and the theoretical minimum achievable by free radical–initiated polymerization is 1.5. The difference is explained by different kinetic characteristics; with anionic polymerization, the rate of propagation can be slower than the rate of initiation, while with free radical polymerization, the rate of propagation is generally faster. It is difficult to approach the theoretical minima in practice; $\bar{P}_w/\bar{P}_n = 2.5$ is typical of reasonably well controlled free radical polymerizations. The other factor involved is sequence length distribution, which is the distribution of sequences of different lengths of non-functional monomers separating functional monomers. If these sequence lengths are short compared to the chain length of the low MW parts of the resin, multiple functional groups will be incorporated in the molecules. But if the sequence lengths of non-functional monomers are long in comparison to chain lengths, molecules with one or no functional monomer units can be expected.

Statistical methods have been used to calculate the proportions of non-functional molecules that would be formed during random copolymerization of monomer mixtures with differing monomer ratios for different MWs and MW distributions [10,11]. Due to the assumptions involved, the calculations are approximate. An example of such results for S/BA/HEA (30 : 50 : 20 wt%) copolymers of varying $\bar{P}_n$ is given in Table 8.1. For $\bar{P}_n = 9.5$ ($\bar{M}_n = 1125$), about 36% of all molecules, corresponding to 13% of the weight, is non-functional. (The mol% and wt% differ because of the MW distribution; low MW molecules are more likely to be nonfunctional than higher MW molecules.) The weight fraction of monofunctional oligomer is more difficult to calculate but would be expected to exceed that of non-functional oligomer. At the higher HEA content (30%) of the example given previously with $\bar{P}_n = 20$, the proportion of monofunctional oligomer molecules would be minimized. But if one wished to have volume solids of about 70 NVV, one would need to have a $\bar{P}_n$ of about 10 with a narrow distribution of MW. The calculations show that the functional monomer content would have to be very high; so high that the XLD of the cross-linked film would be too high for acceptable film properties.

TABLE 8.1. Percentage of Non-functional Molecules Statistically Predicted for S/BA/HEA (30 : 50 : 20 by wt%) Copolymers

$\bar{P}_n$	$\bar{M}_n$	Mol%	Wt% Nonfunctional
36.8	4357	15	1.8
19.2	2273	24	5.8
9.5	1125	36	12.8

Source: Ref. [12].

The viscosity of acrylic resins can be reduced by changing the proportions of comonomers to reduce T_g. However, this approach also reduces the T_g of the cross-linked film, other factors being equal. The effect of reduced T_g on film properties can be offset to an extent by increasing cross-link density, but if carried too far, this approach leads to an unsatisfactory combination of properties. Methacrylate esters of relatively rigid alcohols, such as 3,3,5-trimethylcyclohexyl [12] and isobornyl [13] methacrylates, with a compact shape can combine relatively low viscosity and high T_g. Accordingly, such esters can be used as partial replacements for MMA and S.

MW is reduced by using chain-transfer agents, but some chain-transfer agents can have an adverse effect on exterior durability [9]. Use of a chain-transfer agent with a functional group is an interesting approach. For example, when 2-mercaptoethanol is used as a chain-transfer agent, initiating free radicals bearing a hydroxyl group are formed. These lead to a high fraction of molecules with a hydroxyl group on one end, reducing the fractions of non- and monofunctional molecules in the resin [14]. Improved film properties are obtained, but the unpleasant odor of mercaptoethanol causes handling problems and may leave residual odor in the resin.

High levels of initiator with close control of variation of temperature and concentrations during polymerization can minimize polydispersity. Although no basic studies have been published, it appears that with high initiator concentration, polydispersity; is narrower than theory predicts. Proprietary acrylic resins for general-purpose white coatings with moderately demanding durability requirements have been reported with sprayable viscosities at about 54 to 56 NVV (70 to 72 NVW) [15]. Another commercial resin with $\bar{M}_n$ of 1300 and $\bar{M}_w/\bar{M}_n = 1.7$ can be formulated with class I MF resins in white coatings at about 77 NVW [16]. These resins provide hard, chemical resistant films with many good properties, although the films tend to be brittle.

Initiator choice can be critical. Benzoyl peroxide gives wide distributions due to chain transfer to polymer resulting from hydrogen abstraction. Azo initiators such as azobisisobutyronitrile (AIBN) give less branching; AIBN is also generally preferred over benzoyl peroxide because exterior durability of films is superior. Initiators based on *t*-amyl peroxides, such as ethyl 3,3-di(*t*-amylperoxy)butyrate, are reported to give narrow distributions [17]. Other workers recommend initiators derived from *t*-butyl peroxide, such as *t*-butyl peracetate [18]. A comparison of the use of azobis(2-methylbutyronitrile (ABMBN) with *t*-butyl peroctanoate as initiators showed that the azo initiator gave narrower MW distributions [19]. It was also shown that with ABMBM, hydroxy-functional acrylic resins could be polymerized in solutions of MF resin. In the presence of mercaptan chain-transfer agent, ABMBN gave narrower MW distribution than did *t*-butyl peracetate.

Copolymers of hydroxy-functional allylic monomers and acrylate esters are reported to give copolymers with more uniform distribution of hydroxy groups than copolymers with hydroxy-functional acrylates. The allylic monomers are less reactive than the acrylate monomers; hence, allylic monomers rarely react with each other, leading to more uniform incorporation of hydroxy functionality. Also, they are chain-transfer agents, which increases the amount of terminal hydroxy functionality. Three allylic monomers were used in the study: allyl alcohol, allyl monoethoxylate, and allyl monopropoxylate. Resins were designed for use in 2K urethane coatings [20].

Controlled free radical polymerization (CFRP), a living free radical polymerization, permits the synthesis of block copolymers with narrow MW distribution and controlled introduction of functional groups (Section 2.2.1.1). An acrylic resin prepared by CFRP is being used in automotive clear coats. The solids of the SuperSolids clear coat are reported to be 65% with the possibility of future coatings having up to nearly 90% solids. At the same time the scratch and mar resistance are substantially higher. Dupont has been awarded the EPA clean air achievement award for the work [21].

Another example of the use of CFRP is the preparation of acrylic resins for use in powder coatings [22]. The resin had a $\bar{M}_w/\bar{M}_n$ of 1.25, compared with 1.95 for a similar resin made by conventional free radical polymerization. The melt viscosity at 180°C of the ATRP polymer was 11.2 Pa•s, compared with 57.2 for the conventional resin. A powder coating using bis(*N*,*N*-di-2-hydroxyethyl)adipamide as a cross-linker was compared with a similar powder coating made with the conventional free radical copolymer. The ATRP powder coating gave cured films with better leveling than the conventional polymer and had superior storage stability. The lower melt viscosity due to the narrow MW distribution resulted in better leveling. The reduced amount of very low MW molecules reduced the fusion of the powder particles during storage.

Another approach to increasing solids is to blend acrylic polyols with other low viscosity polyols, such as polyesters. Some reduction in VOC can be achieved in this way. The film properties, such as exterior durability and chemical resistance, with such blends are often not quite as good as those of straight TSA–MF coatings, but they may be adequate for many uses, and some highly weather resistant coatings have been reported [23].

In general, acrylic resin coatings do not show good adhesion to metals and are used over primers. However, phosphate-functional (meth)acrylate esters are now available. Resins prepared with 1 to 4% of such a monomer are reported to give acrylic coatings with excellent adhesion to a broad range of metals [24].

8.2.2. Acrylics with Other Functional Groups

Carbamate-functional acrylics can be cross-linked with Class I MF resins to give films with better environmental etch resistance than MF cross-linked hydroxy-functional acrylics while retaining the advantage of mar resistance [25] (Section 11.3.4). Carbamate-functional acrylic resins can be prepared by reacting isocyanato-functional acrylic resins with hydroxypropyl carbamate [26,27], by reacting acrylic resins with urea [27] and by ester interchange between a hydroxyl group on a hydroxy-functional acrylic and the carbamate from propylene glycol monomethyl ether [28]. Use of a combination of a carbamate-functional acrylic resin, a carbamate-functional urethane, and MF resins has been disclosed [29]. Carbamate-functional acrylics can be blended with hydroxyl-functional resins to reduce costs while retaining satisfactory levels of mar resistance.

Trialkoxysilylalkyl-functional acrylics can be prepared using a trialkoxysilylalkyl methacrylate as a comonomer [30]. They provide high-performance clear coats by moisture-cure in the air (Section 16.2). Trialkoxysilyl-functional acrylics have also been synthesized by copolymerization of vinyltrimethoxysilane and butyl acrylate. Studies of the structure indicate that some Si—O—Si bonds form during the polymerization. Films of the resin cure rapidly with an acid catalyst by reaction with atmospheric water [31].

Carboxylic acid–functional acrylic resins are made using acrylic or methacrylic acid as comonomers; they are cross-linked with epoxy resins (Section 11.3.4). Note that close quality control of acrylic acid monomer is required because it can dimerize during storage.

Acrylics with amide groups can be used in several ways. Acrylic copolymers containing acrylamide can be cross-linked with MF resins by reaction with the amide group; the curing temperature required is higher than for hydroxy-functional resins. Alkoxymethyl derivatives of acrylamide copolymers can be made by reacting the amide groups with formaldehyde, followed by etherification, analogous to the preparation of amino resins, as described in Section 11.4.4. These resins can be used as cross-linkers for hydroxy-functional TSAs. Alternatively, one can make alkoxymethyl derivatives of monomeric acrylamides for use as comonomers. For example, *N*-(isobutoxymethyl)methacrylamide has been used as a comonomer along with hydroxy-functional comonomers to make copolymers that are "self cross-linking" [32]. Acrylic copolymers containing acrylamide and HEMA can also be reacted with formaldehyde and then with an alcohol to make a self cross-linking resin.

Epoxy-functional acrylics are made using glycidyl methacrylate (GMA) as a comonomer (Section 13.3.2). Such resins are used in powder clear coats for automobiles [33–35] (Section 28.1.4). They can be cross-linked with dicarboxylic acids such as dodecanoic acid [33,34] or with carboxylic acid-functional acrylic resins [35]. GMA acrylic copolymers, which contain 4-hydroxybutyl acrylate (HBA), have also been combined with an acrylic resin using maleic anhydride as a comonomer that has been reacted with methanol to give a half ester. During curing the half ester cyclizes to re-form anhydride groups that react with the hydroxy groups from the HBA; epoxy groups react with the COOH groups generated after the anhydride reacts with the OH group. The cured films are reported to exhibit excellent mar and acid resistance as automotive clear coats [36]. Three alternative systems based on GMA acrylic copolymers have been proposed. A GMA copolymer can be cross-linked with carboxy-functional polyesters. Copolymers using both GMA and acrylic acid as comonomers are self cross-linking resins. Also, an acrylic using GMA and *t*-butyl acrylate are self cross-linking; with heat the *t*-butyl group leaves as isobutylene, leaving a COOH to cross-link with the epoxy groups. The coatings are reported to exhibit excellent mar and acid resistance and to be useful not only in high-solids solventborne systems but also in powder coatings and, with a nonionic emulsifier, in waterborne coatings [37].

Isocyanato-functional acrylics can be prepared by copolymerizing isopropenyl dimethylbenzylisocyanate (TMI) with acrylates (Section 12.3.2) [38]. They can be cross-linked with polyols and hydroxy-functional acrylic resins.

New under body plastisol coatings prepared from core–shell acrylic copolymers have been reported. For example, an emulsion copolymer with a core of isobutyl methacrylate with 2% 1,6-hexanediol diacrylate and a shell of MMA with 6% 1,6-hexanediol diacrylate is converted to a dry powder and dispersed in dioctyl phthalate or tricresylphosphate [39].

8.3. WATER-REDUCIBLE THERMOSETTING ACRYLIC RESINS

Another way to reduce VOC emissions from TSA coatings is to make TSA resins that can be diluted (reduced) with water. Such resins are sometimes called "water-soluble resins," but this terminology is misleading since the resins are not soluble in water. Rather, solutions of amine salts of these resins in organic solvents can be diluted with water to form reasonably stable dispersions of polymer aggregates swollen by solvent and water. To minimize confusion, we have chosen to use the following terminology: *waterborne* is used broadly for all coatings with aqueous media, including latex coatings; *water-reducible coatings* is used only for waterborne coatings based on resins having hydrophilic groups in most or all molecules, which excludes latexes; and *water-soluble* is limited specifically to substances that are soluble in water.

A typical water-reducible acrylic resin is a copolymer of MMA/BA/HEMA/AA, in a weight ratio of 60 : 22.2 : 10 : 7.8, prepared by free radical–initiated polymerization using an azo initiator [40]. The polymerization is carried out at high solids (generally, 70 NVW or higher) in a water-miscible solvent. Glycol ethers, such as 1-(*n*-propoxy)-2-propanol or 2-butoxyethanol, and butyl alcohols are the most widely used solvents. Except for the solvent and the higher proportion of acrylic acid, such resins are similar to conventional solids TSAs, having $\bar{M}_w$ and $\bar{M}_n$ of about 35,000 and 15,000, respectively, as described in Section 8.3.

Water-reducible acrylic resins typically have acid numbers of 40 to 60. (The acid number is determined by titration and is defined as milligrams of KOH required to neutralize 1 g of resin solids. Equivalent weight equals 56,100/acid number.) Residual monomer is removed by distilling off a small fraction of the solvent, and the resin is stored as a concentrated solution. The first step in preparing a coating is to add an amine, such as 2-(dimethylamino)ethanol (DMAE). As discussed later, less than the theoretical amount of amine required to neutralize all of the carboxylic acid groups is commonly used. The ratio used is called the *extent (of) neutralization* (EN). For example, if 75% of the theoretical amount were used, the EN would be 75. Other coating components (pigments, MF resin, sulfonic acid catalyst) are dispersed or dissolved in this solution and the coating is diluted with water prior to application.

The change in viscosity with dilution of water-reducible resins is abnormal. An example is given in Figure 8.1 showing the log viscosity as a function of concentration for a model resin [41]. The height of the peak in the dilution curve is dependent on the particular resin and formulation, and the systems are highly shear thinning in the peak region. Another abnormality is that when water-reducible resins are neutralized and reduced with water, their pH is over 7 (commonly 8.5 to 9.5), even though less than the theoretical amount of amine necessary to neutralize the carboxylic acid is used. For comparison purposes, a dilution curve for the same resin using an organic solvent (*t*-butyl alcohol in this case) is included in the figure, as is a typical dilution curve of a latex.

The morphology of water-reducible TSAs has been studied fairly extensively [41–43]. In Figure 8.1, the water-reducible resin is a 54% solution of a 90 : 10 butyl methacrylate (BMA)/AA copolymer in *t*-butyl alcohol at 75 EN with DMAE. The solvent dilution curve of log viscosity versus concentration is fairly linear, which is typical for most resin solutions in good solvents. The water dilution curve shows the abnormal response that is typical for water-reducible resins. During dilution with water, two kinds of changes are occurring simultaneously: The concentration is reduced, as is the ratio of solvent to water.

In the first stages of dilution, viscosity drops more rapidly with water than with solvent. It is hypothesized that the viscosity is high before dilution because of association of ion pairs on different molecules. Water associates strongly with ion pairs, separating most of the intermolecular ion pairs and causing rapid reduction in viscosity. However, as dilution with water continues, the viscosity levels off and then increases, passing through a maximum. Further dilution causes a very steep drop of viscosity. At an application viscosity of about 0.1 Pa•s, such systems typically have solids in the range 20 to 30 NVW. Thus, the application solids of coatings made with such resins is low; however, since a major part of the volatile components is water, VOC emissions are still low.

The viscosity changes on dilution with water are explained as follows. The amine salt of the resin is soluble in the *t*-butyl alcohol and in *t*-butyl alcohol–water solutions in which the

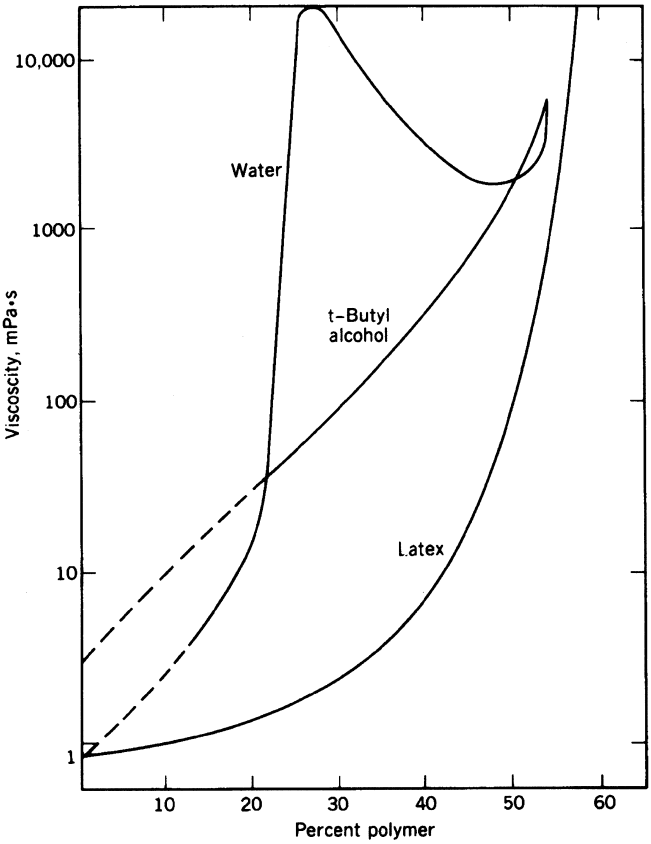


Figure 8.1. *Viscosity dependence on concentration for a 10 mol% acrylic acid copolymer, 75 EN with DMAE, dissolved in* t*-butyl alcohol and then diluted with water. Also shown are curves for dilution of the same resin with* t*-butyl alcohol and a typical viscosity–solids latex dilution with water. (From Ref. [41], with permission.)*

ratio of solvent to water is high. But as additional water is added, the ratio of solvent to water decreases to the point where some of the molecules are no longer soluble in the mixed solvent. These molecules do not precipitate in a separate macrophase, but the nonpolar segments of various molecules associate with each other to form aggregates. The predominantly nonpolar parts of the molecules are in the interior of the aggregates, and the highly polar carboxylic acid salt groups are on their periphery. As dilution continues, more and more molecules join in aggregates. Since the solvent is soluble in the resin, some dissolves in the aggregates, swelling their volume. Also, water associates with the salt groups, and some dissolves in the solvent inside the aggregates, further swelling them. As the aggregates form, the system changes from a solution to a dispersion of aggregates in a continuous phase. As the number and volume of aggregates grow, the volume fraction of internal phase increases and the aggregates get more and more closely packed, leading to an increase in viscosity. (See Section 3.5 for discussion of the factors controlling the viscosity of liquids containing dispersed phases.) At the maximum viscosity, the material is predominantly a dispersion of highly swollen aggregates in water containing some solvent. The high viscosity can lead to difficulty in stirring. On still further dilution, the viscosity drops rapidly. This drop results from two factors. There is a dilution effect, that is, the decrease in volume fraction internal phase. However, the drop is even steeper than would result from this effect alone. The balance of the decrease is due to a decrease in the swelling of the aggregates. The partitioning of solvent and water between the aggregates and the continuous phase changes throughout the dilution process, and as more water is added, more solvent moves to the continuous phase, shrinking the swollen aggregates.

The viscosity of the solutions in the organic solvent is Newtonian, as it is when only small amounts of water have been added. However, in the midrange around the peak of the water dilution curve, the dispersions show a high degree of shear thinning [42]. The dilute systems show little or no shear thinning. This behavior can be explained on the basis that in the shear thinning stage, the swollen aggregate particles (internal phase) are not rigid. When shear is applied, the particles distort, decreasing the shape factor, increasing the packing factor, and as a result, decreasing the viscosity as a function of increasing shear rate. With further dilution, some of the organic solvent is extracted from the aggregates into the continuous phase, and the aggregates become smaller and less easily distorted. In the more dilute stage, the viscosity is lower, so the shear stress exerted on the aggregates at a given shear rate is less, reducing the probability of distortion. Thus, the flow properties are Newtonian or only slightly shear thinning at application viscosities.

The abnormal pH effect noted earlier can be explained in a way consistent with this picture of the morphology of the system [44]. When one neutralizes a simple carboxylic acid, such as acetic acid, with 75% of the theoretical equivalent amount of an amine such as DMAE, the pH is about 5.5. However, the situation with the carboxylic acid groups on the polymer chain is different. The acrylic acid groups are relatively randomly spaced along the polymer chain. In some cases, there are carboxylic acid groups near each other; in other cases, there are single acrylic acid groups separated from others on both sides by several hydrophobic ester monomer units. As aggregation occurs during dilution, many of the carboxylic acid groups are near the surface, where all, or almost all, are neutralized by the water-soluble amine. However, geometric factors require that many other carboxylic acid groups reside in the interior of the aggregates; those most widely separated from other carboxylic acid groups by hydrophobic monomer residues are presumably most likely to be “hidden” in the interior of aggregates. DMAE partitions among the continuous (water–solvent) phase, the surface region of the aggregates, and the interior of the aggregates. Since DMAE and DMAE salts are highly soluble in water, it is expected that DMAE concentrates in the first two regions, leaving a fraction of carboxylic acid groups unneutralized in the interior of aggregates. Even when there is only 75% of the amine necessary to neutralize all of the carboxylic acid groups, there is more than enough to neutralize those carboxylic acid groups at or near the surface of the aggregates. Part of the amine is in the continuous phase, resulting in a basic pH reading. Since the interaction is between a weak base and a weak acid, the change of pH with amine addition is slow. Due to this insensitivity, pH is not appropriate as a quality control specification.

This description of the morphology of a water-reducible system accounts for its behavior but does not provide direct evidence for the presence of aggregates. Evidence was found by studying the effects of changing solvent to water ratios at a constant resin/amine concentration. A BMA–AA copolymer (mole ratio 84 : 16) at 75 EN with DMAE was “dissolved” in a series of solvent/water solutions at the same concentration of 21.2% of resin plus DMAE [42]. The viscosity of this series of dispersions goes through a peak at 30 : 70 solvent to water. The samples were then subjected to ultrafiltration. No resin was retained on the filter in the case of samples with a ratio of 80 : 20

solvent to water up to pure solvent. As the solvent ratio decreased from 80 : 20 to 30 : 70, the amount of resin retained increased until at 30 : 70, essentially all of the resin was retained by the ultrafilter. All of the resin in samples with still less solvent was also retained. The samples were also examined by phase contrast microscopy, which revealed the presence of particles in all those samples where resin was retained by the ultrafilter.

Many variables affect the morphology of these systems. The shape of the viscosity–concentration (dilution) curve varies. In some cases, there is a very high viscosity peak—higher than the viscosity of the original undiluted material; in other cases, there may be only a shoulder in the dilution curve. Dependence of the viscosity on the MW depends on solvent structure and the ratio of solvent to water, in addition to the concentration [42]. The effect of MW on viscosity is different at different stages of dilution. The log viscosity of the all solvent solution varies with approximately the square root of the MW. The viscosity in the peak area of the dilution curve is very dependent on MW. As the MW increases, the viscosity of the interior of the aggregate particles is higher, so they are more difficult to distort; hence, the viscosity of the entire system does not decrease as much at any given shear rate. Very high peak viscosity leads to difficulty in dilution. It is necessary to limit the MW so that the coating can be thoroughly agitated throughout the dilution cycle with the available mixing equipment. The viscosity of systems diluted with water to application viscosity is independent of MW. This advantage permits application of coatings using resins having a MW in the same range as those used in conventional solventborne TSA coatings but with VOC contents substantially lower and comparable to that of relatively high solids coatings.

The dilution behavior of TSAs depends on their carboxylic acid content. The effect of varying the mole percent of acrylic acid in a series of BA/AA copolymers from 10 to 50% is shown in Figure 8.2. With 50% acrylic acid, the salts exhibit a viscosity dependence on dilution behavior approaching that of solution systems. As the carboxylic acid content is reduced, the abnormal rheological properties become more pronounced. Notice that the concentration at viscosities near those required for application are highest for the lowest acid content systems. This is an important reason that resins of this type are designed with the lowest carboxylic acid content (acid numbers 40 to 60) that still provides a stable dispersion at application viscosity. Low acid numbers favor formation of relatively unswollen aggregates, keeping viscosity down, but if the acid numbers are too low, the system separates into macrophases instead of forming a stable microphase dispersion.

The required acid content is lower for resins with increasing hydroxyl group content. Although salts of carboxylic acid groups are much more hydrophilic than hydroxyl groups, hydroxyl groups are sufficiently hydrophilic to promote the solubility in water–solvent blends, as indicated by the water solubility of the homopolymer of 2-hydroxyethyl acrylate. Therefore, the minimum required acid content decreases as the content of hydroxyl groups increases.

Polycarbonate-modified water-reducible acrylic resins, having pendant carbonate groups, are synthesized by copolymerizing MMA and styrene with a monomer obtained by reacting 5,5-dimethyl-1,3-dioxane-2-one with HEMA. Aqueous dispersions of the resins exhibited excellent hydrolytic stability; and formulations with MF resin cured more rapidly than did conventional water-reducible acrylic resins [45].

Various types and amounts of amine can be used [41,46,47]. Generally, less than the stoichiometric amount of amine is used. The lower the amine content, the lower the

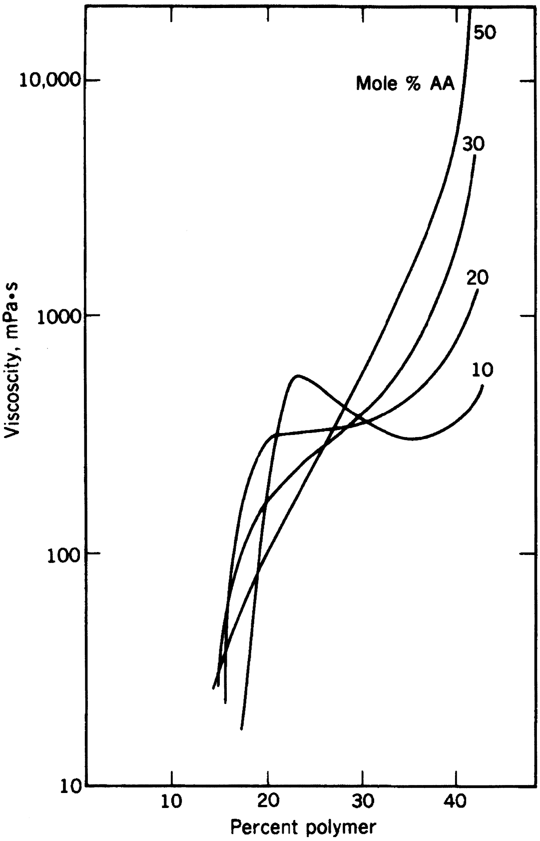


Figure 8.2. Viscosity variations during water dilutions of 42 NVW copolymers having 50, 30, 20, and 10 mol% AA, each at 75 EN with DMAE. (From Ref. [41], with permission.)

viscosity of the fully diluted systems, corresponding to higher solids at a fixed application viscosity. Figure 8.3 shows viscosity response to dilution as a function of extent neutralization of a 90 : 10 BMA–AA resin with DMAE. For any resin–amine combination, there is a minimum amount of amine required to give a stable dispersion at application viscosity, that is, to prevent macrophase separation. In the example shown in Figure 8.3, the 50 EN sample could not be fully diluted without macrophase separation. In a similar experiment using an 80 : 20 BMA–AA resin, 50 EN with DMAE gave a stable dispersion even when diluted until the viscosity was below 0.1 Pa•s. Viscosity at application viscosity changes rapidly with concentration, and it is possible to overshoot a desired reduction. The viscosity is also sensitive to amine content, so if a coating has been reduced with too much water, resulting in too low a viscosity, the viscosity frequently can be brought back up by addition of small amounts of amine.

Another variable is the structure of the neutralizing amine. Although there may be some effect of base strength (less amine may be required with increasing base strength), the principal variable seems to be the water solubility of the amine. The amount of amine required for stable dispersions increases in the order DMAE < triethylamine (TEA) < tripropylamine. Hydroxyl-substituted amines are the most widely used, but morpholine derivatives

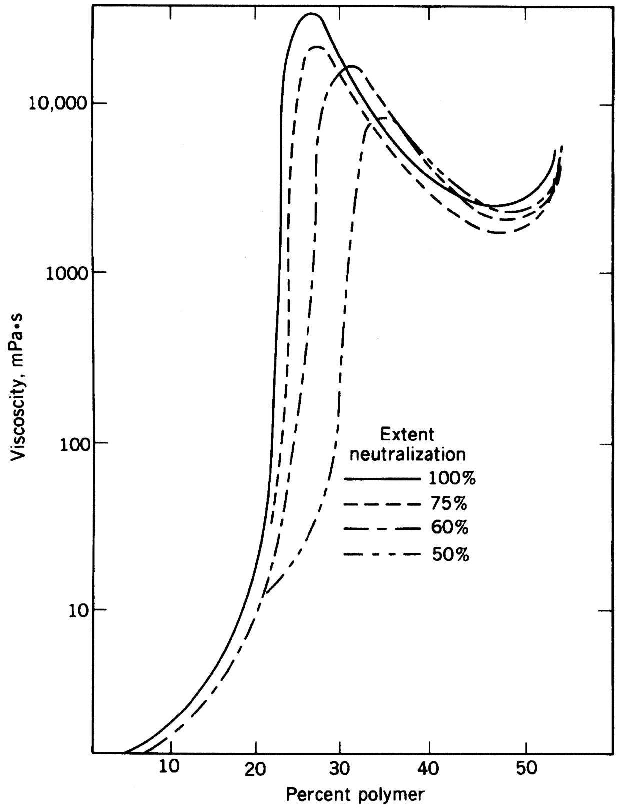
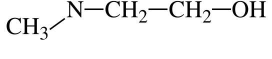


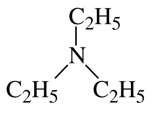
Figure 8.3. Viscosity as a function of weight percent resin when neutralized with varying levels of DMAE. Resin has 10 mol% AA; dilution started at 54 wt% solids. (From Ref. [41], with permission.)

such as *N*-ethylmorpholine (NEM) are also effective. Potential toxic hazards of the amines should be assessed carefully.



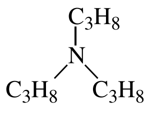
$\begin{matrix}CH_3\\ CH_3\end{matrix}\!>\!N{-}CH_2{-}CH_2{-}OH$

DMAE



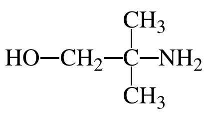
$\overset{C_2H_5}{\underset{C_2H_5\quad C_2H_5}{N}}$

TEA



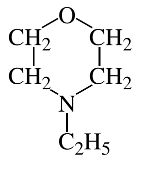
$\overset{C_3H_8}{\underset{C_3H_8\quad C_3H_8}{N}}$

TPA



$HO{-}CH_2{-}\overset{CH_3}{\underset{CH_3}{C}}{-}NH_2$

AMP



NEM

In selecting amines it is important to consider not only the effect on dispersion stability, but also the effect on package stability and curing of the coating [44]. The amine improves the package stability by minimizing reactions of MF resins during storage. If Class II MF resins are to be used, the amine must be tertiary. If, as is more common, Class I MF resins are used, primary or secondary amines can also be used.

DMAE, although widely used, has a disadvantage. It has been shown that transesterification occurs between ester groups on the acrylic resin and the hydroxyl of the amino alcohol, thereby covalently bonding part of the amine to the resin [46]. Since bound amine cannot volatilize during application and baking, it inhibits the acid-catalyzed cross-linking reactions. NEM, which has essentially the same boiling point as DMAE, permits faster curing, since it cannot undergo transesterification. 2-Amino-2-methyl-1-propanol (AMP) can be used with Class I MF resins. It provides stable dispersions and despite its higher boiling point, gives coatings that cure more rapidly than even those neutralized with NEM. AMP has a hydroxyl group that can transesterify, but also a primary amine that can undergo aminolysis reactions with ester groups on the resin [46]. By reacting at both sites, AMP can act as a cross-linking agent, supplementing cross-linking with the MF resin. Furthermore, AMP has been shown to cyclize to an oxazolidine under curing conditions, reducing basicity and increasing the cure rate [47]. The difference in curing response with DMAE and AMP has also been demonstrated by dynamic mechanical analysis [48].

Another factor involved in the choice of amine is the effect on wrinkling [46]. When using TEA as the neutralizing amine, it is common to get low gloss coatings. The low gloss results from the development of a fine wrinkle pattern on the surface during curing of the film, which is caused by faster curing of the surface layer than the interior of the film. When the interior of the film does cure, it shrinks, causing the immobilized surface of the film to wrinkle. (See Section 24.6 for further discussion of wrinkling.) This phenomenon occurs when amine is essentially absent near the surface of the film but still present in the lower layers of the film; the MF resin readily cross-links the acrylic at the surface, whereas the reaction is still inhibited in the lower layers.

The probability of wrinkling increases as film thickness increases because there is more likely to be a differential in amine content as film thickness increases. The probability of wrinkling is also affected by amine structure. A series of amines gave decreasing probability of wrinkling in the order TEA $>$ DMAE $>$ NEM [46]. TEA is a relatively strong base (pK_a of conjugate acid $= 10.9$) and hence diffuses slowly through a film containing COOH groups; it also has a relatively low boiling point (90°C), so on reaching the surface, it volatilizes rapidly. This combination of factors leads to a differential amine content even with relatively thin films. NEM, which is a weaker base (pK_a of conjugate acid $= 7.8$) and has a higher boiling point (139°C), can diffuse relatively more rapidly through the film, but volatilizes more slowly from the surface. The result is a more nearly uniform amine gradient and more uniform timing of curing of surface and lower layers of a film. DMAE has an intermediate base strength ($pK_a = 9.3$) and a relatively high boiling point (134°C) and exhibits intermediate behavior between that of TEA and NEM.

Melamine–formaldehyde resins are most commonly used as cross-linkers for the coatings. Class I and Class II monomeric methylolated MF resins are miscible in these systems. They cross-link the TSA by reacting with hydroxyl and carboxyl groups. The reaction with OH groups is faster, and the resulting ether bonds are more stable to hydrolysis than are ester bonds resulting from cross-linking with COOH groups. Thus, while the cross-link density of the final film depends on the total functionality of COOH and OH groups, it is generally desirable to attain as much of the cross-linking as possible through OH groups and to adjust cross-link density by varying the $\bar{f}_n$ of OH. A further advantage of using the lowest possible level of COOH is that less amine is required. Amines are relatively expensive and must be included as part of the VOC emissions. 2K waterborne urethane coatings use polyisocyanates as cross-linkers for water-reducible acrylics (Section 12.7.3).

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9

Latexes

A *latex* is a dispersion of polymer particles in water. Most synthetic latexes are made by a free radical–initiated chain-growth polymerization process in which the monomers are emulsified in water at the start; hence, the process is called *emulsion polymerization*. It is not surprising that latex paints are sometimes misnamed *emulsion paints*, but this terminology is best avoided, since it can cause confusion with systems that are true emulsions. Aqueous dispersions of polymers are also prepared by other methods; for example, polyurethane dispersions in water are prepared by step-growth polymerization. Usually, these materials are called *aqueous dispersions* rather than latexes; they are discussed in Section 12.7.1. To further confuse the terminology, some authors call latexes *colloidal dispersions* or *polymer colloids*.

Molecular weights (MW) of polymers prepared by emulsion polymerization are generally high; an $\bar{M}_w$ of 1,000,000 or higher is common. However, unlike solution polymers, the MW of the polymer in latex particles does not affect the viscosity of the latex. Instead, latex viscosity is governed by the viscosity of the medium in which the polymer particles are dispersed (the continuous phase), by the volume fraction of particles, and by their packing factor. (See the discussion of the Mooney equation in Section 3.5.) This lack of dependence of viscosity on MW makes it possible to formulate latex coatings at higher solids than those of solutions of polymers having high MW. Latexes are used as the principal vehicle in a large majority of architectural coatings in the United States. A growing part of the OEM (original equipment manufacture) product and special purpose coatings markets is latex based. Most latex paints form films by coalescence at ambient temperatures (Section 2.3.3). A limitation of most latex-based coatings is the inability to achieve very high gloss. On the other hand, the durability of the films is superior to that of films formed from drying oil and alkyd paints; and VOC emissions are often lower.

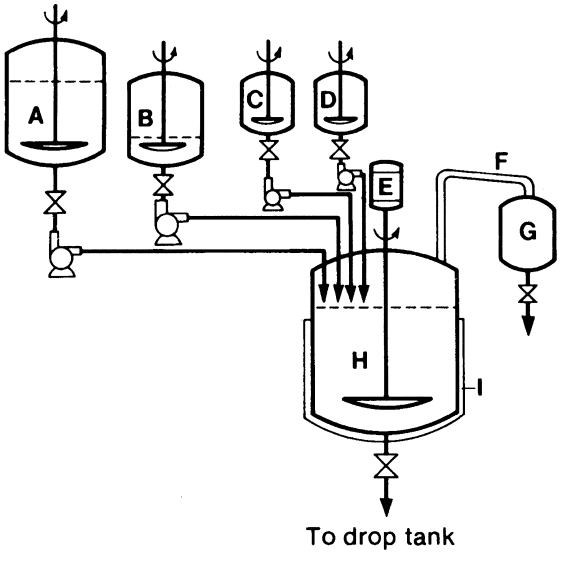
Organic Coatings: Science and Technology, Third Edition, by Zeno W. Wicks, Jr., Frank N. Jones, S. Peter Pappas, and Douglas A. Wicks

9.1. EMULSION POLYMERIZATION

Emulsion polymerization is carried out in water using monomer(s), surfactant(s), and a water-soluble initiator. Many of the same monomers are used as in solution polymerization, and the reactions are broadly similar at the molecular level. However, the physical circumstances of polymerization are different, affecting the polymerization chemistry. The process is easily varied, and the properties of the latex are affected by changes in physical conditions of the polymerization.

There have been many studies of the mechanisms of emulsion polymerization; however, there are so many variables that no general theory has been developed that can predict the results obtained in all emulsion polymerizations. Monomer structure, solubility, and concentration; surfactant(s) structure and concentration; initiator concentration and rate of radical generation; presence and concentration of added electrolytes; and temperature are some of the critical variables. The rate of agitation and reactor design can affect the results as well. A qualitative discussion of proposed mechanisms is provided in Section 9.1.2. The reader is referred to the general references provided at the end of the chapter for extensive discussion and proposed equations for predicting the number of particles and particle sizes of latexes.

Many early laboratory studies were carried out by a small-scale *batch process* in which all of the ingredients were put into a sealed bottle, which was then shaken in a temperature controlled water bath. This process is often called the *pop-bottle process*. Many papers describing the mechanism of emulsion polymerization are based on such studies. However, batch processes cannot be used commercially because the heat evolved by the exothermic polymerization process would be uncontrollable in a large vessel. Instead, commercial latexes are produced by a *semicontinuous batch process*, using apparatus such as that shown schematically in Figure 9.1. Monomers and initiators are added in proportions and rates such that rapid polymerization occurs. In this way, the monomer



A — Main monomer feed tank
B — Auxiliary monomer feed tank
C,D — Initiator feed tanks
E — Stirring motor
F — Condensor
G — Receiver
H — Reactor
I — Heating/cooling jacket

Not shown: Safety vents, pressure and temperature gauges, filters, coolers for feed tanks.

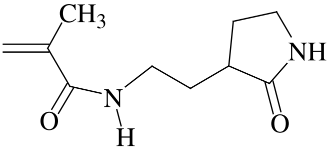
Figure 9.1. *Semicontinuous batch process production unit. (Adapted from Ref. [1], with permission.)*

concentration at any time is low; the polymerization is said to be done under *monomer-starved conditions*. This facilitates temperature control. Furthermore, the composition of copolymers formed under monomer-starved conditions approximately equals the composition of the monomer feed, regardless of the relative reactivity of the various monomers. This procedure also permits changing monomer composition during the course of a polymerization, as discussed in Section 9.1.3. It is common to start the polymerization in the presence of a seed latex (Section 9.1.2). A laboratory scale process involving a seed latex is described in detail in Ref. [2].

The products obtained from batch and semicontinuous emulsion polymerizations of the same monomers are often quite different. The differences are particularly large when copolymers are prepared by the two methods (Sections 9.1.2 and 9.3). Care must be exercised in reading the literature since conclusions derived from studies on the batch process are often misleading when applied to the semicontinuous process, and vice versa. Since many variables affect the composition and properties of the latex produced, it is vital to plan laboratory procedures to simulate eventual production operations as closely as possible to minimize problems in scaling up to production equipment.

9.1.1. Raw Materials for Emulsion Polymerization

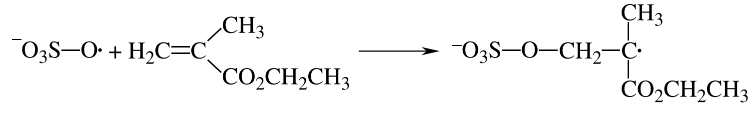
9.1.1.1. Monomers Many monomers have been converted to latexes by emulsion polymerization. The main requirements are that the monomers can undergo free radical chain polymerization and that they do not react with water. Monomers with limited solubility in water are most useful, although water-miscible comonomers can be used in small amounts. Monomers with very high or very low solubility in water pose some difficulties but can be accommodated in copolymerization. The two major classes of latexes used in coatings are based on acrylic and methacrylic esters (Section 9.2) and on vinyl esters (Section 9.3). Vinylidene chloride/acrylic ester copolymer latexes give films with exceptionally low water permeability (Section 9.2). The earliest latexes used in coatings were copolymers of styrene with butadiene; they are seldom used today in architectural coatings, but are used in coatings for paper. Various functional monomers are also used. Methacrylic acid (MAA) and acrylic acid (AA) improve colloidal stability, affect flow properties, improve adhesion, and give carboxylic acid groups to serve as cross-linking sites. Hydroxyethyl acrylate (HEA) and hydroxyethyl methacrylate (HEMA) provide hydroxyl groups for cross-linking. Monomers have been developed that promote wet adhesion to painted surfaces; methacrylamidoethylethyleneurea is used widely for this purpose. Phosphate-functional (meth)acrylate esters are available that can be used as comonomers to promote adhesion to metals [3].



Methacrylamidoethylethyleneurea

9.1.1.2. Initiators The principal initiators used in emulsion polymerization are soluble in water. The most common initiators are persulfate salts, especially ammonium persulfate (more correctly, ammonium peroxydisulfate). Persulfates cleave thermally in the water phase to sulfate anion radicals (Eq. 9.1) that initiate polymerization, as shown with ethyl acrylate in Eq. 9.2. Note that the terminal group is a sulfate half ester anion.

$$^{-}O_3S{-}O{-}O{-}SO_3^{-} \longrightarrow {}^{-}O_3S{-}O\cdot \qquad (9.1)$$



$$^{-}O_3S{-}O\cdot + H_2C{=}C\begin{matrix}\diagup CH_3\\ \diagdown CO_2CH_2CH_3\end{matrix} \longrightarrow {}^{-}O_3S{-}O{-}CH_2{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CO_2CH_2CH_3}{\overset{|}{\underset{|}{C}}}}\cdot \qquad (9.2)$$

The sulfate anion radical can also abstract hydrogen from water, leading to the formation of bisulfate and a hydroxy free radical (HO·). Although this reaction is not favored thermodynamically, it occurs to some extent under conditions in which monomer concentrations are low. Initiation by HO· leaves a terminal hydroxyl group. Bisulfate lowers the pH, often requiring the addition of a buffering agent.

$$^{-}O_3S{-}O\cdot + H_2O \longrightarrow HSO_4^{-} + HO\cdot$$

The half-life of persulfate is such that a 0.01 M solution of $(NH_4)_2S_2O_8$ at pH 10 produces 8.4×10^{12} radicals per mL s^{-1} at 50°C and 2.5×10^{15} radicals per mL s^{-1} at 90°C. For rapid polymerization at lower temperatures, radical production can be accelerated by reducing agents. For example, mixtures of ferrous, thiosulfate ($S_2O_3^{2-}$), and persulfate salts react faster than persulfate alone as a result of a sequence of oxidation and reduction reactions. Processes using this type of initiation are called *redox* emulsion *polymerization.*

Using redox systems, polymerization can be initiated at room temperature; the exothermic polymerization reaction warms the reaction mixture to the desired temperature (often, 50 to 80°C). Cooling is required to prevent overheating. Sometimes, redox initiation is used in the first stage of polymerization, and the latter stages are continued using thermal initiation. A variety of reducing agents have been used. Sodium formaldehyde sulfoxylate has been widely used. Since it generates formaldehyde, it has been largely replaced by ascorbic acid, isoascorbic acid, and sodium erythorbate. However, all three tend to give yellowing. A mixed reducing agent consisting of 2-hydroxy-2-sulfinatoacetic acid disodium salt, sodium sulfite, and 2-hydroxy-2-sulfanatoacetic acid disodium salt have been introduced. It is reported to be very effective as a reducing agent and not to give yellowing [4].

It is common to add a second, more lipophylic "chaser" initiator in the late stages of the semicontinuous process to facilitate conversion of monomer to high levels, preferably greater than 99%. An initiator such as *t*-butyl hydroperoxide, which is more soluble in polymer particles than in water, is more effective than ammonium persulfate in the late stages, when most of the unreacted monomer is dissolved in the polymer particles. Even when an auxiliary initiator is used, latexes still contain some unreacted monomer. *t*-Butyl hydroperoxide has also been recommended as the sole initiator together with sodium formaldehyde sulfoxylate instead of potassium persulfate; higher conversion of monomers is obtained and the problem of residual persulfate ion is eliminated [5].

9.1.1.3. Surfactants Surfactants are an important component in emulsion polymerizations. A variety of both anionic and nonionic surfactants is used. An example of an *anionic surfactant* is sodium lauryl sulfate (often incorrectly called sodium lauryl sulfonate):

$$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2OSO_3^-Na^+$$

Among *nonionic surfactants*, nonylphenylethoxylates have been popular. However, they now require eco-topological labeling in Europe. Reference [6] reviews the biodegradation of nonylphenylethoxylates to toxic products. Ethoxylates of C_{12-14} mixed primary and secondary aliphatic alcohols are effective surfactants, are biodegradable and do not require labeling. They are available with different lengths of the ethoxyl chain, since the most suitable chain length can vary depending on the monomers to be polymerized. For example, acrylic latexes can be started with a seed latex, made using sodium lauryl sulfate as the surfactant, followed by adding the nonionic surfactant with 40 ethoxyl groups [6]:

$$CH_3(CH_2)_{12\text{–}14}O(CH_2CH_2O)_{40}H$$

Surfactants generally have limited solubility in water. Above that solubility limit, the *critical micelle concentration* (CMC), nonpolar ends of surfactant molecules associate with each other in clusters called *micelles*. Micelles are submicroscopic aggregates typically containing 30 to 100 surfactant molecules, with the hydrophobic parts of each molecule oriented toward the center and the hydrophilic parts oriented outward in contact with water. The CMCs of different surfactants vary over a wide range from about 10^{-7} to 10^{-3} gL^{-1}. (See Ref. [7] for a review of surfactants.) Surfactants play a critical role in stabilizing the dispersion of polymer particles and preventing coagulation of the latex on standing. If the particles approach each other closely, van der Waals forces tend to hold them together and the particles *flocculate*. As noted in Section 3.5, flocculation of a dispersed phase system leads to changes in flow properties; the viscosity increases and the flow becomes shear thinning.

There are two general mechanisms by which stabilization of dispersions is affected; one is by *charge repulsion* in which the surfaces of the particles have an excess of one electrostatic charge, most commonly negative. For example, a latex can be stabilized by an anionic surfactant adsorbed on the surface of the polymer particles. The surfactant molecules orient with the long hydrophobic hydrocarbon tails in the polymer and the hydrophilic salt groups on the periphery associated with the water. As a result, the surface of the particles is covered with anions; each anion has an associated cation. This surface layer of cations, called a *Stern layer*, is somewhat rigid and behaves as if it were physically part of the particle. Its presence induces a second diffuse layer of anions to surround the particle, giving it a negatively charged *double layer*. When two particles approach each other, their diffuse, negatively charged layers repulse each other electrostatically. The stability of such dispersions can be affected by the addition of salts. The stability is particularly sensitive to the presence of multivalent ions with the opposite charge of the stabilizing charge; hence, deionized water is generally used.

The second general mechanism for stabilization is by repulsion resulting from the outer layers of the particle. Three terms are widely used in the literature to characterize this type of stabilization: steric, entropic, and osmotic repulsion, which may be described as follows. If the outer surface of the particles is hydrophilic, water is absorbed and swells the surface. If this swollen layer is thick enough, the particles are not able to approach each other closely enough to flocculate: hence the term *steric repulsion*.

If a nonionic surfactant, for example, a surfactant with a hydrophobic nonpolar segment and a relatively long chain of repeating ethylene ether groups as a hydrophilic segment, is adsorbed on the surface of a latex particle, the hydrophilic ether groups will be on the outer surface. The ether groups hydrogen bond with water, and more water is absorbed in the layer. The absorbed layer can exist in a very large number of conformations, and water molecules can move in and out of the layer. When two particles approach each other, the layers are compressed, leading to a reduction in the number of conformations that molecules in the layers can assume. As a result, the system becomes less random, corresponding to a reduction in entropy. Resistance to the reduction in entropy leads to repulsion: hence the term *entropic repulsion*.

Some authors prefer to focus on the reduction in the amount of water in the layer if compression occurs. There is a tendency for the water to return to equilibrium concentration in the layer; some consider this to be analogous to osmosis and call the result *osmotic repulsion*. Other authors prefer to avoid the controversy over terms by simply calling the repulsion *steric repulsion*, which includes both entropic and enthalpic factors. We favor *entropic repulsion*, because the principal factor is considered to be entropy. In industrial practice, stabilization of the dispersion of polymer particles in a latex is found to be most effective when charge repulsion and entropic repulsion are combined.

Surfactants are a major factor controlling the particle size and particle size distribution of latexes (Section 9.1.2). In general, anionic surfactants are used at levels of 0.5 to 2 wt% based on polymer; they cost less than nonionic surfactants, and they reduce particle size more efficiently on a weight basis. On the other hand, nonionic surfactants, used at levels of 2 to 6 wt%, are more effective in stabilizing the latex against coagulation during freeze–thaw cycling, make it less sensitive to coagulation by salts (especially, salts of polyvalent cations), less sensitive to changes in pH, and sometimes less likely to stabilize foam. In general terms, anionic surfactants stabilize primarily by charge repulsion, and nonionic surfactants stabilize primarily by entropic repulsion. The two surfactant types impart different rheological characteristics to the latex. Anionic surfactants lead to formation of essentially rigid particles. Such latexes can have low viscosity at relatively high solids. On the other hand, with nonionic surfactants, the thicker, swollen layers on the surface of entropically stabilized particles lead to lower polymer solids or higher viscosity at a given solids. The surface layer of an entropically stabilized latex particle is not rigid, so can be distorted when shear stress is applied, imparting shear thinning characteristics. Commonly, both anionic and nonionic surfactants are used in an emulsion polymerization recipe. More explicit generalizations about the use of surfactants in emulsion polymerization are imprudent because there are exceptions to almost any statement that can be made.

All surfactants impart some water sensitivity to films from latex paints. This sensitivity is reflected, for example, in the tendency of house paints to waterspot if rained on soon after application and in the somewhat limited corrosion resistance of most latex coatings on steel. Selection of surfactant combinations that minimize such shortcomings is an ongoing subject of research. So-called "soap-free" latexes have been developed in which emulsion polymerization is effected without the use of conventional surfactants. Such approaches may reduce the water sensitivity associated with surfactants. (Emulsifier-free latexes have been reviewed extensively in Ref. [8].) The most widely used approach is to incorporate a hydrophilic comonomer such as (meth)acrylic acid.

Another approach to the problem of water sensitivity is to use polymerizable surfactants [9]. For example, it has been shown that a surfactant composed of allyl alcohol, butylene oxide, ethylene oxide, and a sulfonate salt terminal group can be used to make vinyl acetate/butyl acrylate latexes [10]. The surfactant is reported to be completely incorporated into the latex during the polymerization. Presumably, a hydrogen is abstracted from the surfactant, yielding a free radical that initiates growth of another polymer chain, covalently bonding the surfactant to a polymer molecule. Alkenyl-functional surfactants in latex preparation have been reported to copolymerize with the monomers during polymerization, giving latexes having superior shear stability and freeze–thaw resistance. Paints prepared with such latexes overcome the problems (e.g., surfactant blooming) associated with the use of conventional surfactants [11].

Additional entropic stabilization can be achieved by including in the polymerization recipe a small amount of water-soluble polymer (sometimes called a *protective colloid*) that can form graft copolymers readily. A polymer commonly used for this purpose is poly(vinyl alcohol) (PVA), which has many abstractable hydrogens. During polymerization, initiator radical ions abstract a hydrogen from PVA to form a free radical on a PVA chain. A graft of the monomers being polymerized grows on the PVA chain; more than one such graft can grow on a single PVA molecule. As the graft chain becomes longer, it becomes hydrophobic and associates with other polymer molecules in particles, carrying the PVA part of the molecule to the particle surface. The PVA part associates with water to form an entropic stabilizing layer analogous to that formed by nonionic surfactants. Such layers can be thicker than the layer from adsorbed surfactant molecules and are effective in promoting stability. The water sensitivity of films may be reduced because less water-soluble surfactant is needed. Hydroxyethyl cellulose (HEC) can also be used. It has been shown that grafting occurs and that the resulting latex exhibits thixotropy and is more shear thinning than a latex prepared with no water-soluble polymer [12]. Although monomer–HEC grafting improves latex stability, it favors large particle size, broad particle size distribution, and low film clarity [13].

9.1.1.4. Water and Other Additives Variations in water quality can cause a variety of problems, especially when anionic surfactants are used. Therefore, deionized water is used in emulsion polymerization and is generally used in latex paint production. Water is somewhat soluble in some polymers and acts as a plasticizer, reducing film formation temperature. Other ingredients sometimes used in emulsion polymerization processes include buffers, which protect sensitive monomers from hydrolysis and sensitive surfactants from deactivation, and thickeners, which control viscosity.

9.1.2. Emulsion Polymerization Variables

Many quantitative theories for the mechanisms of emulsion polymerization have been proposed, but none has proven to be applicable to all systems, because of the wide range of variables involved. Various theories and mathematical models that have been proposed are reviewed concisely in Ref. [14], an example of current theoretical efforts is provided in Ref. [15], and controversial issues as of 2004 are reviewed in Ref. [16]. Since none of the theoretical models have proven to be generally applicable, the discussion here is limited to qualitative discussion of important considerations.

The monomers are emulsified in water with surfactant molecules oriented at the surface of the emulsion droplets, stabilizing the emulsion. There is also surfactant dissolved in the water and excess surfactant present in micelles. In most systems of interest in coatings, at least one of the monomers is somewhat soluble in water, so there are monomer molecules in solution as well as in the emulsion droplets. For example, the solubility of methyl methacrylate (MMA) and ethyl acrylate (EA) is approximately 1% in water. The initiator is also dissolved in the water.

There are three potential sites for initiation and initial propagation of polymerization: (1) in the monomer swollen micelles, (2) in the aqueous phase (called *homogeneous nucleation*), and (3) in the emulsion droplets. It is suggested that all three of these modes may occur in any given polymerization, but that the ratio of the three modes is system dependent [14]; monomer solubility in water, surfactant composition, and emulsion droplet size may be particularly important variables. Usually, initiation in the emulsion droplets is minimal. The number of particles predicted and the particle size are different in each of the three cases (or combinations of them). However, qualitatively, one can say that particle size decreases and number of particles increases as surfactant concentration increases.

When at least one of the monomers is somewhat soluble in water, it is commonly assumed that initiation occurs predominantly in the water phase. The initiating radical reacts with a monomer molecule, forming a new free radical that is soluble in water; these free radicals can react with additional dissolved monomer molecules to form oligomers with terminal free radicals. As the MW of the growing oligomer chain increases, its solubility in water decreases, and one of three things can happen: (1) the growing chain may enter a micelle, where propagation continues, as monomer molecules also enter the micelle; (2) surfactant from the solution may be adsorbed on the surface of the growing oligomer molecule; or (3) the growing chain can enter a monomer droplet. In any case, a surfactant-stabilized polymer particle containing a single free radical is formed. Such particles rapidly imbibe monomer, and propagation continues within the particles.

When all of the monomers are low in solubility, initiation in micelles may predominate. Again, the monomer in the micelle polymerizes rapidly to form a surfactant-stabilized polymer particle containing a single free radical.

Termination (by combination or disproportionation, as described in Section 2.2.1) occurs only after a second free radical enters a particle. After termination, the surfactant-stabilized polymer particle is temporarily inactive because it contains no free radicals. More monomer molecules then migrate into the inactive polymer particle. A third free radical (IMMMMM·) enters the monomer-swollen particle and initiates polymerization. Chain growth continues until a fourth free radical enters the particle and causes termination. Dissolution of monomer from the monomer droplets replenishes the monomer in solution. The process is repeated over and over, leading to formation of additional polymer molecules in the particle. (This model does not apply to cases in which the T_g of the polymer is higher than the polymerization temperature, but this is not usually the case.)

As the polymer particles grow, surface expansion requires additional surfactant. This need is satisfied by adsorption of more surfactant molecules from solution, which, in turn, is replenished by dissolution of micelles in which polymerization has not occurred. The result is the growth of particles that acquired a polymer molecule early on and disappearance of micelles that did not. Polymer particle growth continues until unreacted monomer or initiator is used up; enough initiator is used to assure high conversion of monomer. After the early stages of the process, much of the polymerization occurs within a fixed number of polymer particles. The number of particles per unit volume depends on the concentration of micelles in the early stages. If the concentration of micelles is high, the number of particles is high, and hence the particle size at the end of the polymerization is small. At the same surfactant concentration, a surfactant with a low CMC gives a smaller particle size latex than a surfactant with a higher CMC.

In the homogeneous nucleation mechanism, surfactant is absorbed on the surface of the growing oligomer chains. As the number of particles and their size increase, the amount of surfactant becomes too small to stabilize them, and particles coalesce to form fewer and larger particles until the surfactant concentration is just high enough to stabilize the particles.

The third mechanism, initiation in the droplets of monomer emulsion, is usually unfavorable. In most cases, the size of the droplets of monomer emulsion is relatively large and their surface area is small relative to the surface area of the more numerous micelles, so that the probability of an initiating radical or a growing oligomer radical entering an emulsion droplet is small. However, if the rate of agitation is very high and/or a high surfactant concentration is used, emulsion droplet size becomes smaller, and the probability of propagation in emulsion droplets increases. If a water-insoluble initiator were used in the early stages of polymerization, most of the polymerization would occur in the emulsion droplets, resulting in large, unstable particles. This method is the basis for a different polymerization method, called *suspension polymerization*.

The number of particles, and hence their particle size, are also affected by the rate of initiation (a function of the type of initiator, its concentration, and the temperature). The faster the rate of formation of initiating radicals, the larger the number and the smaller the size of the particles, everything else being equal.

Latexes are frequently made starting with a *seed latex*, a small particle size latex [17]. Monomer and initiator are added slowly, and the polymerization occurs primarily in the seed particles, resulting in a constant number of particles as polymerization proceeds. The seed latex can be prepared as the first step in a polymerization so that it contains 10 to 20% solids. Alternatively, it is common practice to produce a large batch of seed latex and subdivide it for subsequent use in many batches. The seed latex is diluted to 3 to 10% solids. Increasing the number of seed particles, with other factors being equal, yields a latex of smaller average particle size. This practice can improve batch-to-batch reproducibility and is particularly useful in sequential polymerizations.

The $\bar{M}_w$ obtained by both batch and semicontinuous processes is generally very high; an $\bar{M}_w$ over 1,000,000 is common. In many cases, there is a broad distribution of MWs. A high $\bar{M}_w$ results from several factors. First, during polymerization, the fraction of polymer particles containing more than one free radical at a given instant is low. As a result, the rate of termination reactions within the particle is reduced, and a single growing chain may consume most of the monomer present in the particle before it terminates. Second, the viscosity inside the particles is very high, reducing the mobility of the polymer chains. It is then easier for more mobile monomer molecules to diffuse and to add to the growing chain and increase the MW than for two less mobile growing chains to react with each other and terminate growth. Third, hydrogen atoms on polymer chains can be abstracted, leading to chain transfer to polymer and formation of branched-chain molecules. The environment within the polymer particle favors chain transfer to polymer because the concentration of free radicals is low (often, one per particle) while the concentration of polymer approaches 100%. Chain transfer to polymer increases $\bar{M}_w$ and $\bar{M}_w/\bar{M}_n$ because it is statistically probable that when the growth of short chains is ended by chain transfer, the new chain will grow as a branch on a polymer molecule that already has a high MW. Sometimes a chain transfer agent is added to the monomer mixture deliberately to reduce the MW, and sometimes a very small amount of difunctional monomer is added to increase it.

In a study comparing batch and semicontinuous homopolymerization and copolymerization of vinyl acetate and butyl acrylate, $\bar{M}_w/\bar{M}_n$ for batch homopolymers and copolymers was broad, ranging from 15 to 21; and the semicontinuous process gave even broader distributions, ranging from 9 to 175 [18]. The semicontinuous process commonly afforded bimodal distributions with considerable amounts of relatively low MW polymer. Semicontinuous poly(vinyl acetate) homopolymer had the broadest distribution; GPC indicated substantial fractions of material with MW below 660 and above 1,700,000.

Particle size distribution is an important variable in the formulation of latex paints. Particle size distribution is commonly measured by light scattering and can also be measured by hydrodynamic chromatography, ultracentrifuge, or transmission electron microscopy. It may be expressed as number average diameter ($\bar{D}_n$) and volume average diameter ($\bar{D}_v$). The ratio $\bar{D}_v/\bar{D}_n$ is a convenient index of particle size distribution. A broad or bipolar distribution is often advantageous because the packing factor is affected by particle size distribution. The volume fraction of latex particles that can be present at a standard viscosity is highest with broad particle size distribution.

The particle size of a latex is determined by the number of particles relative to the amount of monomer. The number of particles is governed primarily by the amount and type of surfactant(s) and initiator(s). Anionic surfactants tend to produce more particles than do nonionic surfactants when used on an equal weight basis and hence, lead to smaller particles. The specific anionic surfactant used affects the particle size; for example, use of $NP(OCH_2CH_2)_{20}OSO_3^-\ NH_4^+$ (NP stands for the nonpolar part of the molecule) in making an acrylic latex gave a particle diameter of 190 nm, whereas use of the less hydrophilic $NP(OCH_2CH_2)_9OSO_3^-\ NH_4^+$ gave a diameter of 100 nm [19]. In general, particle size distribution is broader with anionic surfactants and more nearly approaches a monodisperse particle size with nonionic surfactants. The effect of changing the ratio of nonionic surfactant (nonylphenol ethoxylate with 40 mol of ethylene oxide) to anionic surfactant (sodium dodecylbenzenesulfonate) on particle size and particle size distribution with a constant amount of total surfactant in the polymerization of a vinyl acetate/dibutyl maleate copolymer has been studied [18]. The lowest ratio gave the smallest particle size and the broadest distribution of particle size.

Particle size is also affected by agitation intensity and turbulence during polymerization. High turbulence leads to larger particle size, thus influencing rheological properties. (See Ref. [20] for a study of the relationship of agitation during polymerization of styrene–acrylic latexes and particle size.) The effect increases the problem of scaling up of laboratory synthesis to production requiring designing lab equipment to approximate the agitation to be encountered in plant reactors.

Emulsion polymerization usually produces latexes with essentially spherical particles. During the 1980s, latexes were commercialized in which groups of a few particles were fused together into nonspherical lobed particles [21]. At equal concentration, the viscosity of these latexes was higher than the viscosity of comparable latexes with spherical particles, since the packing factor is smaller than for a spherical particle latex. Paints formulated with a lobed latex are shear thinning and give a higher high shear viscosity at the same low shear viscosity than do conventional latexes. The higher viscosity at shear rates experienced during application leads to thicker films with low levels of thickener and hence, lower cost. Adhesion to chalky surfaces is said to be improved over that of paints formulated with conventional latexes.

9.1.3. Sequential Polymerization

When latexes are prepared by semicontinuous polymerization under monomer-starved conditions, the composition of the monomer feed can be changed during the course of the polymerization. Depending on a number of variables, the resulting latex particles can have a variety of morphologies. In some cases, latexes having *core–shell morphology* can be made by shifting from the initial monomer feed composition to a different feed partway through the process. Many such core–shell latexes display two T_gs after coalescence. In some cases the composition of the polymer in the center of each particle (the *core*) reflects the initial monomer feed composition, and the composition near the surface (the *shell*) reflects the second monomer feed composition. In other cases, an *inverse core–shell morphology* can be obtained, with the composition of the core polymer being that of the second monomer feed and the shell polymer derived from the initial monomer feed. In yet other cases, a homogeneous composition is obtained despite a change in monomer feed composition. In still other cases, it is possible to make a gradient morphology by changing the monomer feed composition continually during the polymerization. There is an extensive literature on sequential polymerization. (The literature applicable to latexes of interest in coatings and discussion of the variables involved is reviewed briefly in Ref. [22].)

Several factors affect the morphology of particles obtained in sequential polymerization. Formation of outer layers having the lowest interfacial tension with the water phase is favored; thus, when different monomer compositions are fed, the one containing the most polar monomers is likely to end up as the shell, regardless of its place in the sequence. Morphology can be affected by the amount of free monomer present during the polymerization, since free monomer acts as a plasticizer; hence, formation of core–shell morphology tends to be favored under highly monomer-starved conditions. The presence of di- or trifunctional cross-linking monomers in at least one of the monomer combinations increases the probability of phase separated morphology. In latexes designed for coatings, generally only limited amounts of polyfunctional monomers can be used because of the need for coalescence for good film formation. But it is a common practice to use a low level of cross-linking monomer in the first composition to increase the likelihood that it will remain in the core. Examples of applications of sequential polymerization are given in Section 9.2.

9.2. ACRYLIC LATEXES

Acrylic latexes are widely used for exterior paints because of their resistance to photodegradation. They are also more resistant to hydrolysis and saponification than are vinyl acetate latexes. These properties are critical for exterior paints; they also make acrylic latex paints useful for alkaline substrates such as masonry and galvanized metal and for applications in which there is exposure to high humidity. Acrylic and styrene–acrylic latexes are being used increasingly for industrial maintenance coatings. Acrylic latexes are finding increasing interest for kitchen cabinet finishes and for OEM automotive applications. For example, base coats based partially on latexes are being developed for OEM automotive waterborne base coats. Hybrid acrylate–urethane dispersions have become increasingly important (Section 12.7.2).

A critical decision in designing a latex is monomer selection. An important consideration is to select a monomer combination that produces a copolymer with the appropriate T_g. Monomer cost is also important; the paint business is highly price competitive. For lower priced paints, adequate film properties must be attained using low cost monomers. The T_g must be low enough to permit coalescence of the latex at the lowest anticipated application temperature, yet high enough to assure adequate film hardness and toughness. T_g in the vicinity of 5 to 15°C is common for exterior house paints, which might be applied at temperatures as low as 2°C. The *minimum film forming temperature* (MFFT) (Section 2.3.3) of latexes is related to T_g but is influenced by other factors, such as particle size, phase separation within the latex particles, and the plasticizing effects of water and surfactants. The MFFT tends to be somewhat lower than T_g. A T_g and MFFT in the desired range are usually attained by copolymerizing monomers whose homopolymers T_g values are much higher and much lower than the target values.

As a high T_g comonomer, MMA imparts excellent exterior durability and hydrolytic stability at moderate cost. Styrene is often substituted partly or completely for MMA because it costs less and provides a similar T_g effect. Such products are sometimes called styrene–acrylic latexes but usually, simply acrylic latexes. Styrene imparts excellent hydrolytic stability, but its effect on overall exterior durability is not clear cut. Styrene homopolymer degrades relatively rapidly outdoors. However, in a copolymer, some MMA can be replaced with styrene without decreasing exterior durability substantially. The amount of styrene that can be substituted apparently varies, depending on the other comonomers and probably on other variables, such as process conditions. For example, processes that would tend to produce blocks of homopolystyrene are suspect. It is safest to test each composition thoroughly outdoors before use. It is interesting that styrene acrylics are said to be used more in northern Europe than in southern Europe, where weather exposure is more severe. Other properties may also be affected. For example, it cannot be assumed that the mechanical properties of the copolymer will be equal when styrene is substituted for MMA, even though its T_g is about the same. Polystyrene has a significantly higher brittle–ductile transition temperature than poly(MMA), even though it has a slightly lower T_g (Section 4.2).

Acrylic esters are generally used as the low T_g monomer(s), the choice of which is affected by cost and durability considerations. If the cost of the common acrylic esters is intermediate between that of MMA and of styrene, it is more economical to use ethyl acrylate (EA; homopolymer $T_g = -24$°C) than butyl acrylate (BA; homopolymer $T_g = -54$°C) in styrene-free latexes in order to get the highest possible proportion of EA in the composition. However, with styrene–acrylic latexes, BA may be more economical when styrene is less expensive than EA or BA. Presumably, the different acrylic esters impart different film properties at a given T_g, but published data are inadequate to evaluate the effects. Recent decades have seen an industry trend toward use of BA in preference to EA [23]. While published data are scarce, one can speculate that BA has given better durability in proprietary tests. One can also speculate that it imparts better resistance to hydrolysis.

An example of a laboratory semicontinuous batch process for preparation of a 40 : 59 : 1 MMA/EA/MAA copolymer latex is provided in Table 9.1. Many more examples are provided in Ref. [24], and very detailed directions for laboratory-scale seeded emulsion polymerization with a more contemporary composition are given in Ref. [2]. Note from Table 9.1 that the measured MFFT of the latex at 9°C is somewhat lower than the T_g of 17°C estimated by the Fox equation for a 40 : 60 MMA/EA copolymer. Also, note that changing to a 50 : 50 MMA/EA ratio increases MFFT to 21°C, while the Fox equation predicts a T_g value of 28°C. These figures give a general picture for how T_g and MFFT relate to composition.

TABLE 9.1. Laboratory Procedure for Preparation of a MMA/EA/MAA Copolymer Latex

Materials

1 L	Deionized water
96 g	Triton X-200 (sodium salt of an alkylaryl polyether sulfate ester) (Union Carbide Co.)
320 g	Methyl methacrylate (10 ppm MEHQ stabilizer) (MEHQ is the monomethylether of hydroquinone)
480 g	Ethyl acrylate (15 ppm MEHQ stabilizer)
8 g	Methacrylic acid (100 ppm MEHQ stabilizer)
1.6 g	Ammonium persulfate

Procedure

Prepare an emulsion of all reactants in 800 mL of water. Place 200 mL of the emulsion and 200 mL of water in a 3-L flask fitted with an inert gas inlet tube, a thermometer, a stirrer, an addition funnel, and a reflux condenser. Heat in a 92°C water bath while stirring until the internal temperature reaches 82°C. The mixture will begin to reflux, and its temperature will rise to about 90°C within a few minutes, indicating rapid polymerization. When refluxing subsides, add the remaining emulsion continuously over a period of 1.5 hours. Heat to maintain refluxing; the internal temperature will be 88 to 94°C. After monomer addition is complete, heat to 97°C to complete conversion of the monomer. Cool and strain.

Properties

NVW 42.9 (calculated 43.1); pH 2.7; viscosity (Brookfield), 11.5 mPa·s; MFFT 9°C; film hardness (Tukon), 1.2 KHN. A similarly prepared 50 : 50 MMA/EA copolymer latex (no MAA), had similar properties, except that MFFT was 21°C and film hardness was 6.2 KHN.

Source: Ref. [43].

Commercial suppliers of latexes provide little information as to the composition of the latexes they offer. Although a simple acrylic latex made as described in Table 9.1 could be used to make a house paint, it would not be competitive. Commercial production involves many process nuances that are held confidential by the latex producing companies. It is difficult to replicate commercial latexes, even though the monomer composition can be analyzed precisely.

Acrylic acid (AA), or the somewhat less water-soluble methacrylic acid (MAA), is commonly used in preparation of acrylic latexes, usually on the order of 1 to 2 wt% of the monomer charge. The carboxyl functionality incorporated with these monomers enhances the mechanical stability of wet latex paint, reducing the amount of surfactant needed. The effects of acid monomers on stability and viscosity are maximized when they are incorporated in the last part of the monomer feed and the polymerization medium is acidic [1,25]. The viscosity of a latex made in this way depends on pH. As ammonia is added, there is little change in viscosity until the pH reaches about 7. Above pH 7, viscosity increases steeply until pH reaches 9 or 10; at still higher pH levels, viscosity decreases. The pH of acrylic latex paints is usually adjusted to about 9, where there is a substantial viscosity effect: Not only is the viscosity high, the paint exhibits shear thinning, which is sometimes a desirable application characteristic (Chapter 31).

Hoy describes a latex that shows this effect [1]; it is a MMA/EA/BA/AA (40 : 52 : 6 : 2 by weight) copolymer, in which the acrylic acid was added late in the process. The T_g of this copolymer was 15°C. Neutralization with ammonia to pH 9 caused the surface layer of the particles to expand, so the diameter of the particles was about 1.8 times that at pH 7. The corresponding increase in volume was almost sixfold. The expansion resulted from the association of water with the highly polar salt groups in the polymer near the particle surface. The presence of the expanded layer at pH 9 increased the viscosity at low shear rates. However, because this layer could be distorted by shear forces, the viscosity decrease at high shear rates was less marked.

In the same paper, Hoy describes the effects of using sequential polymerization during semicontinuous batch polymerization [1]. In one experiment, an MMA/BA ratio of 40 : 60 was used, with 2 wt% of AA added late in the process. When the 40 : 60 ratio was maintained throughout monomer addition, the product, called a *uniform feed latex*, had a T_g of 20°C. A second *staged feed* latex of the same overall composition was made by a process designed to yield core–shell particles [1] (Section 9.1.3). In the first half of the monomer addition, the MMA/BA ratio was 70 : 30, and in the second half, it was 10 : 90. The resulting latex showed two T_gs, one at 60°C and the other at -10°C. Because the shell of this latex has a low T_g, its MFFT is substantially lower than that of the uniform feed latex. However, coalesced films are cloudy. Apparently the high T_g cores remain uncoalesced; the composition of the cores and the shells is sufficiently different that the polymers are not miscible with one another. Because the refractive index of the two polymers is different, light passing through the film is scattered, making the film cloudy. Since the T_g of the continuous phase is low, the blocking resistance of a film of the staged feed latex is inferior to a film of the uniform feed latex.

Hoy describes a third latex with the same monomer composition made by a process called *linear power feed addition*, using the apparatus sketched in Figure 9.2. In this process there are two stirred tanks for monomer mixtures. The near tank was loaded with half of the monomer charge at an MMA/BA ratio of 70 : 30, and the far tank was loaded with the other half at a 10 : 90 ratio. During polymerization, monomer was pumped from the near tank into the reactor in the usual way. At the same time, monomer was being pumped at the same rate from the far tank to the near tank. Again, 2 wt% of AA was added in the late stage of the process. In this procedure, the monomer feed starts at 70 : 30 MMA/BA and ends at 10 : 90, but changes continuously through the process. Each latex particle presumably contains high T_g polymer at its center and low T_g polymer (with COOH groups) near its surface. It differs from the usual core–shell latex in that there is a linear gradient of

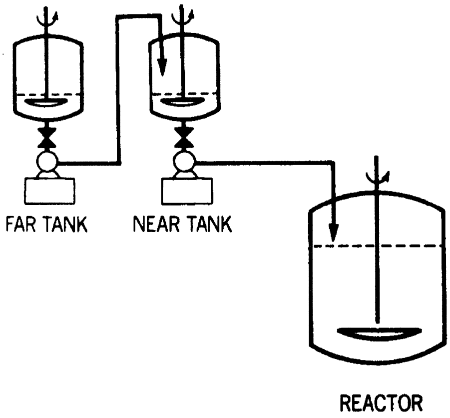


Figure 9.2. Apparatus for semicontinuous latex polymerization using a linear power feed addition. (Adapted from Ref. [1], with permission.)

composition and T_g from the center to the surface. Films cast from this latex have equal clarity and the same T_g, about 20°C, as those cast from the uniform feed latex. However, the glass transition is much broader for the linear power feed latex than for the uniform feed latex. The linear power feed latex has a lower MFFT than that of the uniform feed latex and also has a higher blocking resistance temperature.

Exterior house paints for large surfaces are usually formulated at low gloss in the United States; the formulations are heavily pigmented. Block resistance requirements are modest, and the pigment helps improve this property; T_g values of about 5 to 15°C are adequate. Latex paint films are more permeable to water than films from oil or alkyd paints, an advantage because it reduces blistering of paints applied to wood surfaces, but it is a disadvantage for coatings applied over metal.

Applications such as gloss trim and door paints, as well as interior trim paints (for kitchen cabinets, windowsills, etc.) have different requirements; to be glossy, they must be formulated at lower pigment levels, yet block resistance is required. This situation presents a challenge to designers of latexes. The problems have been at least partly overcome, as described by Mercurio [26]. A latex T_g of about 55°C is reported to be required to achieve adequate block resistance. Coalescence of acrylic latexes having this T_g can be attained by using a small particle size latex with substantial amounts of carefully selected coalescing solvent(s). The coalescing solvent increases VOC to near the current regulatory limit of 250 g of VOCs per liter of paint as applied, excluding water. Commercial products based on these principles are available; details of how they are made are proprietary.

Although the VOC of latex paints is usually lower than that of solventborne paints, there is increasing pressure to reduce VOC further. Reducing the amount of coalescing solvent required is the most evident approach to this end. Sequencing the composition of the monomer feed during polymerization so that the last part of the monomer feed has a higher fraction of monomers, which impart a low T_g, as in the power feed approach discussed previously, permits reduction of coalescing solvent (Section 9.1.3). Addition of acrylic acid in the later part of the comonomer feed may permit reduction of coalescing solvent. Water associates with the neutralized carboxylic acid salt, plasticizing the surface of the particles, promoting coalescence, and reducing the need for coalescing solvent. Another method is to use cross-linkable latexes having a lower T_g; cross-linking after film formation increases block resistance to offset the effect of the lower T_g (Section 9.4). It may also be possible to design a coalescing solvent that would cross-link after film formation. Another approach for eliminating the need for coalescing solvent is to use blends of high and low T_g latexes [27,28]. When a film of such a blend dries, the high T_g latex does not coalesce, but is dispersed in the continuous phase from the low T_g polymer. The hard particles act to reinforce the low T_g polymer film increasing the modulus of the film so that its block resistance is superior to that of a film using only low T_g latex. It is critical that the ratio of the two latexes be such that there is enough low T_g latex so that there is enough to enclose the high T_g latex particles completely. It would be interesting to compare the results with those of a film from the low T_g latex with a volume content of pigment equal to that of the high T_g latex.

Acrylated castor oil has been used as a comonomer, resulting in latexes that are formulated into semigloss paints with better block resistance while still permitting low-temperature film formation. The latexes have the further advantage that coalescing solvents are not needed [29].

Another approach to eliminating VOC is to make nano polymer/nano clay composite latexes. The latexes are made with relatively low T_g acrylic monomers polymerized with clay dispersed in the water in which the emulsion polymerization is carried out. Films prepared from the latex have unusual toughness without compromising film formation. They also exhibit low tack and dirt pickup in zero VOC paints [30]. Polymerization of BA, MMA, and MAA, with sodium montmorillonite dispersed in the water phase has been disclosed [31]. The latex is reported to give coatings with improved block, print, and dirt pickup resistance, as well as enhanced barrier properties.

For latexes to be used over metal, it is desirable to have low moisture vapor permeability. Acrylic latexes give films with quite high permeability. One approach to reducing water permeability is to use vinylidene chloride as a comonomer. Reference [32] provides details of procedures for the copolymerization and characterizations of several vinylidene chloride/acrylate latexes. Since the reactivities of vinylidene chloride and acrylic ester monomers are quite different, monomer-starved polymerization conditions are used to achieve reasonably uniform compositions. Although the moisture vapor permeability is greatly reduced, stabilizing the chlorinated copolymer against photodegradation may be difficult.

A different use for an acrylic emulsion polymerization is for the preparation of microgel particles. For example, acrylic latexes containing some cross-links by using a small fraction of divinylbenzene as a comonomer were prepared by emulsion polymerization using a water-soluble azo initiator, 4,4′-azobis(cyanovaleric acid) [33]. The latex polymer was isolated as a powder by precipitating with an equal volume of isopropyl alcohol, washing with a 4 : 1 methyl alcohol/water ratio, and drying under vacuum at 50°C. The resultant powder readily dispersed in aliphatic hydrocarbon to yield a dispersion of an acrylic microgel. Among other applications, acrylic microgels are used as additives to control sagging of high-solids coatings (Section 24.3).

9.3. VINYL ESTER LATEXES

Vinyl acetate (VAc) is less expensive than (meth)acrylic ester monomers. However, VAc latexes are inferior to acrylic latexes in both photochemical stability and resistance to hydrolysis. When an acetate group on a PVAc chain hydrolyzes, the liberated acetic acid catalyzes hydrolysis of more acetate groups, and the hydroxyl group may exert a neighboring group (anchimeric) effect that promotes hydrolysis of adjacent acetate groups. Hence, PVAc latexes find their principal use in interior coatings that do not have to withstand high humidity exposure or frequent wetting. One such use, flat wall paints, is the largest volume type of paint sold in the U.S. market. The T_g of PVAc homopolymer is 29°C, too high for film formation under ambient conditions. Thus, one must either formulate PVAc with a plasticizer or copolymerize VAc with a monomer that reduces T_g. A widely used comonomer is *n*-butyl acrylate (BA), although other comonomers, such as 2-ethylhexyl acrylate and di-*n*-butyl maleate, have been used. Longer chain vinyl esters are also being used as comonomers; the resulting latexes have superior hydrolytic stability and exterior durability. Use of diesters of 3-butene-1,2-diol to reduce the T_g of vinyl acetate copolymers has been reported. Best hydrolytic resistance was obtained using the di(2-ethyl)hexanoate ester [34].

Copolymerization of VAc with BA poses potential problems because of reactivity ratios; specifically, the rate of reaction of a free radical on a terminal BA group with another molecule of BA is greater than its rate of reaction with VAc; furthermore, the rate of reaction of a free radical on a terminal VAc group is much greater with BA than with VAc. Thus, a 50 : 50 mixture of BA and VAc will produce a copolymer very rich in BA at the outset of batch polymerization and very rich in VAc in the late stages. This problem is overcome by a semicontinuous batch process, wherein the monomer mixture is added at a rate equal to the polymerization rate. A steady state is reached in which the concentration of unreacted VAc is low but the concentration of BA is even lower. Under these monomer-starved conditions, a relatively uniform copolymer forms with a composition similar to the ratio of monomers being fed. Such copolymers are made commercially on a large scale. An extensive study of the copolymerization of VAc with BA by batch and semicontinuous batch processes, as well as characterization of the copolymers, has been reported [18,35] and is discussed in part in Section 9.1. Since the reactions rates are relatively low, the rate of monomer addition must be quite slow. If the initial charge is high in the least reactive monomer, the addition can be made faster while still producing reasonably uniform copolymerization. Mathematical simulations can predict the effects of different addition modes [36].

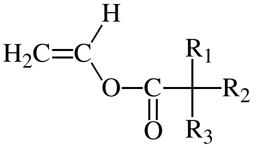
Vinyl acetate is more soluble in water than acrylic esters, as are the initial oligomeric free radicals formed from VAc than those from oligomeric radicals of acrylic esters at equal chain length. This factor increases the probability of termination of VAc-rich oligomers, while still in aqueous solution, and leads to low MW fractions. On the other hand, chain transfer to polymer is more facile with polyvinyl acetate, leading to high MW and broad MW distribution. The high water solubility of VAc also increases the need for effective initiator systems to remove residual monomer. Vinyl acetate latexes, including the effect of different initiator combinations, are reviewed in Ref. [37].

An essential component of the recipe for polymerization of VAc is a buffer, such as sodium bicarbonate, to maintain the pH near 7. A buffer is essential because VAc monomer hydrolyzes at appreciable rates under either acidic or basic conditions. The hydrolysis is irreversible because the products are acetaldehyde and acetic acid. At pH less than 7, hydrolysis is autocatalytic because acetic acid catalyzes further reaction. Furthermore, acetaldehyde is oxidized by persulfate, which consumes initiator and generates still more acetic acid to catalyze hydrolysis.

$$CH_3CO_2CH{=}CH_2 + H_2O \longrightarrow CH_3CO_2H + CH_3CHO$$

Copolymer latexes of VAc and (meth)acrylic monomers have been designed for dual-purpose use in both exterior and interior flat paints. The objective is to save cost in two ways: lower raw material cost for exterior paints and lower inventory and storage costs by basing all production on a single resin. This approach has been successful commercially, although the latexes undoubtedly represent a compromise between the best resins for exterior and interior use. The amount of vinyl acetate in an acrylic latex can be increased by sequential polymerization to form inverse core–shell latexes, lowering the cost with minimal loss of properties [38]. For example, a seed latex of MMA/BA/MAA made with persulfate initiator was further reacted with vinyl acetate using azobisisobutyrylnitrile as initiator. Since the initial polymer has polar acrylate salt groups, the acrylate polymer becomes the shell, with a polyvinyl acetate core.

Copolymer latexes of the vinyl ester of a C_{10} branched acid (vinyl neo-decanoate, Vinyl Versatate) with VAc are used in both interior and exterior paints. These copolymers have better hydrolytic stability than conventional vinyl acetate copolymers [39]. A combination of ethoxylated undecyl alcohol, a cellulose ether, and sodium vinyl sulfonate can be used as a surfactant/protective colloid in preparing the latexes. A study has been published covering the effect of changes in chain length of the ethylene oxide units on the properties of latexes and paints. Increasing the degree of ethoxylation gave smaller-particle size latex particles and higher viscosity. In flat paints, optimum properties are obtained with 2 to 3% emulsifier concentration and 17 to 28 degrees of ethoxylation. In gloss and semigloss paints, the gloss improves with increased emulsifier content up to about 4%, where it levels off, and as the degree of ethoxylation increases to 17. Above 4% concentration and 17 ethoxyl units, blocking increases drastically. Similar results were obtained with vinyl acetate–ethylene latexes [40].



Vinyl neo-decanoate

(R_1, R_2, and R_3 are alkyl groups totaling C_8H_{19})

The use of a variety of vinyl esters, including vinyl pivalate and vinyl 2-ethylhexanoate, in latexes is discussed in Ref. [41]. Such monomers yield polymers that are more hydrophobic than vinyl acetate homopolymers and that have superior hydrolytic stability and scrub resistance. The advantages of using vinyl neo-decanoate in both vinyl acetate and acrylic copolymers is reported in Ref. [42].

Emulsion copolymerization of VAc with vinyl neo-decanoate can be problematic because of the very low water solubility of the latter. Satisfactory processes have been developed, and the mechanism of copolymerization is reasonably well understood [43].

Copolymers of ethylene and VAc are made by emulsion polymerization under high pressure. The copolymers are often called *VAE latexes*. Their use, especially in interior wall paints, has been increasing rapidly; consumption of the latexes (on a solids basis) in 2003 was 27,000 metric tons in the United States and 20,000 metric tons in Europe. The number average MW of VAc/ethylene is lower than that of most emulsion polymers. In one series of varying MW, a latex having $\bar{M}_n$ value of 89,700 showed improved scrub resistance. Scrub resistance increased further with still higher $\bar{M}_n$, but films cracked with touch-up at 40°F. Water permeability and scrub resistance are superior to VAc/BA latexes. Lower-VOC paints can be prepared and the odor is much lower than with VAc/BA latexes [44]. Ethylene is not only a more effective monomer than butyl acrylate for reducing the T_g of VAc polymers, and it appears to provide more effective plasticization. Paints made with VAc/ethylene latexes require less coalescing solvent and are said to show better touch-up properties at low and room temperatures, as well as higher scrub resistance [45]. Copolymer latexes with a hydrophobic comonomer give paints with enhanced water, block, and scrub resistance [46]. An example of such a terpolymer latex is vinyl acetate/ethylene/vinyl neo-decanoate [47].

9.4. THERMOSETTING LATEXES

Although the majority of latexes are thermoplastic polymer latexes, there are applications for thermosetting latexes as well, as reviewed in Refs. [48] and [49]. The reviews emphasize experimental results related to the importance of the rate of interdiffusion and cross-linking in films of thermosetting latexes. To develop good properties, significant interdiffusion must occur before extensive cross-linking. Film properties depend on the relative rate of interdiffusion between polymer particles and the rate of cross-linking. If the rate of cross-linking is fast in comparison to the rate of diffusion, cross-linking within the particles will occur and interfere with good film formation. If the rate of cross-linking is too slow, achievement of desirable film properties may take excessive time. A balance between the two is needed. In some cases, the functional groups on a latex particle are on the particle surface and an external cross-linker serves to cross-link the particles together. In other cases, the functional groups are on the same polymer, and interdiffusion is required to bind the particles together.

The rate of interdiffusion is controlled by $T - T_g$ and the chain length of the latex. Thus, thermosetting latexes are designed with lower MW, which both reduces T_g and shortens chain length. Straight chains diffuse more rapidly than branched chains. A copolymer of isobutoxymethylacrylamide (IBMAA) with MMA and BA having 2% IBMAA and $\bar{M}_w = 200{,}000$ was studied. The MW was controlled with dodecyl mercaptan chain transfer agent. IBMAA groups react with each other to form $\text{—CO—NH—CH}_2\text{—O—CH}_2\text{—NH—CO—}$ cross-links, a reaction catalyzed with acid. It was found that interdiffusion increases more rapidly with temperature than does cross-linking. At 80°C with 0.5% pTSA, the cross-linking occurred in 40 min. Similarly, copolymers of BA/IBMAA/HEA/MAA showed good film formation. In addition to self cross-linking, IBMAA reacts with the OH groups of HEA; the COOH group of MAA serves as a catalyst [48].

In many cases, two package coatings are required, but they are useful only for industrial applications; a few stable systems have been developed that can be used for architectural paints. Cross-linked films have better mechanical properties and increased resistance to solvents. In general, a lower T_g latex can be used in coatings, which permits coalescence without addition of a coalescing solvent and/or at lower film formation temperatures.

For two package coatings, a variety of cross-linkers for hydroxy-functional and carboxylic acid–functional polymers can be used. Hydroxy-functional polymers are readily prepared by using hydroxyethyl (meth)acrylate as a comonomer. The resulting latexes can be formulated with urea–formaldehyde (UF) or melamine–formaldehyde (MF) resins as cross-linkers. UF resins tend to evolve high levels of formaldehyde from hydrolysis; MF resins evolve less formaldehyde. MF resins are soluble in BA/HEMA/MAA latex polymers, so that they act as plasticizers to promote interdiffusion [48]. As temperature increases, interdiffusion rate increase faster than the rate of cross-linking until many of the potential reactions have occurred, but at some point the cross-link density (XLD) reaches a point that interdiffusion ceases. The rate of cross-linking can be increased by the addition of a catalyst such as pTSA. Although this permits shorter cure times, the pot life of the coating decreases and the residual acid in the final film can lead to reduced stability of the films to hydrolysis since the catalyst also catalyzes hydrolysis.

An approach to assuring distribution of the MF resin through the polymer particles is to dissolve the MF resin in the monomer mixture before polymerization [50]. Premature cross-linking is minimized by controlling pH at above 5. With addition of catalyst, films cross-link; the pot life of the resin after adding catalyst is 1 to 2 days.

The following examples in this section illustrate specific applications and/or specific cross-linkable systems.

Traffic paints must dry very rapidly so that vehicles can be driven over them soon after application. Three-package traffic marking paints have been patented. The first component is a white (or yellow) pigmented carboxylic acid functional latex paint, the second paint is pigmented with $CaCO_3$, the third component is a polyamine. The polyamine is a copolymer of dimethylaminoethyl methacrylate and MAA, dissolved in aqueous methanol and neutralized with NH_4OH. The packages are mixed and applied; as the water and ammonia evaporate, the COOH functional latex and the polyamine rapidly form a cross-linked salt [51].

Acetoacetate-functional (Section 17.6) latexes can be cross-linked with polyamines, but pot life is short before coalescence is adversely affected [52]. A BA/MMA/MAA/acetoacetoxyethyl methacrylate latex made using dodecyl mercaptan for MW control is used in traffic paint with aminoethylaminopropyltrimethoxysilane and a dimethylaminoethyl methacrylate/AA latex, neutralized with ammonia. Pot life is said to be adequate [53].

Carbodiimides (Section 17.8) can be used as cross-linkers [54]. A water-emulsifiable polycarbodiimide that is terminated with a mixture of the methyl ether of diethylene glycol and the methyl ether of a polyethylene glycol is used as a cross-linker for COOH-functional latexes. The design of the latex markedly affected properties. The best properties were obtained with a BA/MMA/MAA latex that was prepared with the core containing 2% MAA and the shell 1% MAA [55].

Another system studied used two latexes with different functional groups. One latex was a copolymer of *t*-butylcarbodiimidoethyl methacrylate and 2-ethylhexyl methacrylate (EHMA), the other was a copolymer of MA, EHMA, and MAA. The carbodiimide group and COOH group react to form *N*-acylurea groups. This graft copolymer is said to increase the solubility of one latex in the other. The reaction occurs at ambient temperature, but improved properties were obtained at 60°C, because interdiffusion increases more rapidly with temperature than the cross-linking reaction [48].

Polyfunctional aziridines (Section 17.7) such as the propylene imine addition product with pentaerythritol triacrylate serve as cross-linkers for carboxylic acid-functional latexes [56]. Pot lives of 48 to 72 hours are reported.

Carboxylic acid–functional latexes can also be cross-linked with epoxysilanes, such as β-(3,4-epoxycyclohexyl)ethyltriethoxysilane [57]. Addition of an emulsion of this cross-linker to the latex increased solvent resistance and hardness, especially when baked 10 minutes at 116°C. Latexes with a high COOH content and equivalent amounts of epoxysilane showed the largest improvements. Package stability is reported to be at least one year. Cross-linking can be catalyzed: for example, using 1-(2-trimethylsilyl) propyl)-1*H*-imidazole. *m*-Isopropenyl-α,α-dimethylbenzyl isocyanate (TMI) (Section 12.3.2) reacts slowly with water and can be used to make thermosetting latexes [58].

Acrylic latexes with surface methacrylate groups are prepared by treating a carboxylic acid–functional acrylic latex with an emulsion of cyclohexylcarbodiimidoethyl methacrylate. The carbodiimide group reacts with COOH groups on the surfaces of latex particles to give surface methacrylate ester groups. Films prepared with the latex (to which *t*-butyl peroxybenzoate was added) were cured at 160°C for 30 minutes, or by UV after adding a photoinitiator [59].

There have been fewer reports of thermosetting latexes that cross-link at room temperature and are storage stable for the long times required for architectural paints. One approach is to use a cross-linking mechanism based on autoxidation. A latex with allylic substitution cross-links on exposure to air after application [60,61]. Hybrid alkyd–acrylic latexes have been prepared by dissolving an oxidizing alkyd (Section 15.1) in the monomers used in emulsion polymerization, yielding a latex with alkyd grafted on the acrylic backbone [62–64]. Stable thermosetting latexes can be prepared using triisobutoxysilylpropyl methacrylate as a comonomer [57]. In contrast to the ethoxy derivative, the isobutoxy derivative has sufficient hydrolytic stability to permit emulsion polymerization at 80 to 90°C without extensive reaction with water. The resulting latex has a package stability of over a year, yet cross-links after application in a week using organotin catalysts. This unusual combination of storage stability and reactivity may signify that the trialkoxysilyl groups hydrolyze during storage, but in the presence of large amounts of water, do not cross-link until the water evaporates after the coating is applied.

Acrylic latexes prepared using vinyltriethoxylsilane as a comonomer are reported to be package stable if buffered with $NaCO_3$. Compared to a similar latex without the silane comonomer, films show increased solvent resistance and exterior durability and improved heat flow resistance [65].

Core–shell latexes, prepared using *N*-(3-keto-2,2-dimethylbutyl)acrylamide (diacetoneacrylamide) as a comonomer, resulting in ketone groups in the shell for cross-linking with adipic dihydrazide, have been reported [66], as have corresponding latexes having a continuous gradient composition rather than a core–shell structure. Diffusion of the cross-linker through the latter particles before cross-linking is said to afford better film properties than reaction with keto groups at the surface of the core–shell particles [67].

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10

Polyester Resins

In fibers and plastics, *polyester* refers to high molecular weight (MW), partially crystalline, linear, thermoplastic polymeric esters of a short-chain diol and terephthalic acid. In coatings, however, it is used to describe a different sort of material. Most coating polyesters have relatively low MWs and are amorphous and branched, and they must be cross-linked to form useful coating films. Furthermore, the term is applied only to certain polyesters, those prepared from polyols and polybasic acids. Alkyd resins are also polyesters in the chemical sense of the word, but they are not called polyesters in coatings. As discussed in Chapter 15, alkyds are prepared from polyols and dibasic acids, and in addition, monobasic acids, usually derived from vegetable oils. Coating polyesters are sometimes called *oil-free polyesters* or *oil-free alkyds* to distinguish them from alkyds.

Polyesters are made by step-growth polymerization; the general principles are discussed in Section 2.2.2. The relatively low MW polyesters used in coatings are usually made from mixtures of diols, triols, and dibasic acids. Most commonly, excess polyol is used; hence, the polyesters are *hydroxy-terminated polyesters*. They are most commonly cross-linked with melamine–formaldehyde (MF) resins or polyisocyanates. Resins with excess carboxylic acid are also made; these *carboxylic acid–terminated polyesters* are cross-linked with epoxy resins, MF resins, or 2-hydroxyalkylamides. *Water-reducible polyesters* are synthesized with both terminal hydroxyl and carboxylic acid groups; they are usually cross-linked with MF resins.

Branched polyesters are made from monomer mixtures that include one or more monomers having functionality $F > 2$. Kinetic analysis of such polymerizations is complex, but a few generalizations can be pointed out. As the proportion of monomer of $F > 2$ increases, $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and the number average functionality $\bar{f}_n$ all increase. The average $\bar{F}$ must be controlled to avoid gelation at high extents of reaction.

Organic Coatings: Science and Technology, Third Edition, by Zeno W. Wicks, Jr., Frank N. Jones, S. Peter Pappas, and Douglas A. Wicks

In general terms, thermosetting polyesters give coatings with better adhesion to metal substrates and better impact resistance than thermosetting acrylics (TSAs) (Section 8.2). On the other hand, TSAs give coatings with superior water resistance and exterior durability. The differences can be attributed to the presence of the ester linkages in the backbone of polyesters: linkages that impart flexibility but are vulnerable to hydrolysis. Thus, polyesters tend to be used for one-coat coatings on metal, and TSAs tend to be used in applications for which exterior durability and moisture resistance are particularly important, often with primers that assure excellent adhesion of the coating system to the metal. The superior exterior durability of TSAs results partly from the greater effectiveness of UV screeners in acrylics than in polyesters. Many exceptions to these generalizations can be found (Section 5.2.1).

10.1. HYDROXY-TERMINATED POLYESTER RESINS FOR CONVENTIONAL SOLIDS COATINGS

Most hydroxy-terminated polyesters are made by coesterifying four types of monomers: two polyols (a diol and a triol) and two diacids (an aliphatic dibasic acid or its anhydride and an aromatic dicarboxylic acid or its anhydride). Tribasic and cycloaliphatic acids are used to some extent. The ratio of moles of dibasic acid to polyol must be less than 1 to give terminal hydroxyl groups and avoid gelation. MW is controlled by this ratio; the smaller the ratio, the lower the MW. The MW distribution, $\bar{M}_n$, and $\bar{f}_n$ are all controlled by the diol/triol ratio; $\bar{f}_n$ is critical because it affects the potential cross-link density after cure. With the same mole ratio of dibasic acid to total polyol, an increase in triol component increases the average number of hydroxyl groups per molecule, decreases hydroxy equivalent weight, broadens MW distribution, and increases cross-link density of a fully cross-linked film. The ratio of aromatic to aliphatic dibasic acids is the principal factor controlling the T_g of the resin, but differences in polyol structure also affect T_g. Mixtures of polyols and diacids also reduce the tendency of the resins to crystallize.

In commercial processes, mixtures of the monomers are esterified at 220 to 240°C while water is removed. Organotin compounds, titanium orthoesters, or zinc acetate are frequently used as catalysts. Strong protonic acids also catalyze esterification but can cause side reactions and discoloration. The reaction is continued until a high conversion has been reached. Acid numbers of resins to be cross-linked with MF resins are generally 5 to 10 mg KOH per grams of resin solids; those for use with polyisocyanates are commonly esterified until the acid number is less than 2. Polyesters made from polyfunctional reactants can cross-link during polymerization, causing gelation. Since the probability of gelation increases with conversion, and high conversions are generally desirable, an equation relating formula composition, extent of reaction, and probability of gelation would be useful. Progress has been made in predicting gelation in simple systems in which the reactivity of all hydroxyl groups and carboxylic acid groups are equal, but even with these "simple" systems, the equations give only fair predictions because they do not take into consideration the formation of cyclic esters (see Ref. [1] for a discussion of such equations). In the case of polyesters used in coatings, the situation is far from simple; the reactivity of the various functional groups commonly varies substantially, and side reactions occur. Therefore, the textbook gelation equations are of little value for polyesters used in coatings. If the mole ratio of dibasic acid to polyol exceeds, or even closely approaches 1, gelation may occur before esterification is essentially complete. This is seldom a problem in making hydroxy-functional polyesters for coatings, but it can become critical in synthesis of alkyds (Section 15.1).

Misev [2] has published equations that permit calculation of ratios of polyols and polybasic acids to use to make polyesters with a desired $\bar{M}_n$ and $\bar{f}_n$ at a desired extent of reaction of the acid groups. The equations are complex and require iterative computer solution. The equations are simplified if the choice of raw materials is limited, as it generally is, to diols, triols, and dibasic acids, and if essentially all of the acid groups are to be esterified. In commercial practice, polyesters are cooked until about 98 to 99.5% of the carboxylic acid groups are esterified. Therefore, an assumption of complete esterification is reasonable. In these simplified equations N_{p2} represents the number of moles of diol; N_{p3}, the number of moles of triol; and N_a, the number of moles of dibasic acid. M_{p2} represents the MW of the diol; M_{p3}, the triol; and M_a, the dibasic acid. If more than one dibasic acid (or other component) is used, additional terms would be added to the equation for each additional component. Using these equations, one can calculate how much diol, triol, and dibasic acid should be used in an initial laboratory cook for a desired $\bar{M}_n$ and $\bar{f}_n$.

In making hydroxy-terminated polyesters, the number of moles of polyol is one more than that of dibasic acid:

$$N_{p2} + N_{p3} = N_a + 1 \tag{10.1}$$

or

$$N_a = N_{p2} + N_{p3} - 1 \tag{10.2}$$

The relationship between the average functionality and the moles of reactants is expressed as

$$\bar{f}_n = 2N_{p2} + 3N_{p3} - 2N_a \tag{10.3}$$

Substituting the value of N_a from Eq. 10.2 into Eq. 10.3 gives Eqs. 10.4 and 10.5

$$\bar{f}_n = N_{p3} + 2 \tag{10.4}$$

or

$$N_{p3} = \bar{f}_n - 2 \tag{10.5}$$

When the esterification is carried out 2 mol of water (total MW = 36) is split out for each mole of dibasic acid, resulting in Eq. 10.6 for $\bar{M}_n$:

$$M_n = N_{p2}M_{p2} + N_{p3}M_{p3} + N_a(M_a - 36) \tag{10.6}$$

If an anhydride is used, only 1 mol of water ($M = 18$) is split out for each mole of anhydride, and the appropriate adjustment in Eq. 10.6 is needed. Substituting in

TABLE 10.1. Starting Formulation for a Conventional Polyester Resin

Raw Material	Weight (g)	Moles	Equivalents
NPG	2050	19	38
TMP	270	3	9
IPA	1740	10.5	21
AA	1530	10.5	21

Eq. 10.6 for N_a using Eq. 10.2 and for N_{p3} using Eq. 10.5 gives Eq. 10.7, which relates $\bar{M}_n$ to $\bar{f}_n$:

$$\bar{M}_n = N_{p2}M_{p2} + (\bar{f}_n - 2)M_{p3} + (N_{p2} + \bar{f}_n - 3)(M_a - 36) \tag{10.7}$$

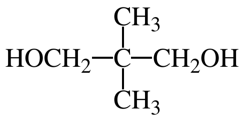
A wide range of polyesters has been used commercially. In conventional polyester–MF coatings, polyesters with $\bar{M}_n$ on the order of 2000 to 6000, $\bar{M}_w/\bar{M}_n$ on the order of 2.5 to 4, and with $\bar{f}_n$ of 4 to 10 hydroxyl groups per molecule are usual. Table 10.1 gives an example of an initial laboratory formulation calculated for a polyester with an $\bar{M}_n$ of 5000 and an $\bar{f}_n$ of 5 using Eqs. 10.1 to 10.7. Neopentyl glycol is NPG, trimethylolpropane is TMP, isophthalic acid is IPA, and adipic acid is AA. Structural formulas for these compounds are given in Sections 10.1.1 and 10.1.2.

A formulation such as that in Table 10.1 does not take into consideration all of the complexities of polyesterification; thus, it can only be expected to provide a starting point for experimentation. A common complication is partial loss of monomer from the reactor by volatilization. The diol is usually the most volatile component, so it is generally necessary to use excess diol. The amount of excess diol depends on the particular reactor and conditions, the efficiency of separating water and diol, the rate of flow of inert gas, the temperature of reaction, and so on. A formula established in the laboratory has to be adjusted when production is scaled up in a pilot plant, again when it is scaled up in a production reactor, and yet again when production is shifted from one reactor to another.

Esterification is a reversible reaction, the formation of high yields of ester requires removal of the water. A few percent of a reflux solvent, such as xylene, may be added to accelerate removal of water and to assist in return of volatilized diol to the reactor. Alternatively, an inert gas purge can be used in the later stages of the process to help remove the last of the water. Polyols can undergo self-condensation to form polyethers, which also produces water. Ester groups that form during the process may hydrolyze or transesterify and re-form many times, leading to a mixture of kinetic and thermodynamic control in formation of the final products.

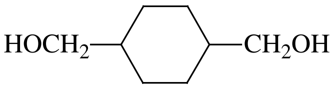
10.1.1. Selection of Polyols

Polyols are selected on the basis of cost, rate of esterification, stability during high temperature processing (minimal decomposition and discoloration), ease of separation from water during processing, viscosity of esters at equal MW and functionality, effect on T_g, rate of cross-linking with MF resins (or other cross-linkers), and hydrolytic stability of their esters. Obviously, compromises are necessary. The following polyols are representative of the many available:

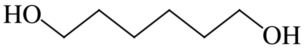


$$\begin{array}{c} CH_3 \\ | \\ HOCH_2{-}C{-}CH_2OH \\ | \\ CH_3 \end{array}$$

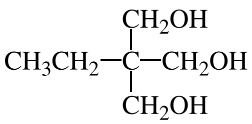
Neopentyl glycol (NPG)



Cyclohexanedimethanol (CHDM)

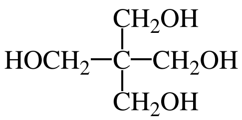


Hexane diol



$$\begin{array}{c} CH_2OH \\ | \\ CH_3CH_2{-}C{-}CH_2OH \\ | \\ CH_2OH \end{array}$$

Trimethylolpropane (TMP)



$$\begin{array}{c} CH_2OH \\ | \\ HOCH_2{-}C{-}CH_2OH \\ | \\ CH_2OH \end{array}$$

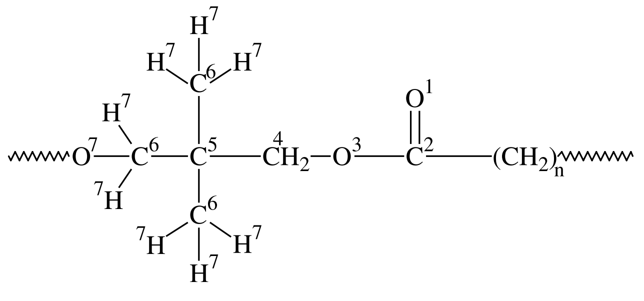
Pentaerythritol (PE)

The most widely used diol is probably NPG, and the most widely used triol is TMP. CHDM esterifies significantly more rapidly than NPG, and trimethyl-1,3-pentanediol (TMPD) more slowly [3]. Generally, but not always, the slower the rate of esterification, the greater the resistance of the ester to hydrolysis. The hydrolytic stability of esters of NPG and TMP is better than those from less hindered glycols such as ethylene glycol or propylene glycol. Neopentyl glycol (bp 213°C) is volatile at esterification temperatures, so well designed fractionating and condensing equipment are needed to permit the removal of water with a minimum loss of NPG during processing at 220 to 240°C. Most diols start decomposing in the presence of strong acids at temperatures above about 200°C, so strong acid esterification catalysts should be avoided. Organotin compounds and titanium orthoesters are examples of appropriate catalysts.

Although the kinetics and mechanisms of esterification and hydrolysis reactions have been extensively studied from a fundamental point of view, the literature contains few basic data dealing with polyols of most interest in coatings resins. Turpin [4] has proposed an empirical *steric factor* based on *Newman's rule of six* that may be useful in predicting the relative hydrolytic stability of esters. The steric factor is based on the number of substituents in the 6 and 7 positions of an ester, starting with the carbonyl oxygen as 1:

$$\text{steric factor} = 4(\text{No. 6 position atoms}) + (\text{No. 7 position atoms})$$

For example, for an NPG ester,



3 No. 6 atoms × 4 = 12

9 No. 7 atoms $\quad = \underline{9}$

Total = 21

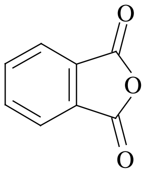
The value of 21 for NPG esters is the same for TMP esters, but for ethylene glycol and

1,6-hexanediol esters, the steric factors are only 13 and 15, respectively. Turpin's steric factor seems to correlate reasonably well with experience and with the limited published data for esters of acyclic alcohols. Turpin also pointed out that an *anchimeric*, or *neighboring group*, effect may be involved. For example, the location of the hydroxyl group in a half ester of ethylene glycol may promote the hydrolysis of its neighboring ester through a cyclic transition state and contribute to the poorer hydrolytic stability of ethylene glycol esters as compared to those of 1,6-hexanediol [4]. TMPD is also used frequently. Despite its relatively low steric factor, some polyesters made from it have good exterior durability.

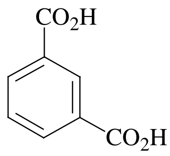
Esters of cycloaliphatic diols, such as cyclohexanedimethanol (CHDM), seem more resistant to hydrolysis than predicted by Turpin's steric factor. A comparison of the results of testing films of coatings made with a series of polyesters from several polyols has been published [5]. Coatings based on CHDM polyesters cross-linked with MF resins showed the best test results for properties related to hydrolytic stability. In contrast to general behavior, CHDM also esterifies more rapidly than NPG [3]. It has also been shown that CHDM polyesters give cured films with MF resins more rapidly than NPG-based polyesters [6]. A 1 : 1 mixture of (*cis,trans*) 1,3-cyclohexanedimethanol and (*cis,trans*) 1,4-cyclohexanedimethanol is a liquid that is reported to give polyesters for cross-linking with either MF resins or polyisocyanates that exhibit an excellent balance of hardness and flexibility with excellent acid etch resistance and durability [7]. The enhanced hydrolytic resistance of CHDM may arise from hydrophobicity of the cyclohexane ring.

10.1.2. Selection of Polyacids

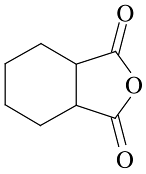
Most polyesters are made using a mixture of aromatic and aliphatic diacids. The ratio of aromatic to aliphatic acid is a major factor that controls the T_g of the resin.



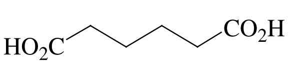
Phthalic anhydride
(PA)



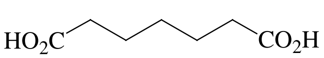
Isophthalic acid
(IPA)



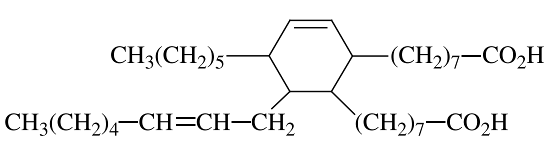
Hexahydrophthalic anhydride
(HHPA)



Adipic acid



Azelaic acid



Dimer fatty acid
(one of isomer mixture)

Aromatic acid esters hydrolyze more slowly than aliphatic esters, unless there is an anchimeric effect. Isophthalic acid (IPA) is the predominant aromatic acid used even though phthalic anhydride (PA) can be processed at lower cost. The preference for IPA is based on superior exterior durability of coatings made with IPA polyesters; this has been attributed to greater hydrolytic stability of isophthalic esters. Half esters of (ortho)phthalic acid are more easily hydrolyzed than half esters of isophthalic acid in the pH range 4 to 8 [8]. This difference results from anchimeric assisted hydrolysis by the *ortho*-carboxylic acid group. During exterior exposure, resistance to hydrolysis in contact with rainwater, which has a pH in the range 4 to 6, is most important. Under these conditions, isophthalic acid polyesters are more resistant than phthalic acid polyesters. On the other hand, mono- and diesters of isophthalic acid hydrolyze more rapidly than those of phthalic acid under alkaline conditions [9,10].

A processing cost advantage of phthalic anhydride results from its lower melting point (131°C); it can be handled as a molten liquid, it is readily soluble in the reaction mixture, and its reactive anhydride structure rapidly forms monoesters at about 160°C. Isophthalic acid (mp > 300°C) is more difficult to process because it dissolves more slowly in the reaction medium, and lower reactivity slows the processing. Due to a longer time at high temperatures, volatilization losses and acid catalyzed side reactions (e.g., etherification or dehydration of polyols) are more serious problems with IPA than with PA (Section 15.5.2).

Adipic acid is probably the most widely used aliphatic dibasic acid. Succinic and glutaric acids give esters with inferior hydrolytic stability, presumably due to the anchimeric effect [4]. Longer chain acids such as azelaic and sebacic acids may give somewhat better hydrolytic stability and greater reduction of T_g (on a molar basis) than those given by adipic acid, but are more expensive. Dimer acids, derived from dimerization of drying oil fatty acids and hence predominantly C_{36} acids, are widely used. Fatty acid dimerization is discussed in Section 14.3.1. Dimer acids are relatively inexpensive and are available in various grades. The high quality grades of dimer acids normally used in polyesters have little monobasic or tribasic acid contaminants and have been hydrogenated to saturate the double bonds in order to reduce oxidative degradation. Dimer acid–isophthalic polyesters impart an excellent balance of properties to MF cross-linked coil coatings, providing high resistance to marring combined with excellent resistance to cracking during fabrication of coated metal.

Cycloaliphatic dibasic acids or anhydrides can be used. Hexahydrophthalic anhydride (HHPA) is said to give exterior durability comparable to IPA. Aside from being aliphatic, HHPA half esters may be less susceptible to anchimeric assisted hydrolysis than are phthalic acid half esters possibly owing to isomerizing to the *E* (*trans*) isomers during processing. 1,4-Cyclohexanedicarboxylic acid (CHDA) provides a good balance of hardness, flexibility, and stain resistance. CHDA esters are much more stable than IPA esters to hydrolysis at pH 8 to 9, but somewhat less stable to hydrolysis at pH 4 to 5 [9,10].

A statistically designed evaluation of the factors affecting the exterior durability of IPA/adipic acid polyester/MF coatings showed that the major factor was the IPA/adipic acid ratio. The polyols were NPG and TMP. Higher IPA content polyesters gave coatings with improved durability [11].

10.2. POLYESTER RESINS FOR HIGH-SOLIDS COATINGS

Low viscosity polyesters are required for reduction of VOC emissions; viscosity of concentrated polyester solutions depends on several variables. MW and MW distribution are two important factors. The number of functional groups per molecule also affects the viscosity; increasing the number of hydroxyl groups (and to an even greater extent, the number of carboxylic acid groups) increases the probability of intermolecular hydrogen bonding, in turn increasing viscosity. The hydrogen-bond effect can be minimized, but not eliminated, by using hydrogen-bond acceptor solvents such as ketones. The T_g of the resin also affects viscosity at a given concentration. For this reason, reducing the ratio of aromatic to aliphatic dibasic acids and using acyclic polyols rather than cyclic polyols, such as CHDM [5,6], give lower viscosities, but there is a lower limit of T_g below which desired film properties cannot be attained.

Polyesters have significant advantages over thermosetting acrylics (TSAs) in high-solids coatings. In contrast to the difficulty of making low MW TSAs with at least two hydroxyl groups on essentially all molecules, the synthesis of polyesters with two or more hydroxyl groups on essentially all of the molecules is relatively easy. With the low mole ratios of dibasic acids to polyols (2 : 3 is typical) required to make low MW resins, the probability of cyclization reactions to form nonfunctional materials is small. Virtually all of the final reactions result in terminal hydroxyl groups. While the lowest viscosity is obtained with difunctional resins, such resins also require the most careful formulation and curing to achieve good film properties. If a hydroxyl is left unreacted on a conventional polyester with an average of five or so hydroxyl groups per molecule, the effect on film properties would probably be relatively small. However, failing to react all of the hydroxyl groups on a resin with only two hydroxyl groups per molecule would magnify the effect. A compromise is required; commonly, an $\bar{f}_n$ of between two and three hydroxyl groups per molecule is used.

The major factor controlling the MW ($\bar{M}_n$) of a polyester is the mole ratio of dibasic acid to polyol. A ratio on the order of 2 : 3 is typical. Loss of polyol during production of a polyester results in a higher MW than predicted from the starting ratio. Condensers are designed to remove water rapidly while returning a high fraction of NPG (or other polyol), but none is completely efficient. It is necessary to add some extra glycol to compensate for losses. Since production equipment and conditions vary, the final decision on the mole ratio to load must be based on experience with the particular reactor and with the particular formula. The amount of glycol being lost can be estimated by checking the refractive index of the water being removed from the reaction.

Some low MW components of a resin may volatilize when a thin film is baked. Such loss has to be counted as part of the VOC emissions, together with solvent loss. Belote and Blount studied this volatility both in the absence of cross-linking agent and in its presence [12]. They made a series of model resins from NPG and a 1 : 1 mole mixture of AA and IPA; the polyacid/polyol ratio was varied from 1 : 2 to 1 : 1.15. The presence of the cross-linker (class I MF resin) reduced volatile loss. They concluded that an $\bar{M}_n$ of about 800 to 1000 was optimum for achieving the lowest VOC with resins having normal MW distributions. At $\bar{M}_n$ around 600, so much low MW fraction volatilized that the total VOC was higher than at an $\bar{M}_n$ of 800, *even though the amount of solvent required was lower*. A broad MW distribution not only increases volatile losses because of the low MW material, but also gives a higher viscosity because of the disproportionate effect on viscosity of the high MW fraction. Lowest viscosity results from making as narrow a MW distribution as possible.

The use of TMPD in combination with a two-stage addition of the triol TMP during synthesis of a polyester gives lower viscosity and improved film properties [13]. The use of TMPD, an unsymmetrical diol, presumably gives narrower MW distribution because of the differential reactivity of the two hydroxyl groups. A drawback is the need for somewhat higher baking temperatures for coatings, presumably a result of the

TABLE 10.2. High-Solids Polyester Formulations (Equivalents)

Raw Material	Resin 1	Resin 2	Resin 3
TMPD	11.96	11.96	12.24
TMP	1.72	0.86	0.88
IPA	4.56	4.56	4.38
AA	4.56	4.56	4.38
	Second Stage		
TMP	—	0.86	0.88
Resin $\bar{M}_n$	1500	1075	1000
Coating NVW	75.6	76.5	77.6

low reactivity of the hindered terminal hydroxyl groups derived from TMPD. Three of the resin formulations used in this study are given in Table 10.2. Addition of the TMP in two stages resulted in a reduction in $\bar{M}_n$ from 1500 to 1100 (compare resins 1 and 2) with a corresponding reduction in viscosity. Further reduction was achieved by adjusting the monomer ratios (resin 3).

A polyester diol with a narrow MW distribution and a reported $\bar{M}_n$ of 425 is commercially available [14]. This resin is presumably manufactured by preparing a polyester with excess CHDM and then distilling off the low MW fraction with a vacuum thin-film evaporator. Low viscosity polyester diols and triols prepared by reacting caprolactone with a diol or a combination of diol and triol are also available [15]. These types of low-$\bar{M}_n$ resins seldom provide satisfactory coatings when used by themselves, but they are useful in blends to increase the solids content of somewhat higher MW polyester or acrylic-based coatings. They are often called *reactive diluents*.

Linear polyesters made by transesterification of 1,4-butanediol with a mixture of glutarate, adipate, and azaleate methyl esters give low viscosity hydroxy-terminated polyesters having an $\bar{M}_n$ of 680 [16]. They gave solvent-free two package coatings with hexamethylene diisocyanate trimer. However, with Class I MF resins, baked films were soft due to low T_g.

A relatively new analytical method, *matrix-assisted laser desorption ionization time-of-flight mass spectrometry* (MALDI-ToF-MS), has made it possible to study the complex mixtures of molecules in coatings polymers in unprecedented detail. For example, Willemse et al. [17] studied polyesters designed for very high solids and solventless liquid formulations. One such polyester was made from 1,4-butanediol, adipic acid (AA), and isophthalic acid (IPA) in a 1 : 0.375 : 0.375 mole ratio with an organotin catalyst. Figure 10.1(*a*) shows an overall MALDI spectrum of the product. Each cluster of peaks represents molecules with a specific degree of polymerization. Figure 10.1(*b*) is an expanded spectrum focused on molecules composed of seven diol and six diacid monomers. The numbers designate the numbers of AA and IPA residues in the molecules; for example, the peak designated 4-2 with a mass of 1369.57 Da contains four AA and two IPA residues. Here the peaks are clusters because of the presence of molecules containing isotopes (e.g., ^{2}H, ^{18}O). Further expansion makes it possible to identify small peaks from cyclic structures and from molecules with one acid and one hydroxyl end group. A significant finding of this study was that the compositions of molecules within this polyester are close to random as calculated by Bernouillan statistics. Sequences of monomers within molecules cannot be determined by MALDI-ToF-MS alone.

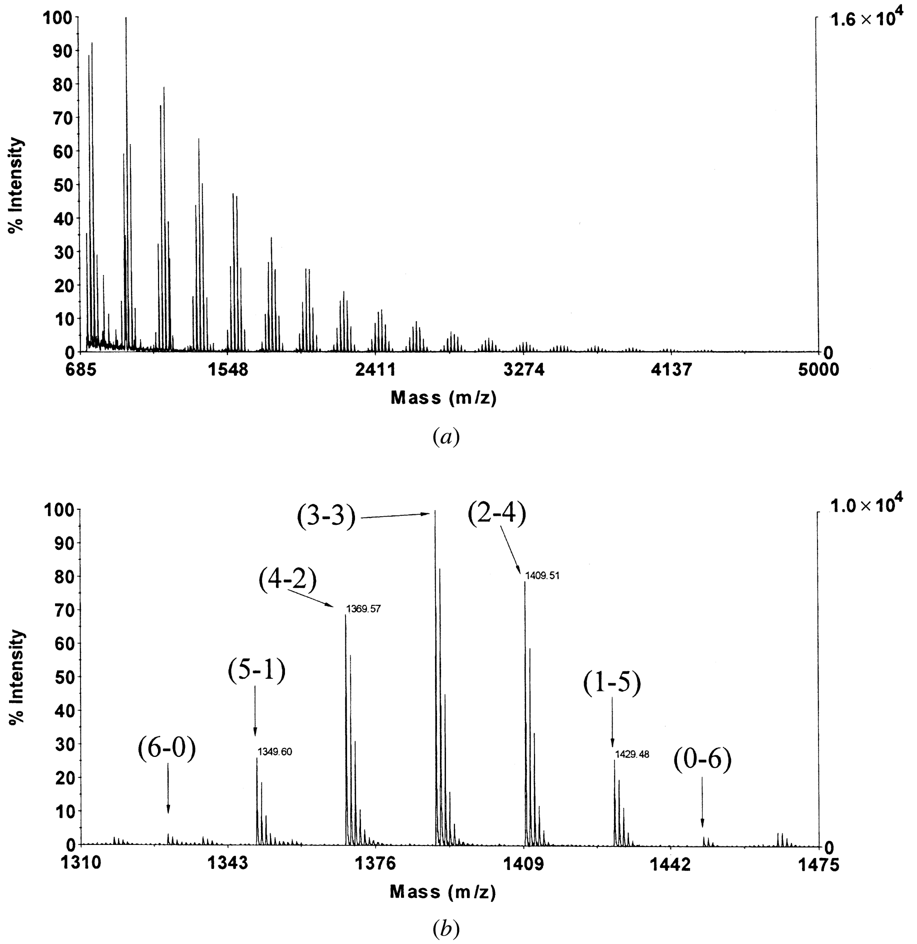


Figure 10.1. (a) MALDI-ToF-MS spectrum of a polyester resin made from 1,4-butanediol, adipic acid (AA), and isophthalic acid (IPA) in a 1 : 0.375 : 0.375 mole ratio; (b) expanded spectrum focused on molecules composed of seven diol and six diacid monomers. (Reprinted with permission from Ref. [17]; copyright © 2005 American Chemical Society.)

In another study, Arnould et al. [18] used MALDI-ToF-MS, tandem mass spectroscopy (MS/MS), and gel permeation chromatography (GPC) to study a higher-MW polyester. It was made from NPG, TMP, TPA, and AA in a 50 : 1 : 45 : 5 ratio, a composition similar to powder coating resins (Section 10.6). The polymer was fractionated by GPC to facilitate study of higher MW fractions. Only low levels of cyclic products were detected. The MS/MS spectra suggested that within individual molecules, certain specific sequences of monomers are favored.

10.3. CARBOXYLIC ACID–TERMINATED POLYESTER RESINS

Carboxylic acid–terminated polyesters are copolymers of a diol and a molar excess of dibasic acid. A modest amount of a tri- or polyfunctional monomer, most commonly trimellitic anhydride (TMA), is almost always included to increase $\bar{f}_n$. Carboxylic acid–functional polyesters can be cross-linked with MF resins but in most cases are cross-linked with epoxy resins or 2-hydroxyalkylamides, as discussed in Sections 13.3.2 and 17.5, respectively. With high ratios of high melting point diacids such as IPA, it is usually preferable to use a two-step process. The slow dissolution and high melting point of IPA prevent a clean reaction when the IPA is used in excess. First, one prepares a hydroxy-functional polyester with the IPA and then reacts the terminal hydroxyl groups with a lower melting acid or anhydride. Careful control is needed to assure reproducible products, since varying degrees of transesterification occur in the second stage. Final product structure is governed both by kinetic and thermodynamic factors; thus, resin properties are affected by reaction time and other process variables.

10.4. CARBAMATE-FUNCTIONAL POLYESTER RESINS

Carbamate-functional resins cross-linked with MF resins have been shown to give clear coats with good mar and acid resistance, exterior durability, and hydrolytic resistance. An example is an oligomer prepared by reacting citric acid with glycidyl neodecanoate and then transesterified with methyl carbamate [19].

10.5. WATER-REDUCIBLE POLYESTER RESINS

Polyesters are also made for use in waterborne coatings with a reduced VOC. Most such polyesters have both hydroxyls and carboxylic acids as terminal groups. As with other water-reducible resins, acid numbers in the range 35 to 60 are required to give amine salt solutions in solvent that can be diluted with water to give reasonably stable dispersions of aggregates of resin molecules swollen with water and solvent. These resins show abnormal viscosity dilution curves similar to those described in Section 8.3 for water-reducible acrylic resins.

In theory, one could prepare such water-reducible polyesters by simply stopping the esterification of a combination of diol, triol, AA, and IPA at the desired acid number; in practice, it is almost impossible to do so reproducibly. Rather, it is necessary to find combinations of polybasic acids that have sufficiently different reactivity to permit control of the ratio of unreacted hydroxyl and carboxyl groups. The most widely used method has been to prepare a hydroxy-functional resin and then add enough TMA to esterify a fraction of the hydroxyl groups, generating two carboxyl groups at each site. Advantage is taken of the higher reactivity of the anhydride groups of the TMA at 180°C relative to the carboxylic acid groups formed in the reaction. Table 10.3 gives an example of a formulation for preparing a water-reducible polyester [20].

This approach has been used on a large scale, but it has disadvantages. Most seriously, the ester linkages in the resin are vulnerable to hydrolysis during storage of the formulated coating. The ester group of partially esterified TMA is particularly sensitive to hydrolysis, owing to anchimeric assistance by the adjacent carboxylic acid group. Hydrolysis of the TMA partial ester results in removal of the solubilizing carboxyl groups and thereby destabilizes the resin dispersion. The film properties may also be affected adversely. In addition, the use of primary alcohols as a solvent, as recommended in Table 10.3, has been found to be undesirable. Primary alcohols have been found to esterify carboxylic acid groups and transesterify ester groups during the thinning at 160°C and at a slow but appreciable rate during storage of the resin. This problem can be minimized by using a secondary

TABLE 10.3. Water-Reducible Polyester Formulation

Material	Weight (g)	Mole Ratio	Equivalent Ratio
NPG	685	1.0	1.0
Adipic acid	192	0.2	0.2
TMA	84	0.067	0.1
IPA (85 : 15 IPA to TPA)	655	0.6	0.6
React at 235°C until the acid number is 16–18; cool to 180°C, then add:			
TMA	84	0.067	0.1
React at 180°C until the acid number is 40–45; cool to 160°C, and thin to 80% solids with diethylene glycol monobutyl ether.			

alcohol as solvent, along with careful control of process temperatures. 1,4-Cyclohexanedicarboxylic acid esters are more stable than IPA to hydrolysis under basic conditions [10]. Water-reducible polyesters are used in applications for which good storage stability and hydrolytic stability are not important, such as industrial coatings with a fast turnover.

An alternative approach that provides somewhat better, but still limited hydrolytic stability is to use 2,2-dimethylolpropionic acid as one of the diol components. The carboxylic acid group of this monomer is highly hindered by being located on a tertiary carbon. The resulting differential reactivity makes it possible to esterify the hydroxyl groups while leaving many of the acid groups unreacted. Although they are too hindered to esterify readily, the acid groups still form salts readily.

Hydrolytic stability is also affected by the choice of polyol. In addition to the steric effect discussed earlier, it has been shown that polyols with low water solubility give polyesters that are more stable than those with higher water solubility to hydrolysis under basic conditions, presumably because the polymers are more hydrophobic [10]. For example, polyesters made with 2-butyl-2-ethyl-1,3-propanediol have greater stability to hydrolysis than do NPG esters.

The problem of hydrolysis can be minimized by making powdered solid polyesters. An example of such a solid polyester is made from purified isophthalic acid, adipic acid, neopentyl glycol, cyclohexanedimethanol, hydrogenated bisphenol A, and trimellitic anhydride [21]. The resin is powdered and stored until a coating is to be made; then it is stirred into a hot aqueous solution of dimethylethanolamine to form a dispersion.

Another possible problem with water-reducible polyesters results from intramolecular reaction of terminal hydroxyl and carboxylic acid groups to form some low MW nonfunctional cyclic polyesters. When coatings are baked, small amounts of cyclic esters can volatilize out of the coating and gradually accumulate in cool spots in the oven. Eventually, sufficient resin can accumulate to drip down on products going through the ovens, marring their finish. Since the amounts are small, dripping may not start until after weeks or months of operation of the coating line.

Water-thinnable polyester coatings have been formulated with low MW oligomeric hydroxy-terminated polyesters [16]. Up to about 20% of water dissolves in a polyester–Class I MF resin binder, reducing the viscosity to about half. This permits making solvent free coatings. Further work is needed, but the idea is appealing not only because of the low VOC from the lack of need of cosolvent, but also because no amine is needed. Absence of amine should reduce the problem of hydrolysis.

10.6. POLYESTER RESINS FOR POWDER COATINGS

Polyester resins for powder coating are brittle solids with a relatively high T_g (50 to 60°C), so the powder coating does not sinter (partially fuse) during storage. These requirements are met with terephthalic acid (TPA) and NPG as the principal monomers. Resins in which much of the TPA is replaced with isophthalic acid (IPA) are said to give coatings with superior outdoor weatherability [22]. Smaller amounts of other monomers are added to increase $\bar{f}_n$ and to reduce T_g to the desired level. The relatively high T_g makes it possible to prepare hard, tough films with relatively low cross-link density. Widely used commercial products are amorphous, not crystalline. Both hydroxy- and carboxy-terminated polyesters are used. The former are most commonly cross-linked with blocked isocyanates (Section 12.5) and the latter with epoxy resins (Chapter 13). Other cross-linkers include 2-hydroxyalkylamides (Section 17.5) and tetramethoxymethylglycoluril (Section 11.4.3). (See Chapter 28 for a discussion of powder coatings.)

1,4-Cyclohexanedicarboxylic acid (CHDA) has been suggested as a replacement for isophthalic acid [23]. CHDA polyesters have a lower T_g and lower melt viscosities; if the T_g is too low, NPG can be fully or partially replaced with hydrogenated bisphenol A to provide for storage stability. Processes involving direct esterification of TPA are used, but since TPA has a very high melting point, it is common to make the hydroxy-terminated polyester by transesterification of dimethyl terephthalate. An appropriate transesterification catalyst is tetraisopropyl titanate. If desired, the hydroxy-terminated TPA polyester can then be reacted with other polyacids to form a carboxylic acid–terminated product in a second stage.

Recycled polyethylene terephthalate (PET) has been evaluated as a raw material for making polyesters for powder coatings. Recycled PET was dissolved in a mixture of NPG and TMP with a catalyst at 200°C. After cooling to 180°C, IPA was added and the reaction mixture heated to 240°C until the required acid number was reached. Properties of powder coated films were identical to those obtained with a polyester prepared from IPA, ethylene glycol, NPG, and TMP [24].

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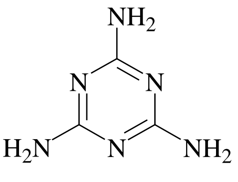
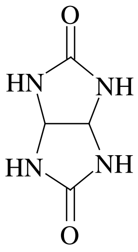
11

Amino Resins

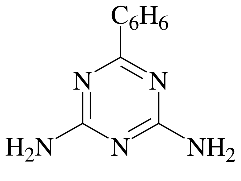
Amino resins, also called *aminoplast resins*, are major cross-linking agents for baked thermosetting coatings; the amino resins most commonly used are derived from melamine: that is, 2,4,6-triamino-1,3,5-triazine. Urea, benzoguanamine, glycoluril, and copolymers of (meth)acrylamide are also used.



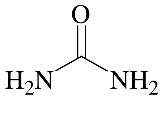
Melamine



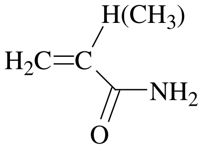
Glycouril



Benzoguanamine



Urea



(Meth)acrylamide

Amino resins for coatings are made by reacting one of these compounds with formaldehyde ($H_2C{=}O$) and subsequently, with alcohols (ROH) to yield activated ethers with

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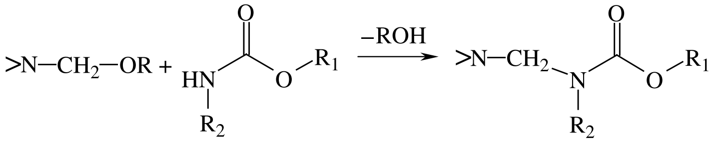
Organic Coatings: Science and Technology, Third Edition, by Zeno W. Wicks, Jr., Frank N. Jones,
S. Peter Pappas, and Douglas A. Wicks

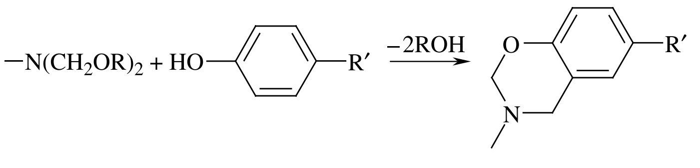
the general structure $>NCH_2OR$. Ethers of amino resins are activated toward nucleophilic substitution by the neighboring N and are much more reactive than aliphatic ethers. When the nucleophile is the alcohol of a polyol (POH), transetherification can occur, as shown in Eq. 11.1, resulting in formation of a cross-linked polymer. The reaction is catalyzed by acid. Carboxylic acids, urethanes, and phenols with an unsubstituted ortho position also react, as shown in Eqs. 11.2, 11.3, and 11.4.

$$>N{-}CH_2{-}OR + P{-}OH \rightleftharpoons >N{-}CH_2{-}OP + ROH \tag{11.1}$$

$$>N{-}CH_2{-}OR + P{-}CO_2H \rightleftharpoons PCO_2{-}CH_2{-}N< + ROH \tag{11.2}$$



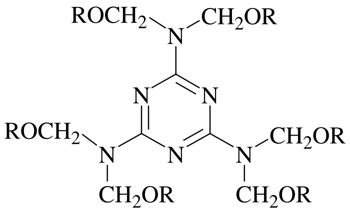
(11.3)



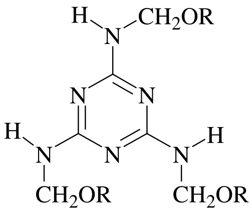
(11.4)

11.1. SYNTHESIS OF MELAMINE–FORMALDEHYDE RESINS

The first step in the synthesis of melamine–formaldehyde (MF) resins is methylolation, the reaction of melamine with formaldehyde under basic conditions. With excess formaldehyde, the reaction can be driven to form a mixture that contains substantial amounts of hexamethylolmelamine (**1**, where R is H). With less than the stoichiometric 6 mol of formaldehyde per mole of melamine, a mixture of partially methylolated derivatives, including species such as symmetrical trimethylolmelamine (**2**, where R is H) is formed. Methylolmelamine resins of this type are often used to fabricate laminates and plastics but are rarely used in coatings.



(**1**)



(**2**)

For coatings, the second step is acid-catalyzed etherification of methylolmelamines with an alcohol, such as methyl or butyl alcohol. Complete etherification of methylolmelamines **1** and **2**, where R is H, yields alkoxymethyl derivatives **1** and **2**, where R is alkyl. Many commercial MF resins are only partially etherified. In addition to monomeric species, commercial MF resins contain oligomeric species in which triazine rings are linked by methylene ($>NCH_2N<$) and dimethylene ether bridges ($>NCH_2OCH_2N<$).

11.1.1. Methylolation Reaction

A probable mechanism for base catalyzed reaction of melamine with formaldehyde is outlined in Scheme 11.1, where —NH_2 represents the melamine amino groups. The first step involves nucleophilic attack by the amino group on the electrophilic C of formaldehyde, which is facilitated by removal of a proton from N by the base (B^-). This is followed by proton transfer from the resulting B—H to the negative oxygen atom, which yields the methylolated product and regenerates the base catalyst; both steps are reversible.

Early studies of the kinetics of the reaction indicate that the presence of one methylol group on N deactivates the group for a second reaction by a factor of 0.5 to 0.6. On the other hand, substitution on one amino group has less effect on the reactivity of the other amino groups. These kinetic factors favor formation of the symmetrical trimethylolmelamine (TMMM) (**2**), where R is H. However, the preference is not strong enough to overcome the kinetic and thermodynamic tendencies to produce mixtures of products. Thus, at equilibrium, the reaction of 6 mol of formaldehyde with 1 mol of melamine yields a mixture of products, including all levels of methylolation and free formaldehyde [1]. A side reaction is methylolation on oxygen, as shown in Scheme 11.1.

Scheme 11.1

Main reaction:

$$\text{—NH}_2 + \text{H}_2\text{C{=}O} + \text{B}^- \rightleftharpoons \text{—NH—CH}_2\text{—O}^- + \text{BH}$$

$$\text{—NH—CH}_2\text{—O}^- + \text{BH} \rightleftharpoons \text{—NH—CH}_2\text{—OH} + \text{B}^-$$

Side reaction:

$$\text{—NH—CH}_2\text{—O}^- + \text{H}_2\text{C{=}O} \rightleftharpoons \text{—NH—CH}_2\text{—O—CH}_2\text{—O}^-$$

$$\text{—NH—CH}_2\text{—O—CH}_2\text{—O}^- + \text{BH} \rightleftharpoons \text{—NH—CH}_2\text{—O—CH}_2\text{—OH} + \text{B}^-$$

11.1.2. Etherification Reaction

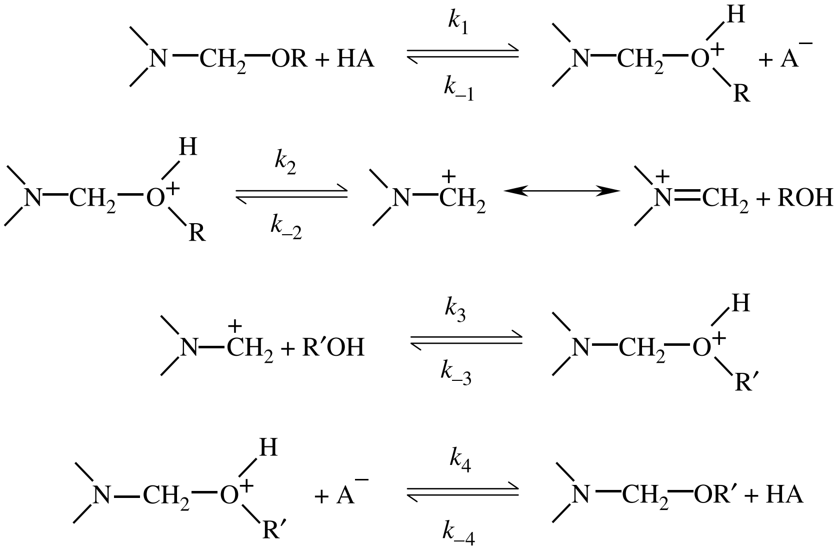
Following methylolation, the base catalyst is neutralized with excess acid and the appropriate alcohol is added. The acid-catalyzed reversible reaction leads to formation of alkoxymethyl groups. Nitric acid is commonly used as a catalyst because nitrate salt by-products are relatively easily removed.

There is disagreement in the literature about the mechanism of the etherification reaction as well as of the closely related transetherification reaction, shown in Eq. 11.1. The contending mechanisms for these substitution reactions are S_N1 and S_N2, both of which are outlined in Scheme 11.2, where R is H and R′OH is methyl or butyl alcohol. Note that the conjugate base (A^-) is omitted from the intermediate steps.

The distinguishing feature is whether the protonated methylol group dissociates to an intermediate, resonance-stabilized carbocation, as in Eq. 11.5, before reacting with the alcohol, characteristic of the S_N1 mechanism, or reacts directly with the alcohol, as in

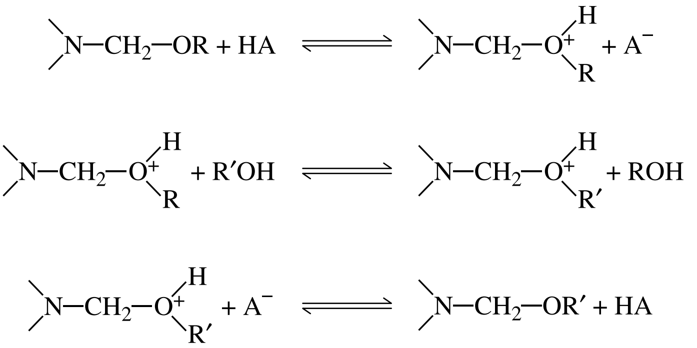
Scheme 11.2

S_N1 mechanism:



(11.5)

S_N2 mechanism:



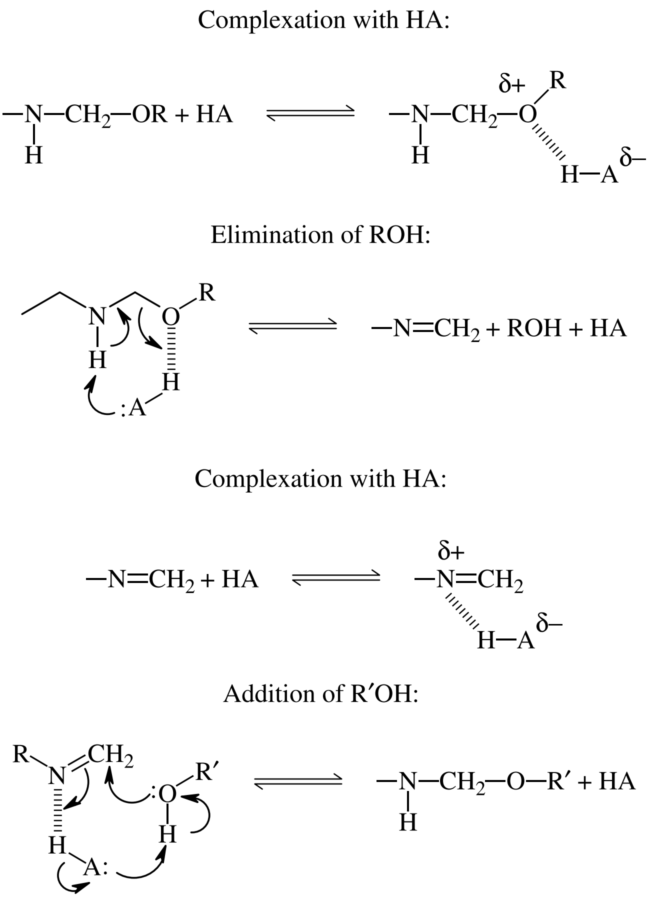
(11.6)

Eq. 11.6, characteristic of the S_N2 mechanism. The controversy about the mechanism in MF resin synthesis also applies to the transetherification reaction involved in cross-linking MF resins with polyols, where R is methyl or butyl and R′OH is the polyol. Experimental evidence bearing on this controversy has been acquired primarily in studies of coatings and is discussed in Section 11.3.2. Based on the available evidence, we favor the S_N1 mechanism.

Etherification of methylol groups on a singly substituted N (i.e., a N that also bears a H atom) is proposed to follow the mechanism outlined in Scheme 11.3, where R is H and R′OH is methyl or butyl alcohol.

The distinguishing feature is formation of the uncharged imine intermediate, shown in Eq. 11.7, which is possible due to the presence of the N—H group. Imines form by elimination of water catalyzed by relatively weak acids, such as carboxylic acids. Complexation of the methylolmelamine by an acid (A—H) is sufficient to yield the imine, either in a concerted push-pull mechanism, as shown in Scheme 11.3, or a step-wise mechanism.

Scheme 11.3



Complexation with HA:

Elimination of ROH:

Complexation with HA:

Addition of R′OH:

(11.7)

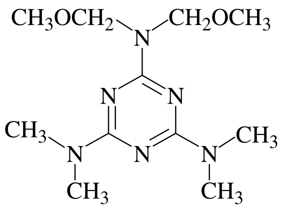
Complexation of the reactive imine by acid is also sufficient to effect subsequent addition of alcohol, resulting in overall substitution of water by alcohol. This reaction is also reversible. Since catalysis in Scheme 11.3 involves complexation rather than protonation by the acid, the rate is dependent on the nature of H—A as well as its concentration. Indeed, both the more positive H end and the more negative A end of H—A participate by facilitating breaking of both the C—O and the N—H bonds, respectively. By convention, this is called *general acid catalysis*. The mechanism in Scheme 11.3 also applies to cross-linking of polyols by MF resins with N—H groups by transetherification, where R is methyl or butyl and R′OH represents the polyol.

In contrast, elimination of water from methylolmelamines lacking N—H groups, either by the S_N1 or S_N2 mechanism (shown in Scheme 11.2), requires protonation of the methylol group, necessitating a strong ionizing acid such as nitric, sulfuric, or a sulfonic acid. Such catalysis, requiring protonation, is called *specific acid catalysis*, signifying that the rate is dependent only on the concentration of protons (H^+) and is independent of the conjugate base (A^-).

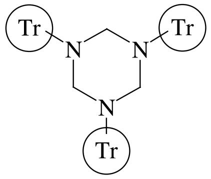
11.1.3. Self-Condensation Reactions

Self-condensation refers to reactions that lead to the formation of bridges between triazine rings, resulting in dimers, trimers, higher oligomers, and ultimately, to cross-linked polymer. The extent of such reactions depends on process factors, including pH, ratio of reactants, reaction temperature, rate of removal of water, and probably others. Two types of linkages occur between triazines: methylene bridges (>NCH_2N<) and dimethylene ether bridges (>NCH_2OCH_2N<) [2,3]. Acid catalysis is said to favor dimethylene ether bridges and base catalysis to favor methylene bridges; furthermore, formation of methylene bridges may occur by base-catalyzed scission of dimethylene ether bridges [4].

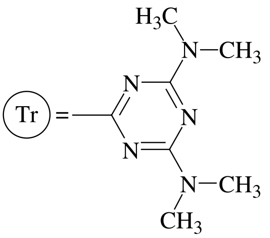
Formation of methylene bridges has been demonstrated in the acid-catalyzed reaction of a model compound *N*,*N*-dimethoxymethyl-*N*′,*N*′,*N*″,*N*″-tetramethylmelamine (**3**) and water [5]. In the presence of *p*-toluenesulfonic acid (pTSA) and water at elevated temperatures, a cyclic trimer (**4**) with methylene groups connecting the three nitrogens is formed. Formation of the trimer is reversible [6]; when trimer **4** is heated with methyl alcohol and formaldehyde at 130°C, compound **3** is regenerated.



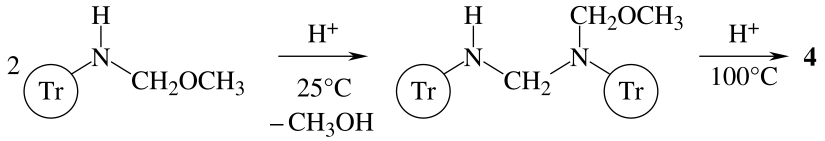
(**3**)



(**4**)



The monomethoxymethyl model compound (**5**) is more reactive than **3** [7]. It rapidly forms the cyclic trimer (**4**) in the absence of water at 100°C. In solution with an acid catalyst, it equilibrates rapidly at 25°C with the methylene ether bridge dimer (**6**).



(**5**) (**6**)

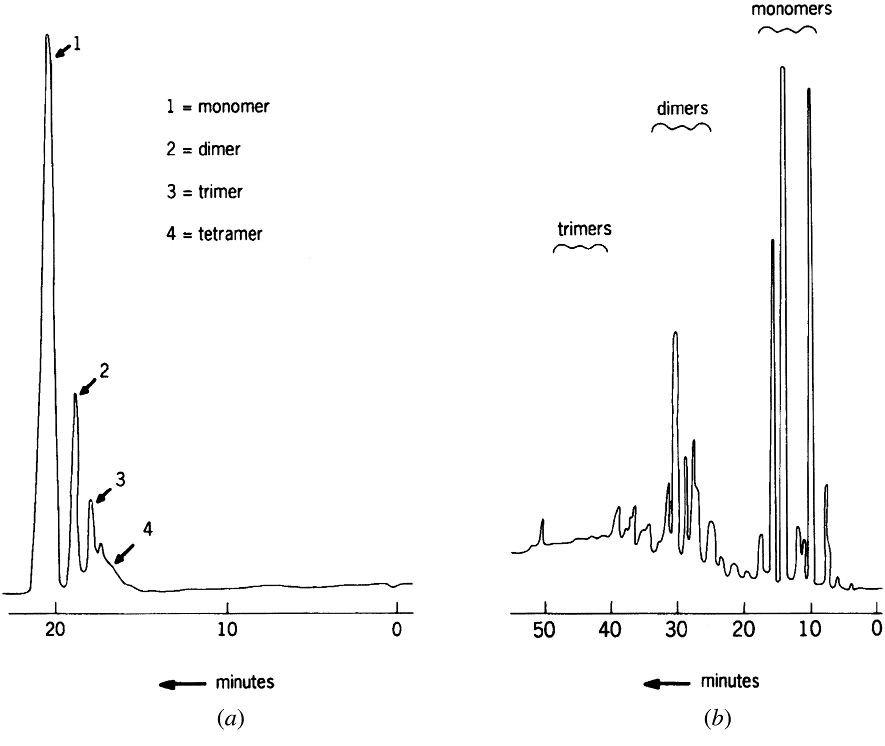
11.2. TYPES OF MF RESINS

A variety of MF resins are made commercially, which differ by the ratio of functional groups, the alcohol used for etherification, and the average degree of polymerization $\bar{P}$. To facilitate discussion, MF resins are classified into two broad groups. Class I resins are made with relatively high ratios of formaldehyde to melamine, and hence most of the nitrogens have two alkoxymethyl substituents. Class II resins are made with lower ratios of formaldehyde, and many of the nitrogens have only one substituent.

From about 1940 through the 1950s, the predominant melamine resins were Class II types used for cross-linking alkyds. These resins have enough bridging so that $\bar{P}$ is 3 or more, and the alcohol is usually *n*-butyl or isobutyl alcohol. Such resins are economical, they are readily miscible in alkyd formulations, and they give a wide latitude; that is, coatings do not require exacting control of formulation to produce acceptable application characteristics and film properties.

Class I MF resins were commercialized in the 1950s. Methylated Class I resins are more compatible than butylated resins with certain coreactant resins, and in some cases, provide tougher films. Introduction of waterborne and high-solids coatings during the 1970s accelerated the shift toward Class I resins. Methylated MF resins are more miscible with the water, solvent, and resin blend used in waterborne coatings; and Class I resins with low $\bar{P}$ values give lower viscosity to high-solids coatings. These generalities are not universal; some Class II resins are used in low-solvent coatings.

A commercial methylated MF Class I resin has been reported to contain 62% monomers (i.e., one triazine ring), 23% dimers, together with 15% trimers and higher oligomers [8]. The equivalent weight of pure hexamethoxymethylmelamine (HMMM) is 65 g equiv.$^{-1}$, but the equivalent weight of this resin is 80 g equiv.$^{-1}$, resulting from the presence of dimers, trimers, and higher oligomers. (In estimating equivalent weight, it is necessary to make an assumption as to whether $>NCH_2N<$ or $>NCH_2OCH_2N<$ bridging groups react to form cross-links. Here, it is assumed that they do not.) Chromatographic analysis of a different, but similar resin of this type is shown in Figure 11.1. The chromatograms show at least 30 different chemical species present in significant amounts [2,9]. While the predominant groups are —$N(CH_2OCH_3)_2$, various species containing incompletely etherified groups [—$N(CH_2OCH_3)(CH_2OH)$] and incompletely formylated groups [—$NH(CH_2OCH_3)$] are present. These methylated MF resins are frequently called *HMMM resins*, but the terminology *high HMMM resin* is more appropriate.



(*a*) (*b*)

Figure 11.1. High-performance liquid chromatograms (HPLC) of a typical Class I high-HMMM resin: (a) SEC chromatogram; (b) gradient HPLC chromatogram. (From Ref. [9], with permission.)

A broad range of Class I resins is available with different degrees of polymerization $\bar{P}$ and with different extents of formylation and etherification. In addition to methylated derivatives, butylated as well as mixed methyl/*n*-butyl, methyl/isobutyl, methyl/ethyl, and methyl/isooctyl derivatives are also available. Class I resins generally have lower $\bar{P}$ and therefore lower viscosity than Class II resins at the same percent solids content. The viscosity is also reduced by the presence of fewer polar groups. At a given $\bar{P}$, butyl ethers exhibit even lower viscosities, attributable to lower T_g values, than the corresponding methyl ethers.

An even broader range of Class II resins is available because the ratio of formaldehyde/melamine and of alcohol/formaldehyde can be varied through a wider range. It is harder to suppress bridge-forming reactions during synthesis of Class II resins, and very low $\bar{P}$ resins cannot be prepared. The predominant reactive group present in Class II resins is $—NHCH_2OR$. Hence, they are frequently called *high NH resins*. They also contain $—NH_2$, $>NCH_2OH$, as well as $—N(CH_2OR)_2$, groups. To minimize viscosity and maximize reactivity, resin producers strive to reduce $\bar{P}$ and maximize the amount of symmetrical TMMM (**3**), where R is Me. This is possible to a degree because the methylolation of $—NH_2$ groups, yielding $—NHCH_2OH$, is kinetically favored over methylolation of $NHCH_2OH$, yielding $—N(CH_2OH)_2$. Owing to advances in HPLC analysis techniques, it is possible to follow the effects of small changes in process conditions on composition. Continuing refinement of processes has permitted commercial production of resins with as high as 50% TMMM. A variety of alcohols are used to make different resin grades.

Amino resins usually contain small amounts of unreacted formaldehyde that may be vaporized during application and baking of the coatings. Additional amounts of formaldehyde vapor may be formed during storage of formulated coatings and/or during the baking process. These small amounts of formaldehyde vapor pose a potential hazard to workers who are exposed daily. Formaldehyde exposure levels are strictly regulated in the United States; and current technology appears adequate to satisfy these regulations. Although the regulations already appear stringent, it is possible that allowable exposure levels will be reduced further. Intensive research on ways to reduce formaldehyde emissions has been under way for some time. Besides improving ventilation, approaches include changing resins, changing formulations, incinerating oven exhausts, and introducing formaldehyde scavengers. MF resin producers offer low-formaldehyde (<0.1 wt%) grades of key resins.

11.3. MF–POLYOL REACTIONS IN COATINGS

Melamine–formaldehyde (MF) resins are used to cross-link coreactant resins having hydroxyl, carboxylic acid, urethane (carbamate), and/or amide groups. Acrylic (Chapter 8), polyester (Chapter 10), alkyd (Chapter 15), epoxy (Chapter 13), and polyurethane (Chapter 12) resins are the most important classes of coreactant resins. It is widespread practice to use combinations of cross-linkers (e.g., MF resins with other types of amino resins) with (blocked) polyisocyanates (Chapter 12), with phenolic resins (Section 13.6), or with resins bearing reactive silanes (Section 16.2).

Polyols (hydroxy-functional acrylics, polyesters, etc.) are the resins most commonly cross-linked by MF resins. The hydroxyl groups of polyols react by either transetherification with the activated alkoxymethyl groups or by etherification of methylol groups of MF resins to form new ether cross-links. The reaction with phenols, as in Eq. 11.4, has the advantage that a C—C bond is formed so that the product is stable to hydrolysis. Strong acid catalysts, such as sulfonic acids, are used for Class I resins, and weak acid catalysts, such as carboxylic acids, are used for Class II resins. The reactions are reversible but are driven toward cross-linking by volatilization of the monofunctional alcohol or water produced, as shown in Eq. 11.8, where R is alkyl or H and POH is the polyol.

$$>\mathrm{N{-}CH_2{-}OR} + \textcircled{P}\!\sim\!\sim\mathrm{OH} \xrightleftharpoons{\mathrm{H}^+} >\mathrm{N{-}CH_2{-}O}\sim\!\sim\textcircled{P} + \mathrm{R{-}OH} \tag{11.8}$$

Rates of reaction with hydroxyl groups depend on the structure of the polyol and the MF resin, the type and amount of catalyst, and the temperature. The rate at which MF resins cross-link polyols increases with increasing volatility of the alcohol, according to the following order: methyl $>$ ethyl $>$ *n*-butyl. These rates are probably influenced by the rate of diffusion of the alcohol from the reactive site and by evaporation from the film.

A widely believed but mistaken conclusion is that steric hindrance limits the number of active ether groups on high HMMM resins that can participate in cross-linking of films to three, or at most four, of the six groups [1]. This conclusion was apparently based on the need to use an excess over the stoichiometric amount of MF Class I resin relative to polyol to achieve the desired film properties at baking schedules such as 30 minutes at 120°C, using around 0.3 wt% (on the total weight of polymers) of pTSA. However, Hill and Kozlowski provide strong evidence in support of an essentially complete reaction of $\mathrm{{-}NCH_2OCH_3}$ groups with certain polyols, showing that all $\mathrm{{-}NCH_2OCH_3}$ groups of high HMMM resins can co-condense if there are enough hydroxyl groups present for them to react with [8]. Their conclusions were based on studies of changes in mechanical properties, as discussed in Section 4.2. These results further substantiate the hypothesis that the excess MF resin used in most formulations is needed not to complete co-condensation cross-linking, but to permit some degree of self-condensation cross-linking that may be necessary to achieve the desired film properties.

Factors in addition to cure response must be considered when selecting the alcohol. For example, viscosity at a given percent solids content can be reduced by substituting Class I mixed ether resins for HMMM types. The alcohols in mixed ether resins are frequently 1 : 6 to 1 : 3 *n*-butyl or isobutyl alcohol to methyl alcohol. Only modest reductions of VOC are attained because mixed ether resins contain a higher weight fraction of volatile by-products; butyl groups represent a higher weight fraction of resins than do methyl groups. Perhaps a greater advantage of mixed ether resins is that they impart lower surface tension to coatings than do high HMMM types. High surface tension is often associated with development of film defects such as crawling, cratering, leveling (Chapter 24), and poor intercoat adhesion (Section 6.5) [10].

The rates of development of solvent resistance and film hardness when a fractionated low NH Class I resin was used to cross-link polyester resins made with cyclohexanedimethanol (CHDM), neopentyl glycol (NPG), and 1,6-hexanediol have been reported [7,11]. Film properties developed most rapidly with CHDM polyesters, followed in order by NPG polyesters a close second, and hexanediol polyesters. It was also found that film properties generally developed more rapidly with acrylic polyols than with polyester polyols.

During acid-catalyzed cross-linking with polyols, *self-condensation reactions* of MF resins also occur, including formation of methylene bridges and dimethylene ether bridges. Self-condensation reactions result in cross-linking, as do reactions of MF resins with polyol (or another coreactant), which have been termed *co-condensation reactions* [12]. Both self- and co-condensation reactions contribute to the structure of the cross-linked polymer network and to its film properties.

With strong acid catalysis, the apparent rate at which Class I resins react with most polyols by co-condensation is faster than self-condensation. However, with Class II resins, the apparent rates of co-condensation and self-condensation are similar. The relatively high levels of $—NHCH_2OR$ and $>NCH_2OH$ groups in Class II resins promote self-condensation reactions. The methylol groups can self-react analogously to reaction with a polyol; and the $—NHCH_2OR$ groups can eliminate alcohol to yield reactive melamine imine ($—N{=}CH_2$) groups, which can form dimethylene ether bridges by reaction with $—NCH_2OH$ groups and methylene bridges by reaction with $>NH$ groups. Based on the time and temperature required to achieve hard films, Class I and II resins have also been classified as high and low cure temperature resins, respectively, which reflects, at least in part, the facility of self-condensation reactions by Class II resins.

Class I resins are used with an excess of alkoxymethyl groups over polyol hydroxyl groups, so final development of film properties depends on the extent of self-condensation reactions as well as on co-condensation. In some cases, this high stoichiometric ratio is dictated by the lower cost of MF resins compared to that of some polyols. It may also be that self-condensation cross-links give some advantage in film properties. The amounts of MF resin and catalyst are determined empirically and are optimized for a specified baking time and temperature. Formulations are designed to achieve optimum properties when co-condensation is nearly complete and self-condensation is partly complete. If the use conditions differ from those for which the formulation was designed, the extent of self-condensation and co-condensation will differ from the optimum levels. Coating properties such as hardness, adhesion, exterior durability, and impact resistance may be affected.

In high-solids coatings in which the hydroxy equivalent weight and the average functionality of the polyol are lower than those for low solids, higher molecular-weight polyols, the results are particularly sensitive to variations in cure temperature and time. These considerations have been addressed in terms of a *cure window*, corresponding to the range of cure times and temperatures that provides films of acceptable properties [13]. The cure window was shown to be smaller for high-solids MF–polyol coatings, especially when Class II resins were used.

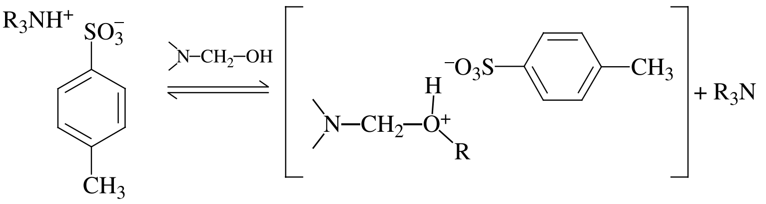
11.3.1. Catalysis of MF–Polyol Reactions

With strong acid catalysts, commonly aryl sulfonic acids, usually in the range 0.5 to 1 wt% of MF resin, reactions of MF Class I resins with polyols give cured films in 10 to 30 minutes at 110 to 130°C. Co-condensation of MF Class I resins with polyols can be catalyzed by weak acids, such as carboxylic acids; however, elevated cure temperatures, generally greater than 140°C, are required [14]. In the case of Class II resins, carboxylic acids are more effective in catalyzing co-condensation in accordance with the mechanism provided in Scheme 11.3. Since many polyol resins contain some carboxylic acid groups, which are present to promote adhesion and facilitate pigment dispersion, no added catalyst may be needed for cross-linking with Class II resins. At the high temperatures (air temperatures as high as 375°C) used in coil coating ovens, strong acid catalysts are needed even with Class II resins, owing to the short cure times.

Cure time and/or temperature may be reduced by increasing the catalyst concentration. However, storage (or package) stability is reduced by this approach, since the reaction at ambient temperature is also catalyzed by acid. Another danger in increasing acid catalyst concentration to reduce cure time and/or temperature relates to the durability of the cured coating. In addition to catalyzing transetherification (and etherification) reactions of MF resins with polyols, acid residues catalyze the hydrolysis of cross-links in cured coatings. The course of the hydrolysis reaction can be followed by reference to Schemes 11.2 and 11.3, where $>N—CH_2—OR$ represents a cross-linked polymer and R′OH represents water. The hydrolysis reaction breaks cross-linked bonds and generates methylol groups that, at least in part, eliminate formaldehyde as follows [12]:

$$>N{-}CH_2OH \rightleftharpoons >N{-}H + H_2C{=}O \qquad (11.9)$$

Free acids such as *p*-toluenesulfonic acid (pTSA) catalyze cross-linking under ambient conditions at a rate that may increase the viscosity of a liquid coating above the range for application in less than 6 months. One-package systems commonly use acid catalysts that are deactivated: variously called *acid precursors*, *latent acids*, and *blocked acids*. Aryl sulfonic acids are strong acids (the pK_a of pTSA $= -6$); their tertiary amine salts are weak acids ($pK_a = 8$ to 10) and do not catalyze the reactions of Class I MF resins. As shown in Eq. 11.10, there is an equilibrium between pTSA amine salt and the protonated MF resin that is the active species for catalysis.



(11.10)

Although the equilibrium favors structures on the left, it may be shifted to the right by volatilization of the amine, increasing the concentration of protonated MF resin, the initial intermediate in the transetherification reaction (Scheme 11.2). Generally, the storage stability of a coating with a blocked catalyst approaches the stability of an uncatalyzed coating. In some cases the cure rate approaches that of a coating catalyzed with free sulfonic acid, whereas in others, the curing rate is somewhat reduced [15]. The balance of the storage stability and cure rate is reported to be particularly favorable for *N*-benzyl-*N*,*N*-dimethylanilinium sulfonates [16]. In this case, the MF resin is probably activated by O-alkylation with the benzyl cation, since quaternary anilinium sulfonates have no available proton.

The acid strength of the medium can be no stronger than that of protonated melamine resin, which exerts a leveling effect on acid strength, just as the strongest acid in water is the hydronium ion. Apparently, pTSA (TsOH) is completely ionized by MF resins, which explains why even stronger acids, such as hexafluorophosphoric acid, exhibit similar catalytic activity. On the other hand, pTSA is more effective for Class I MF resins than weaker acids, such as butylphosphoric and carboxylic acids. With pTSA, the rate of co-condensation of an HMMM resin and acrylic polyol is reported to be proportional to the square root of the acid concentration [17].

Although the acid strength of a strong acid catalyst makes little difference in cure rates, the choice of acid (or blocked acid) catalyst can lead to differences in film properties of cured coatings. The most widely used catalyst is pTSA. The grade of pTSA is important, since some grades contain significant quantities of sulfuric acid, which can lead to pronounced yellowing of films during baking. It has been found that water resistance of films can be improved by use of a more hydrophobic sulfonic acid, such as dinonylnaphthalene disulfonic acid (DNNDSA), which is reported to produce films that are less likely to blister when exposed to high humidity conditions [18]. DNNDSA is particularly effective in coatings applied directly to metal, which, with pTSA are prone to blistering on humidity exposure.

p-Dodecylbenzenesulfonic acid (DDBSA) provides similar catalytic activity and film properties to those of DNNDSA when used in coatings applied over a prime coat. However, when a DDBSA catalyzed coating is used directly on steel, adhesion of the coating is likely to be poor. It seems probable that the sulfonic acid group on DDBSA is strongly adsorbed on the steel surface, causing the surface to become covered with dodecyl groups. The low surface tension of the long hydrocarbon dodecyl groups on DDBSA may cause dewetting by the rest of the coating or formation of a weak boundary layer that reduces adhesion. The better adhesion with DNNDSA catalyzed coatings may be related to the presence of two sulfonic acid groups or weaker surfactant properties.

The activity of acid (or blocked acid) catalysts can be affected by pigmentation of the coating. Some grades of titanium dioxide pigments lead to loss of catalyst activity with storage time. The loss is related to the composition of surface treatments on the TiO_2. Silicon dioxide–treated TiO_2 is preferable to aluminum oxide–treated TiO_2 in this respect, probably owing to the basicity of alumina, which tends to neutralize the acid. When alumina-treated TiO_2 is required for other reasons, a higher concentration of acid catalyst may be necessary to counteract the effect.

In waterborne MF–polyol coatings, the amine utilized to neutralize the solubilizing carboxylic acid groups in the polyol (see Section 8.3 for a discussion) also neutralizes the sulfonic acid. It was shown that commonly utilized hydroxy-functional amines such as *N,N*-dimethylethanolamine (DMEA) may also participate in transetherification of MF resins and/or transesterification of ester groups in the polyol during storage or initial stages of curing, which may retard or prevent their volatilization during cure, causing loss of cure response [19]. It was also shown that 2-amino-2-methylpropanol (AMP) gives a faster cure rate since the primary amine can react with an acrylic resin to form amides, reducing the basicity. Formation of an amide, together with transesterification by the hydroxyl group of AMP, forms cross-links. Furthermore, AMP has been shown to react with formaldehyde to form an oxazolidine, also reducing basicity so that it does not inhibit cure as DMAE does [20]. Dynamic mechanical analysis (DMA) also shows the lesser extent of inhibition by AMP and supports auxiliary cross-linking by AMP [21].

11.3.2. Kinetics and Mechanism of MF–Polyol Co-condensation

Many studies have been directed at elucidating the mechanism(s) of reactions between MF resins and polyols. Until recently, most of these studies were based on following the time necessary to reach some degree of film hardness. However, both co- and self-condensation reactions contribute to hardness [8]. Therefore, one must view with caution conclusions from such studies applied specifically to the co-condensation reaction between hydroxyl groups and MF resins.

It is desirable to develop methods for measuring the extent of co-condensation directly. Infrared (IR) and Fourier transform infrared (FTIR) spectroscopy have been used to follow changes in functional group concentrations using Class I MF resins as a function of time and temperature [17]; particular care must be taken in interpreting results because of band overlap in the hydroxy region. The rate of evolution of volatile reaction products, including formaldehyde and methyl alcohol, has been followed by gas chromatography [12,14] and by thermogravimetric analysis [15]. Major contributions have been made by application of DMA to MF–polyol cross-linking coatings [8,22] (Section 4.2). Oscillating plate rheometry has also been used [23].

A misconception resulting from using hardness results to study kinetics is that the co-condensation reaction of Class I resins was thought to be much slower than it has now been found to be. Disappearance of polyol hydroxyl groups, as followed by FTIR, showed that the reaction is more rapid than the development of film properties [14,23,24]. Relatively slow development of film properties is characteristic of step-growth polymerization processes and may also reflect the slower rate of self-condensation reactions, which probably contribute to achievement of optimal cross-link density.

In Class I resins, it has been observed that reactivity is reduced by the presence of imino (>NH) groups in the resin. Fractionation to remove essentially all of these groups from a commercial HMMM resin yielded a surprising increase in reactivity with hydroxyl functional resins, enabling lower cure temperatures [7,25]. It is speculated that the relatively basic $—NHCH_2OCH_3$ groups present in most HMMM resins tie up a portion of the catalyst.

The mechanism of co-condensation of MF Class I resins with polyols remains controversial, with experimental evidence being interpreted in support of (or against) the S_N1 or S_N2 mechanisms, provided in Scheme 11.2. However, the two mechanisms are not mutually exclusive and may occur simultaneously. Owing to the expectation that the activation parameters, E_a and A, are larger for the S_N1 reaction (Section 2.3.2 and Figure 2.6), the S_N1 mechanism is favored with increasing temperature.

Based on studies with the model analog (**4**) and monofunctional alcohols, it was proposed that both S_N1 and S_N2 mechanisms occur [5]. The novel use of chiral monofunctional alcohols provided kinetic evidence for equal rates of reactivity of primary and secondary alcohols with a high HMMM resin, but higher reactivity in the reverse reaction with secondary alcohols [26]. These findings support the S_N1 mechanism and are consistent with the general order of reactivity in coatings of primary $>$ secondary alcohols, since the curing reactions occur under reversible conditions. However, utilization of an oversimplified rate expression may compromise these conclusions.

Using an HMMM–acrylic composition and following the co-condensation reaction by FTIR, Bauer provided support for the S_N1 mechanism. He also interpreted the role of methyl alcohol in the kinetic order of the reaction and the rate dependence on polyol in support of the S_N1 mechanism [17]. A key point is that the rate of co-condensation by the S_N1 mechanism is expected to depend on the concentration of polyol if the methyl alcohol, formed from HMMM, competes with the polyol for the intermediate carbocation; refer to Scheme 11.2. Water also competes with the polyol for this carbocation. This valid interpretation of the S_N1 mechanism is an important consideration, since dependence of the rate on the polyol had mistakenly been interpreted as evidence against the S_N1 mechanism. Competition for the intermediate carbocation by methyl alcohol is expected to gain relative importance as the reaction proceeds because the methyl alcohol concentration increases, at least temporarily, whereas the polyol concentration decreases with increasing conversion. Thus, kinetic studies based on hardness or other film properties, which tend to develop only at high conversions, are expected to exhibit strong dependence on the concentration and nature of the polyol. Such results had generally been interpreted in favor of the S_N2 mechanism, but are equally consistent with the S_N1 mechanism.

A further complication is the strong possibility that cross-linking with MF resins leads to a gradient of compositions and properties within films. Although relatively few films have been studied in this way, most studies detected a gradient. For example, Haacke et al. used a microtome to separate layers in acrylic–MF clear coats and found that different layers had different compositions [27]. Furthermore, they found that T_g was as much as 15°C higher at the surface than it was deep in the film and that cross-link density was almost twice as high near the surface. They attributed the gradient to the differing effects of escaping by-product alcohol on the cross-linking equilibrium reactions at different levels in the film. There is the additional possibility that catalyst concentrations may not be uniform within the film, especially when catalysts blocked with volatile amines are used. Other studies have suggested that there may be a very thin layer of material at the surface that is quite different than the bulk in composition and properties [28]. These scattered reports suggest that to fully understand the performance of amino resin cross-linked coatings (and perhaps of other types as well), it may be necessary to appreciate the effects of composition and property gradients within the films.

Considerable progress has been made toward understanding the complex combinations of reactions that occur during the curing of MF cross-linked coatings, but the process is not yet fully understood; further research is needed.

11.3.3. Package Stability Considerations

Package stability of coatings containing MF resins is affected by other factors in addition to catalyst levels, discussed in Section 11.3.1. Class II resins generally give poorer package stability than Class I resins due to the preponderance of >NH and >NCH_2OH groups, which participate in slow, weak acid catalyzed reactions during storage at room temperature. Stability is somewhat improved by addition of small quantities of tertiary amines. Primary or secondary amines, which react with formaldehyde, should not be used with Class II resins. Free formaldehyde is in equilibrium with melamine methylol groups in these resins. Reaction of the formaldehyde with primary or secondary amines displaces the equilibrium reaction in favor of formaldehyde formation (i.e., demethylolation), which reduces the methylol group functionality of the MF resins.

An important approach for increasing package stability is to use as much monofunctional alcohol as possible in formulations containing either class of MF resins. The presence of monofunctional alcohol in the formulation extends the storage stability since its reaction with the MF resin does not lead to cross-linking. On the other hand, cross-linking and viscosity buildup occur when the MF resin self-condenses or reacts with the polyol. Generally, it is desirable to utilize the same alcohol that is used to synthesize the MF resin. If a different alcohol is used, undesirable changes may occur. For example, if *n*-butyl alcohol is used in the solvent with a methoxymethylmelamine resin, the cure response gradually becomes slower as the proportion of butyl ether increases. The viscosity of a coating may decrease during storage because butoxymethylmelamine is less viscous (it has a lower T_g) than the corresponding methoxymethylmelamine. Viscosity decrease may also result from breaking dimethylene ether bridges by excess alcohol.

11.3.4. MF Resin Reactions with Carboxylic Acids, Urethanes, Carbamates, and Malonate-Blocked Isocyanates

Carboxylic acid–functional resins react with MF resins to form the corresponding ester derivatives (Eq. 11.2); the reaction is slower than with hydroxyl groups. Carboxylic acid groups are present in substantial levels in waterborne hydroxy-functional resins to enhance dispersibility, as well as in some solventborne polyols, at low levels, to enhance the stability of pigment dispersions. When significant levels of carboxylic acid groups are present, it is desirable to cure under conditions which ensure that they react, since residual carboxylic acid groups increase the water sensitivity of cured films.

As shown in Eq. 11.3, MF resins react with urethane groups. Polyurethanes containing —OC(=O)NH— structures (secondary carbamates), and no hydroxyl groups can be cross-linked with MF resins at temperatures only slightly higher than those used to cross-link polyols [29]. This result indicates that when hydroxy-terminated urethanes are used with MF resins, both groups are involved in cross-linking. Both groups react when polyurethane polyols are used as reactive diluents [30]. A variety of MF resins can cross-link secondary carbamates; Class I resins are more reactive than Class II resins [29]. Secondary carbamates are nearly as reactive as hydroxyl groups, despite their greater steric hindrance. A possible explanation of this surprising result is that the carbamate reaction is irreversible [31]. Thus, the forward reaction might be substantially slower than the forward reaction of hydroxyl groups, but the overall rate could be close to equal if the reverse reaction does not occur with carbamates. The practice of cross-linking polyols with mixtures of MF and polyisocyanate resins has become increasingly common. Formulators should keep in mind the strong possibility that some of the carbamate formed in the isocyanate–hydroxyl reaction will react further with MF resin.

Polymers with pendant —OC(=O)NH_2 structures (primary carbamates) are less hindered than secondary carbamates and would be expected to cross-link more rapidly. Conclusive evidence for this expectation has not been published, but patent examples suggest that it is true; polymers with primary carbamates are cured with Class I MF resins under the same conditions as polymers with primary —OH groups [32,33]. Primary carbamate-functional resins can be made by reacting isocyanate-terminated resins with hydroxypropylcarbamate [32] or from acrylic resins [33]. The isocyanate-based resins can be cross-linked with Class I MF resins, but the cross-link density is too high for some applications. Functionality can be reduced by blocking half of the functional groups of Class I resins with butyl carbamate [32]. Automotive clear coats made from such combinations combine the usual high mar resistance of MF–polyol cross-linked coatings with enhanced resistance to environmental etching.

Class I MF resins also react with malonic ester derivatives of isocyanates at rates similar to their reactions with —OH groups [34]. NMR study of a model compound confirmed that environmentally resistant carbon–carbon cross-links are irreversibly formed in the process. As a result, environmental etch resistance of a coating made from a malonic ester derivative of a triisocyanate and a Class I MF resin is excellent [34]. Malonic ester derivatives of isocyanates can also function as cross-linkers for hydroxy-functional resins, as discussed in Section 12.5.

11.4. OTHER AMINO RESINS

Other amino resins are used on a smaller scale. The structures of the other starting materials are provided at the beginning of this chapter. Although the chemistry of these resins is similar to that of MF resins, there are differences, particularly as a result of differences in basicity of the resins [35].

11.4.1. Urea–Formaldehyde Resins

Substantial amounts of urea–formaldehyde resins are used because of their low cost and high reactivity. Urea reacts with formaldehyde to form methylol derivatives. The first and second formaldehyde units add easily, but trimethylol and tetramethylol derivatives of urea form with more difficulty, if at all. Methylolated ureas can be etherified by reaction with alcohols, analogously to methylolated melamines. Self-condensation reactions also occur under both acidic and basic conditions. A variety of etherified urea–formaldehyde (UF) resins are made with different ratios of formaldehyde to urea and different alcohols for etherification.

In general, UF resins are the most economical amino resins; they are also the most reactive. With sufficient acid catalyst, coatings formulated with UF resins can cure at ambient or mildly elevated temperatures. However, such coatings have poor exterior durability, probably because the cross-links are relatively reactive and have relatively poor resistance to hydrolysis. UF resins are used in coatings for temperature sensitive substrates such as wood furniture, paneling, and cabinetry. In such applications, low temperature baking is essential, and corrosion resistance (related to the hydrolytic stability of the cross-links) is unimportant. Blends of UF and MF resins can be used to achieve fast cure, low cost, and acceptable properties [36].

11.4.2. Benzoguanamine–Formaldehyde Resins

Using benzoguanamine as a starting material, a range of resins analogous to MF resins can be prepared. As with melamine, benzoguanamine may be methoxymethylated and/or butoxymethylated to various extents. The average functionality is lower because there are only two $-NH_2$ groups per molecule. Etherified benzoguanamine–formaldehyde (BF) resins yield cross-linked urethane films with greater resistance to alkali and to alkaline detergents, such as sodium tripolyphosphate, than that of MF resins. They also impart excellent toughness. The exterior durability of BF-based coatings is poorer than that of MF-based coatings. Thus, BF resins are used for applications such as washing machines and dishwashers, in which resistance to alkaline detergents and toughness are more important than exterior durability. The reduced exterior durability of BF-based coatings probably reflects lower photostability arising from the presence of the phenyl group on the triazine ring of benzoguanamine, although evidence supporting this reasonable hypothesis does not appear to be available. Aside from the hydrophobicity of the phenyl groups, a convincing explanation for enhanced alkali resistance is not intuitively forthcoming.

11.4.3. Glycoluril–Formaldehyde Resins

Glycoluril reacts with formaldehyde to give tetramethylolglycoluril (TMGU) [35]. In the pH range 4 to 8, aqueous solutions of TMGU show an equilibrium level of about 3.6 methylol groups per glycoluril, with 0.4 parts of free formaldehyde. Above pH 8.5, demethylolation is more favored. For example, at pH 11 there are approximately equal parts of methylol groups and free formaldehyde. Below pH 3, self-condensation occurs to form glycoluril dimers with methylene ether bridges:

$$>N{-}CH_2{-}OH \underset{}{\overset{pH < 4}{\rightleftharpoons}} >N{-}CH_2{-}O{-}CH_2{-}N< + H_2O \tag{11.11}$$

where $>N{-}CH_2{-}OH$ represents methylolated glycoluril groups. This behavior is unlike that of MF or UF resins. Whereas TMGU does not self-condense above pH 4, methylolated melamines and ureas self-condense at pH 7 and higher.

Tetramethylolglycoluril reacts with alcohols in the presence of strong acid catalyst to form tetraalkoxymethylglycoluril (GF) resins. Tetramethoxymethylglycoluril is a relatively high melting solid and is used as a cross-linker in powder coatings (Section 28.1.3). In solution coatings, (dimethoxymethyldiethoxymethyl)glycoluril and tetrabutoxymethylglycoluril are used, since they are liquids and are handled more readily. The mixed methyl–ethyl ether is water soluble.

Relative to other amino resins, GF resins produce coatings that exhibit greater flexibility at a similar cross-link density. Hence, GF resins are used in applications such as coil coatings and can coatings, where flexibility is important. GF resins possess the further advantage that less formaldehyde is evolved during cure than with MF resins. Also, the glycoluril cross-linked polyols are more resistant than MF cross-linked polyols to hydrolysis under acidic conditions and are said to be UV resistant [35]. The higher cost of GF resins limits their use.

11.4.4. Poly(meth)acrylamide–Formaldehyde Resins

Acrylic copolymers of *N*-isobutoxymethylacrylamide can be prepared by two routes: (1) synthesis of *N*-isobutoxymethylacrylamide monomer (from a step-wise reaction of acrylamide with formaldehyde and isobutyl alcohol), followed by copolymerization with acrylate monomers, and (2) copolymerization of acrylamide, followed by step-wise reaction with formaldehyde and isobutyl alcohol. Analogous reactions can be carried out with other alcohols and with methacrylamide.

Such alkoxymethyl(meth)acrylamide amino resins are used in coil coatings, where with proper design they are weather resistant and more flexible than coatings based on MF–acrylic polyol resins. One can speculate that their flexibility is enhanced by the absence of densely cross-linked clusters of self-condensed MF resins with their rigid triazine rings.

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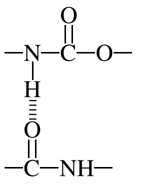
12

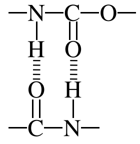
Binders Based on Polyisocyanates: Polyurethanes

Polyurethanes are polymers containing urethane (>NH—CO—O<) linkages; *carbamate* is a synonym for *urethane*. Urethanes are usually formed by reaction of an alcohol with an isocyanate, but they can also be made by other methods. Commonly, urethanes made by a nonisocyanate route are called carbamates. To add to the confusing terminology, the terms *urethane* and *polyurethane* are applied to almost any binder derived from isocyanates even though only part, if any, of the reaction products are urethanes. Isocyanates are used to make urethane-modified alkyds (uralkyds) as discussed in Section 15.7. The market for urethanes in coatings in the United States in 2002 has been reported to be about 250 million kilograms [1].

Urethane groups form intermolecular hydrogen bonds between polymer molecules; they may be acyclic and/or cyclic:



Acyclic H-bond



Cyclic H-bonds

Under mechanical stresses, energy (about 20 to 25 kJ mol^{-1} of acyclic hydrogen-bonds) may be absorbed by separation of hydrogen-bonds, which can re-form (probably in different positions) when the stress is removed. Energy absorption by this reversible bond-breaking/bond re-forming process reduces the likelihood of irreversible breaking of covalent bonds leading to degradation. In addition, the urethanes can be designed

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Organic Coatings: Science and Technology, Third Edition, by Zeno W. Wicks, Jr., Frank N. Jones, S. Peter Pappas, and Douglas A. Wicks

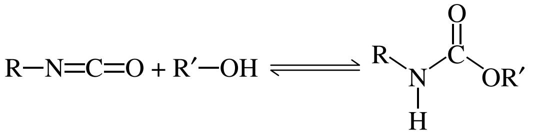
with “soft” and “hard” segments: that is, segments having low T_g and high T_g, respectively. When stress is applied, the soft segments can extend between the hard segment anchors. This factor, combined with the hydrogen-bonding, permits the preparation of coatings with 2H hardness and 300% extension. These properties permit the design of polyurethanes that are abrasion resistant while still resisting swelling with solvents. Polyurethanes tend to absorb water by hydrogen-bonding with water, which plasticizes the coatings.

The isocyanate group is highly reactive, so polyisocyanates can be used to make coatings that cure at ambient temperature or at moderately elevated temperatures. Coatings based on aliphatic diisocyanates exhibit exceptional exterior durability when stabilized with hindered amine light stabilizers (Section 5.3.3). The resistance of urethane coatings to environmental etching is superior to that of many melamine–formaldehyde (MF) cross-linked coatings [2].

The principal limitations of isocyanates are cost and toxicity (particularly of relatively low molecular weight compounds). Any cross-linker that reacts with hydroxyl, amine, and/or carboxylic acid groups near room temperature is likely to be toxic, since the body contains proteins and other materials having such substituents. The important question is not toxicity as much as toxic hazard. Since higher molecular weight reduces vapor pressure and permeability through body membranes, toxic hazard decreases, in general, as molecular weight increases. With adequate ventilation and use of air masks and protective clothing, as commonly done in chemical factories and resin manufacturing plants, even relatively low molecular weight isocyanates can be handled safely. Most low-molecular weight diisocyanates are sensitizers, however, which can result in an allergic reaction on further exposure to isocyanate. The exposure leading to sensitization varies over a wide time period for individuals and may occur only after years of repeated exposure for some. The most common symptoms are hives and asthma. In extreme cases sensitized people cannot be in the same room, or even the same building, in which isocyanates are handled. Isocyanate suppliers supply safety instructions for handling and using isocyanates. Coating applicators, especially amateur users, are less likely than professional chemists to have appropriate facilities or even to follow safety instructions. In using any highly reactive cross-linker, the competence of the user to handle toxic materials should be taken into consideration in establishing formulations. To minimize the hazard, most isocyanates used in coatings are oligomeric or polymeric derivatives.

12.1. REACTIONS OF ISOCYANATES

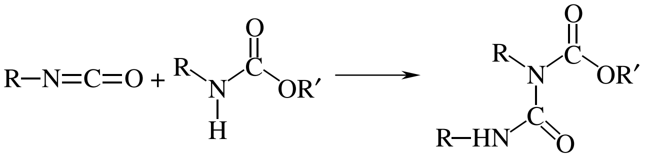
Isocyanates react with any active hydrogen compound. Alcohols and phenols react with isocyanates to form urethanes, as in the following reaction, in which R and R′ can be aromatic or aliphatic groups: The reaction is reversible at elevated temperatures.



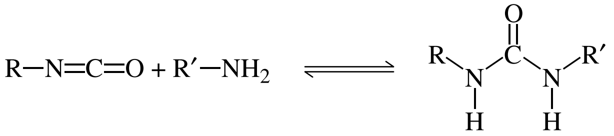
$$R{-}N{=}C{=}O + R'{-}OH \rightleftharpoons R{-}NH{-}C(=O){-}OR'$$

In general, rates of urethane formation decrease in the following order: primary alcohols > secondary alcohols > 2-alkoxyethanols > 1-alkoxy-2-propanols > tertiary alcohols. As a rule, ease of reversion is the inverse of reactivity. Urethanes from tertiary alcohols are relatively unstable and may decompose with heat to give alkenes, carbon dioxide, and amines, rather than alcohols and isocyanates.

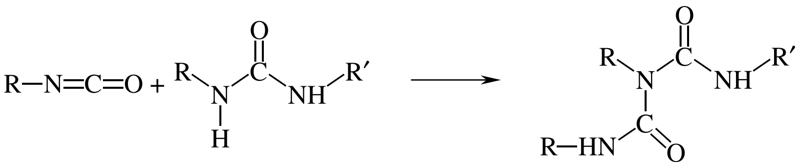
Urethanes react with isocyanates to form allophanates. This reaction is much slower than the reaction of isocyanate with alcohol.



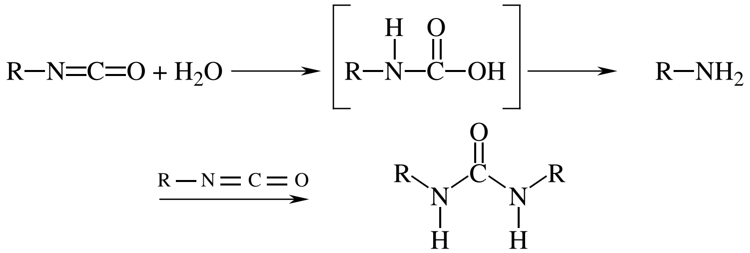
Isocyanates react rapidly with primary and secondary amines to form ureas. The reaction is much faster than the reaction of isocyanates with alcohols. For many coating applications, reactions are too rapid; however, hindered amines have been developed that react sufficiently slowly to permit use in two package (2K) coatings [3,4] (Section 12.4.1):



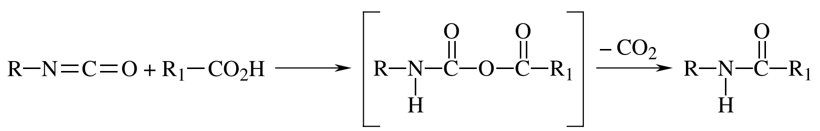
Isocyanates react with ureas to form biurets. Biuret formation is slower than urethane formation, but faster than allophanate formation.



Isocyanates react with water to form unstable carbamic acids, which dissociate into carbon dioxide and an amine. The amine is so much more reactive than water that it reacts with a second isocyanate (in preference to water) to form a urea. The reactivity of water with isocyanates is somewhat slower than that of secondary alcohols but more rapid than that of ureas.

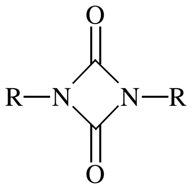


Carboxylic acids react relatively slowly with isocyanates to form amides and CO_2. Hindered carboxylic acid groups such as in 2,2-dimethylolpropionic acid (DMPA) react very slowly; accordingly, DMPA is commonly used to incorporate COOH groups into polyurethanes.

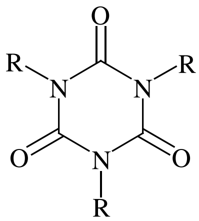


$$\mathrm{R{-}N{=}C{=}O + R_1{-}CO_2H \longrightarrow \left[R{-}\underset{H}{\underset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}O{-}\overset{O}{\overset{\|}{C}}{-}R_1 \right] \xrightarrow{-\,CO_2} R{-}\underset{H}{\underset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}R_1}$$

Isocyanates also react with each other to form dimers (uretdiones) and trimers (isocyanurates). Formation of uretdiones is catalyzed by phosphines. Trimerization to form aliphatic isocyanurates is catalyzed by quaternary ammonium compounds; trimerization of aromatic isocyanates is catalyzed by tertiary amines. Uretdiones decompose thermally to regenerate isocyanates and are used as blocked isocyanates (Section 12.5). Isocyanurates are stable and are used extensively as building blocks for multifunctional isocyanates (Section 12.3).



Uretdione



Isocyanurate

12.2. KINETICS OF REACTIONS OF ISOCYANATES WITH ALCOHOLS

The mechanism and catalysis of reaction of isocyanates with alcohols are not fully understood. One must use caution when evaluating rate data from the literature, especially in interpreting tables of rate constants compiled from different sources. The original literature should be consulted to make sure that comparisons are based on studies done in the same solvents and initial concentrations, since reaction rates depend on these variables. Also, rates of urethane formation are commonly determined by following the disappearance of isocyanate. If other products, such as allophanates and isocyanurates, are also formed, isocyanate disappearance does not correspond to urethane formation. Further, many of the papers do not give the number of replicates, if any, or statistical confidence limits for the data.

Formulators often compare rates of cross-linking by determining the MEK double-rub resistance of films as a function of time and/or temperature and/or catalyst. Usually, the test is stopped when the number of MEK double rubs without marring of the surface exceeds 200. The test is sensitive to cross-link density in the relatively early stages of the reaction but is not sensitive to variations in the high extent of reaction obtained when films are cured. A film that reaches 200+ double rub resistance faster than a second film will not necessarily reach full cross-linking more rapidly, or even as rapidly as the second film. Another technique for following initial cross-linking is determination of the time required for a solution of a triol and diisocyanates to gel. Dynamic mechanical analysis (DMA) or solvent swelling are more reliable ways to measure the cross-link density of more highly cross-linked coatings. Examples of the fact that a 200+ MEK double rub test does not indicate full cure, or even give the same rank order of time to reach 200+ double rubs as the time to reach full cure, are given in Ref. [5] through comparisons of results with the measurement of cross-link density by DMA analysis.

12.2.1. Noncatalyzed Reactions

One might expect urethane formation to follow second-order kinetics, with the rate proportional to the concentration of each reactant: as shown in Eq. 12.1. Indeed, the reaction of *n*-butanol with phenyl isocyanate in the dipolar aprotic solvent acetonitrile has been reported to follow second order kinetics [6].

$$\text{rate} = k[\text{R—N=C=O}][\text{R}'\text{—OH}] \tag{12.1}$$

Other kinetic studies show that the situation is more complex, and often the kinetic order changes as the reaction progresses. In at least some nonpolar or low-polarity solvents, the reaction follows third-order kinetics, at least in its early stages, first order in isocyanate and second order in alcohol concentration. It seems reasonable to assume that in most coating applications, reactions will be occurring in low polarity media. Rate equation 12.2, would apply to such cases: whose implication of Eq. 12.2 is that two molecules of alcohol are involved in the reaction with one molecule of isocyanate.

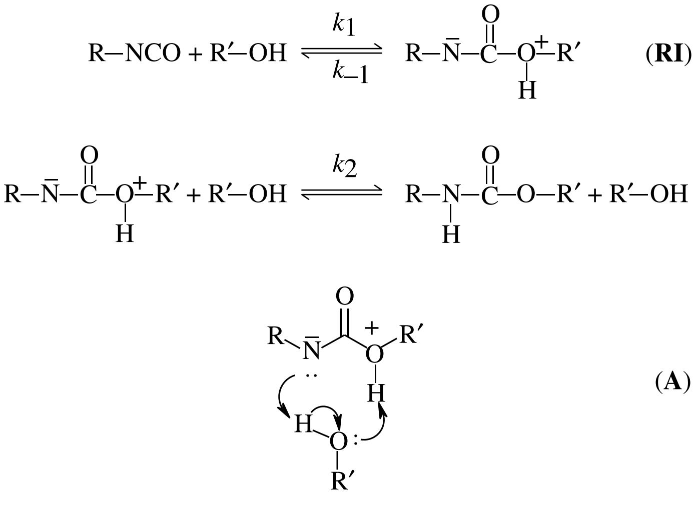
$$\text{rate} = k[\text{R—NCO}][\text{R}'\text{—OH}]^2 \tag{12.2}$$

Such results can be reasonably interpreted in terms of the mechanism provided in Scheme 12.1. Reaction of isocyanate and alcohol (at a rate proportional to k_1) produces a zwitterionic reactive intermediate (**RI**), which can revert to starting materials (k_{-1}) or proceed to product, urethane (k_2). Product formation requires proton transfer from oxygen to nitrogen. The second molecule of alcohol facilitates this transfer by way of a six-membered cyclic activated complex (**A**).

Equation 12.3 is a rate expression that takes into account the sequence of reactions in Scheme 12.1:

$$\text{rate} = k_1[\text{RNCO}][\text{R}'\text{OH}]\frac{k_2[\text{R}'\text{OH}]}{k_2[\text{R}'\text{OH}] + k_{-1}} \tag{12.3}$$

Scheme 12.1



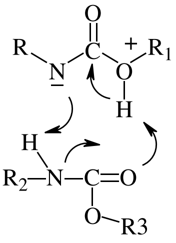
$$\text{R—NCO} + \text{R}'\text{—OH} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{R—}\bar{\text{N}}\text{—}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{—}\underset{\underset{\text{H}}{|}}{\overset{+}{\text{O}}}\text{—R}' \qquad (\textbf{RI})$$

$$\text{R—}\bar{\text{N}}\text{—}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{—}\underset{\underset{\text{H}}{|}}{\overset{+}{\text{O}}}\text{—R}' + \text{R}'\text{—OH} \overset{k_2}{\rightleftharpoons} \text{R—}\underset{\underset{\text{H}}{|}}{\text{N}}\text{—}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{—O—R}' + \text{R}'\text{—OH}$$

If the term k_2[R′OH] is substantially greater than k_{-1}, Eq. 12.3 simplifies to Eq. 12.1. This situation is favored when the alcohol concentration is high, such as at the start of the reaction. If, on the other hand, the term k_{-1} is substantially larger than k_2[R′OH], Eq. 12.3 simplifies to Eq. 12.2 and second-order dependence on alcohol concentration is observed. The latter circumstance is more likely, as alcohol is consumed during the reaction, reducing [R′OH]. As a result, the reaction rate diminishes rapidly as the reaction proceeds (since the rate is proportional to the square of a small, diminishing alcohol concentration). The mechanism in Scheme 12.1 provides an explanation for the strong solvent effects observed. Rates decrease as the hydrogen-bond acceptor potential of solvents increase in the order aliphatic hydrocarbons, aromatic hydrocarbons, esters and ketones, ethers, and glycol diethers. Rates in aliphatic hydrocarbons can be two orders of magnitude faster than in glycol diethers. Hydrogen-bonding of the zwitterionic reactive intermediate **RI** and/or the alcohol with solvent may reduce the rate by reducing the concentration of cyclic activated complex **A**. The mechanism in Scheme 12.1 is also consistent with the higher reactivity observed for aromatic isocyanates. When R is an aromatic group, the negative charge on nitrogen in **RI** is delocalized in the π-electron system of the aromatic ring, resulting in a lower energy (by resonance stabilization) for **RI** and a faster rate of urethane formation relative to aliphatic isocyanates.

Rate constants reported in the literature for reactions of alcohols with isocyanates are commonly apparent initial second-order rate constants. Initial rate constants provide a useful way of comparing reactivities without becoming involved in the complexities of the kinetics, provided that comparisons are made in the same solvent and the same initial concentrations of alcohols and isocyanates. Unfortunately, rate constants are sometimes compared which were determined in different solvents and/or at different initial concentrations. Such comparisons can be misleading.

The kinetics of the isocyanate-alcohol reaction are even more complex than discussed thus far, since the reaction is autocatalyzed by the urethane being formed. Another cyclic transition state, **B**, could be involved, in which a molecule of urethane facilitates proton transfer from oxygen to nitrogen in the zwitterionic reactive intermediate **RI**.



(**B**)

The autocatalyzed reaction would follow third-order kinetics but would be first order in alcohol. The decline in alcohol concentration would be offset by the increase in urethane concentration as the reaction proceeds. The apparent rate constant would change through the course of the reaction depending on the rate constant for the reaction involving activated complex **A** in comparison with that for complex **B**. Sato studied the reaction of various isocyanates with methyl alcohol in di-*n*-butyl ether [7]. In the absence of added catalyst, his results can be expressed by Eq. 12.4, where *a* and *b* are the initial concentrations of isocyanate and methyl alcohol, *x* is the concentration of product (urethane), and k_2 represents the rate constant of the autocatalytic reaction.

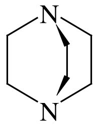
$$\frac{dx}{dt} = k_1(a-x)(b-x)^2 + k_2(a-x)(b-x) \tag{12.4}$$

It is assumed that there are no side reactions; therefore, $a - x$ in Eq. 12.4 equals [RNCO] in Eq. 12.2, and $b - x$ equals [R′OH]. In most cases studied by Sato, k_2 was larger than k_1, but in a few cases, it was comparable. When k_2 is substantially larger, the second term in Eq. 12.4 dominates in the later stages of the reaction (as the urethane concentration builds up). Sato's studies were done in di-*n*-butyl ether; it would be of interest to know what changes in the rate constants would result from changes in solvent polarity. Sato reported that autocatalysis is more important for aliphatic than for aromatic isocyanates, although the rate constants for autocatalysis were similar [7]. This results from the higher reactivity of aromatic isocyanates with alcohols (k_1), which reduces the relative importance of autocatalysis.

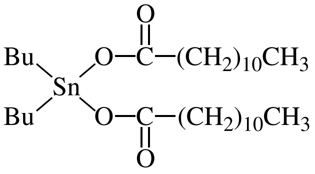
12.2.2. Catalysts

Reactions of isocyanates with alcohols are catalyzed by a variety of compounds, including bases (tertiary amines, alkoxides, carboxylates), metal salts and chelates, organometallic compounds, acids, and urethanes. Most primary aliphatic amines react so rapidly with isocyanates at room temperature that their reaction rates and effect of catalysts have not been determined. The reactions of amines with isocyanates are catalyzed by carboxylic acids and water.

The most widely used catalysts in coatings are tertiary amines, commonly diazabicyclo[2.2.2]octane (DABCO[1]), and organotin(IV) compounds: most commonly, dibutyltin dilaurate (DBTDL).



DABCO



DBTDL

The mechanisms by which these and other catalysts operate are controversial. A reasonable explanation for catalysis by amines is that they facilitate proton transfer from the alcohol to the isocyanate (and similarly to alcohols and urethanes). Proton removal from the alcohol may occur during reaction with the isocyanate, thereby avoiding formation of the positive charge on oxygen and lowering the energy of the reactive intermediate, which may proceed to product by a proton transfer from the protonated amine, as shown in Scheme 12.2 [8]. Proton removal by amines at an earlier stage than by alcohols and urethanes is reasonable, owing to the greater basicity of amines.

Sato included catalysts in the study described in Section 12.2.1 [7]. For triethylamine catalyzed reactions of isocyanates with methyl alcohol in dibutyl ether, Sato's data fit

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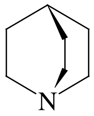
[1] DABCO is Air Products general trademark for a series of different catalysts, including diazabicyclo[2.2.2]octane, which is DABCO L-33. However, DABCO has become widely used just for diazabicyclo[2.2.2]octane.

Eq. 12.5, where k_3 and (cat) represent the rate constant of the catalyzed reaction and the concentration of catalyst, respectively:

$$\frac{dx}{dt} = k_1(a - x)(b - x)^2 + k_2(a - x)(b - x) + k_3(\text{cat})(a - x)(b - x) \qquad (12.5)$$

If the catalyst is effective, k_3 is larger than k_1 or k_2, and when the catalyst concentration is sufficient, the rate is governed by the third term and is first order in [OH]. This is generally observed in amine catalyzed reactions. The mechanism in Scheme 12.2 is consistent with the third term of rate Eq. 12.5. Amine basicity is not the only factor since DABCO, a weaker base, is a more active catalyst than triethylamine. The nitrogen electron pairs are more readily accessible with DABCO than with triethylamine, which could account for the higher catalytic activity. This possibility, that both nitrogen basicity and electron accessibility are important factors, is supported by the even higher catalytic activity (relative to DABCO) of 1-azabicyclo[2.2.2]octane (quinuclidine), which has both the nitrogen accessibility of DABCO and the high basicity of triethylamine.

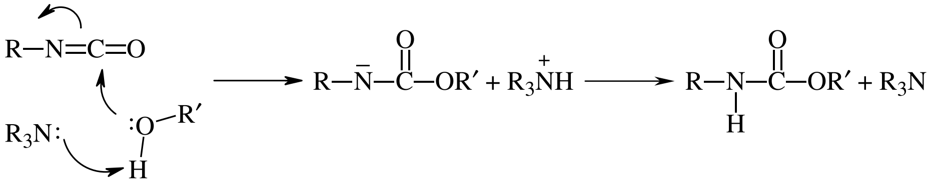


Quinuclidine

Catalysis of urethane formation by 1-8-diazabicyclo[5.4.0]undec-7-ene (DBU) is reported to result from the formation of the ammonium ion and a hydrogen-bond type complex with the polyol [9].

Comparisons are complicated because catalysts also catalyze allophanate formation and trimerization of aromatic isocyanates to form isocyanurates. For example, reaction of phenyl isocyanate with n-butyl alcohol (at 50°C in acetonitrile) in the presence of pentamethyldipropylenetriamine (PMPTA) yielded 30% urethane, while 70% of the isocyanate was converted into triphenylisocyanurate [10]. On the other hand, when DABCO was used as a catalyst, the urethane was the principal product, with a small amount of an allophanate also formed. Possibly, urethane formation is favored by sterically accessible amines (e.g., DABCO) and isocyanurate formation is less sensitive to this factor. The zinc complex of 2,4-pentanedione [Zn(AcAc)$_2$], tin octanoate, and quaternary ammonium compounds such as tetramethylammonium octanoate specifically catalyze allophanate formation [11]. (Rate constants for the formation of urethanes, allophanates, and isocyanurates for a variety of catalysts and co-catalysts are given in Ref. [11].)

Scheme 12.2



Acids also catalyze the reaction, perhaps by protonating the isocyanate group. Carboxylic acids act as catalysts [12]. Acetic acid has been reported to be a more effective catalyst than a carboxylic acid–functional polyether polyester [13]. The effect of temperature on the reaction rate of *m*-chlorophenyl isocyanate with *n*-butanol in heptane catalyzed with acetic acid has been studied and mechanisms proposed for the nonlinear increase in reactivity with temperature [14]. The effect is related to the reduced dimerization of acetic acid at higher temperature. Stronger acids are even more effective [15]. Phenyl acid phosphate is less effective as a catalyst than DBTDL at temperatures below 100°C, but is more effective at 130°C. Blocking the acids by forming amine salts extends the pot life without reducing the cure rate at 130°C.

Catalysis by organometallic compounds of many types has been reported. The majority of these are organotin compounds. Of the many metal derivative catalysts, DBTDL is the most widely used in coatings. It is soluble in a wide range of solvents, comparatively low in cost, colorless, and in general, highly effective at levels on the order of 0.05 wt%. DBTDL promotes urethane formation without promoting allophanate formation [16] or trimerization [10]. Being hydrophobic, it is said to favor urethane formation over hydrolysis of the isocyanate when moisture is present. Dimethyltin diacetate (DMTDA) is usually a somewhat more effective catalyst than DBTDL and is particularly useful with sterically hindered isocyanates. Tin compounds are effective catalysts for reaction of alcohols with aromatic isocyanates and are even more effective with aliphatic isocyanates. Although aromatic isocyanates are more reactive than aliphatic isocyanates in uncatalyzed reactions with alcohols, the reactivity of aliphatics and aromatics can be roughly equal with DBTDL catalysis. On the other hand, amine catalysts are more effective with aromatic than aliphatic isocyanates.

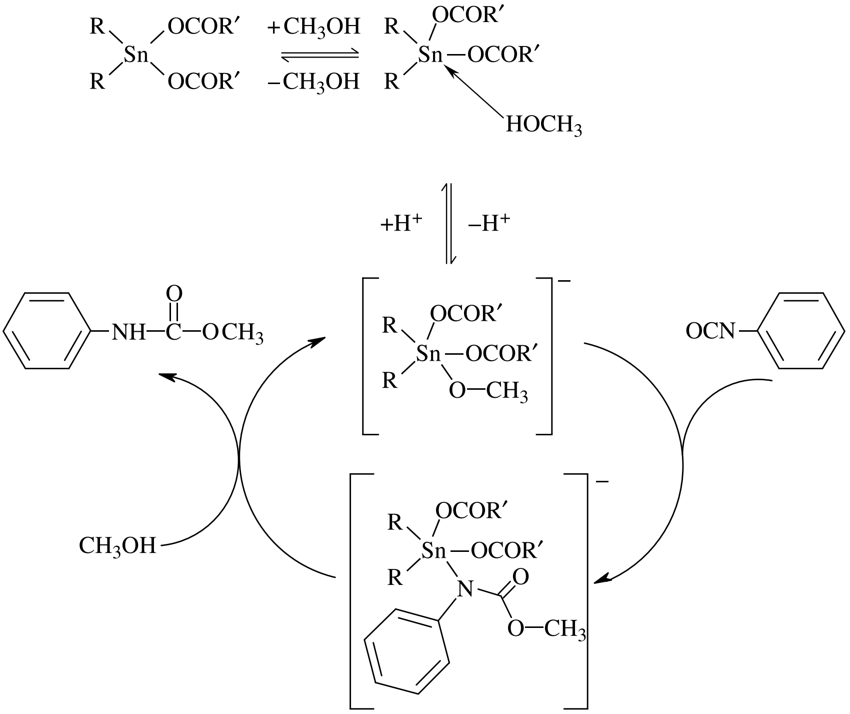
Many mechanisms have been proposed for the catalytic activity of tin compounds, but none has been accepted universally. A plausible proposal is based on studies of reaction of phenyl isocyanate with excess methyl alcohol using dibutyltin diacetate (DBTDA) as catalyst [17]; see also Ref. [18]. The reaction rate is first order in isocyanate concentration and half order in both alcohol and catalyst concentration. Restating the kinetic equation in the same form used thus far gives Eq. 12.6:

$$\frac{dx}{dt} = k_3(\text{cat})^{1/2}(a - x)(b - x)^{1/2} \tag{12.6}$$

Based on kinetic results and the observation that the rate was suppressed by the addition of acid, the mechanism in Scheme 12.3 was suggested. The mechanism involves sequential complexation of alcohol (with loss of H^+) and isocyanate to the tin. The proposed proton loss is consistent with the reduction observed in the activity of tin catalysts in the presence of carboxylic acids. Presumably, addition of H^+ favors decomplexation of alcohol and reversion to starting materials. This proposal is also consistent with the observation that tin compounds are not effective catalysts for reactions of isocyanates with amines.

Coordination of the isocyanate with tin is consistent with the roughly equivalent reactivity of aliphatic and aromatic isocyanates observed with tin catalysts, since stabilization of the reactive intermediate by electron delocalization with the aromatic ring is eliminated as a major factor. Furthermore, tin activates both the alcohol and isocyanate, whereas amine catalysts probably activate only the alcohol by facilitating proton removal.

Scheme 12.3



The rate dependence on alcohol concentration has important implications on the pot life versus curing schedule with isocyanates. If the dependence changes from first to second order (characteristic of the uncatalyzed reaction), the rate will diminish rapidly as the reaction nears completion. With less sensitive half-order dependence, as reported for tin catalysis, the rate at high concentrations (during storage) will be lower and will not slow down as much as the reaction proceeds to completion, thereby favoring both a longer pot life and a shorter cure time (or lower cure temperature). The first-order dependence with amine catalysis results in an intermediate situation. Unfortunately, there are only limited reports in the literature of the effect of solvent on rates of catalyzed reactions.

Another mechanism that has gained favor in recent years is via alcoholization of the organotin ester to the organotin alkoxide:

$$\text{R—OH} + \text{R}'_2\text{Sn}(\text{O}_2\text{CR}'')_2 \rightleftharpoons \text{R}'_2\text{Sn}(\text{O}_2\text{CR}'')_2 + \text{R}''\text{CO}_2\text{H}$$

$$\text{R—OH} + \text{R}'_2\text{Sn}(\text{OR})(\text{O}_2\text{CR}'') \rightleftharpoons \text{R}'_2\text{Sn}(\text{OR})_2 + \text{R}''\text{CO}_2\text{H}$$

Dibutyltin di(2-ethylhexanoate) interacts with an alcohol to form tin alkoxides (mono or di), which then react with the isocyanate to give complexes, which in turn react with the alcohol to give the urethane [19]. The effect of solvent on the catalysis of the reaction of phenyl isocyanate with cyclopentanol in different solvents indicates that the principal reaction pathway is through the dialkyltin monoxide monoester.

The catalytic effect of a series of dibutyltin derivatives on the rate of reaction of phenyl isocyanate with ethylene glycol in THF has been published [20]. Catalytic activity decreased in the order methoxide > laurate > perfluorobutyrate > benzene sulfonate >

TABLE 12.1. Tensile Modulus (psi) (% Elongation-to-Break)

Catalyst	Initial	1 Week	4 Weeks
DMTDC	2450 (270)	1900 (300)	800 (330)
DBTDL	1900 (270)	450 (400)	200 (436)
DBTM	1400 (280)	450 (330)	250 (400)

chloride > hexafluoroarsenate; that is, it decreased with increasing acid strength of the substituent. In the presence of dimethylbenzylamine, rates increased but the order changed to perfluorobutyrate > methoxide = laurate > chloride = hexafluoroarsenate.

Cyclic organotin compounds such as 3,3-di-*n*-butyl-3-stanna-2,4-dioxa-8-thio-spiro[5.3]nonane have been patented as catalysts for the reactions of sterically hindered isocyanates with alcohols [21]. A model compound reaction example given was *t*-butyl isocyanate with 2-ethoxyethyl alcohol.

Catalysts prepared by reacting DBTDL with *p*-toluenesulfonylisocyanate can be used to make storage stable mixtures of polyisocyanate and catalyst in contrast to DBTDL [22]. The catalyst is readily hydrolyzed with water or alcoholized with an alcohol. The protected catalyst can be used in moisture curing coatings.

Metal chelates of 2,4-pentanedione [acetylacetone (AcAc)] also serve as catalysts. It has been proposed that AcAc metal derivatives such as $Zr(AcAc)_4$ activate the hydroxyl group followed by insertion of isocyanate [23]. This catalyst is selective, significantly favoring reaction with hydroxyl groups over reaction with water, so it is particularly useful in two package (2K) waterborne urethane coatings. No significant synergy was observed between $Zr(AcAc)_4$ and tertiary amines [24]. The catalytic effect of $Zr(AcAc)_4$ on the reaction of butanol and butyl isocyanate is reduced by adding excess acetyl acetone or acetic acid [25]. The effect of solvent composition on the reaction rate is reduced substantially by metal AcAc catalysis.

Many metal salts have been shown to be catalysts. There is a wide variation in the extent of catalysis of the NCO–OH reaction, depending on the diisocyanate and catalyst. Stannous octanoate and lead octanoate are particularly effective although less so than DBTDL.

Increased catalyst concentration not only increases reaction rate but can also decrease hydrolytic stability of films after application and curing. The effect is most evident in polyester–polyurethane films. Table 12.1 shows the effect on modulus (a measure of cross-link density) of exposure of films of $H_{12}MDI$–polyestertriol to 95% relative humidity at 70°C for various catalysts: DMTDC, DBTDL, and dibutyltin methoxide (DBTM) [26]. The decreases in modulus observed seem reasonable, since the initial step in the hydrolysis of a urethane may well be the reverse reaction to the reaction of an isocyanate with water. Further studies are warranted with other catalysts, as well as with films cured without catalyst.

Amines can not only catalyze the formation of urethanes, they can also catalyze the thermal decomposition of the polymer. For example, substantial reduction in the physical properties of polyurethane elastomers have been reported when samples are exposed to temperature above 105°C for long periods of time (400 hours), due to the presence of DABCO catalyst [27].

12.2.3. Interrelationships in Catalysis

Combinations of DABCO and DBTDL often act synergistically; that is, the effect of the combination is greater than would be predicted by the sum of the individual effects of the two catalysts. It has been suggested in a study of the mechanism with DBTDL and

DABCO that a highly active complex forms between the tin and the amine. In the presence of an alcohol it is suggested that this complex facilitates the alcoholysis of tin carboxylates to the highly active tin alkoxides, which then rapidly adds isocyanate across the tin–oxygen bond to form the carbamate adduct of tin. The adduct breaks up with another molecule of alcohol to form the urethane and regenerate the tin alkoxide [28]. Metal acetylacetone complexes act synergistically with DBTDL [29].

To increase pot life without reducing cure rate significantly, it is common to add volatile inhibitors to a coating. The mechanism of the inhibition of organotin catalysis of urethane formation by carboxylic acids has been investigated [30]. The pot life of DBTDL catalyzed coatings can be extended by addition of small amounts of volatile carboxylic acids, such as formic or acetic acids; after application the acids evaporate and there is little, if any, effect on cure rate. Pot life can also be extended by the addition of 2,4-pentanedione (acetylacetone) with minimal effect on dry times. For example, coatings with improved pot life and good curing are formulated with 2,4-pentanedione and DBTDL [31].

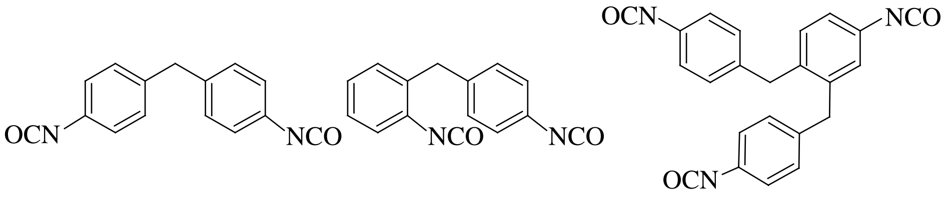
The use of amine salts as blocked catalysts for the reaction of aromatic isocyanates with polyols in 2K systems has been patented [32]. For example, the triethyl amine (TEA) salt of dibutyl phosphate in an MDI–polyether polyol 2K coating had a pot life of 45 minutes at 25°C, in contrast to 3 minutes with a stannous chloride–catalyzed system. Both coatings cured to the same degree at 120°C. Presumably, at the higher temperature there was sufficient free amine and dibutyl phosphate for both to act as catalysts.

12.3. ISOCYANATES USED IN COATINGS

Aromatic and aliphatic isocyanates are used in coatings; the former are less expensive and the latter provide films with better color retention and exterior durability.

12.3.1. Aromatic Isocyanates

The aromatic isocyanates most widely used in coatings are based on MDI. MDI is available in several grades: bis(4-isocyanatophenyl)methane, a mixture of 55% of the 2,4′ isomer and 45% of the 4,4′ isomer; and several oligomeric (frequently called polymeric) MDI with longer chains of methylene phenyl groups. MDI is also used as a prepolymer with polyether polyols. The volatility (particularly of the oligomeric grades) is low enough to reduce toxic hazard, especially as compared to toluene diisocyanate (TDI).



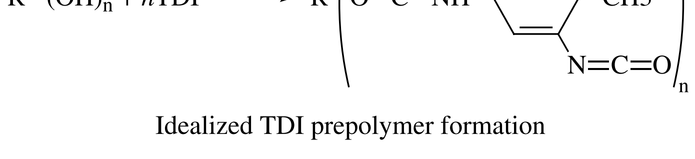
4,4′-and 2,4′-MDI isomers and an example of an oligomer

The most common grade of commercial TDI consists of a mixture of about 80% 2,4- and 20% 2,6-diisocyanate isomers. Nearly pure 2,4-TDI is also available at a premium price. Due to toxic hazards, TDI is not used as such in final coating formulations. For coatings in which unreacted isocyanate groups are needed, TDI is converted into derivatives of higher molecular weight and higher functionality. Higher molecular weight reduces the toxic hazard, and the higher functionality yields solvent resistant films more rapidly.

2,4-TDI has the advantage of a differential in reactivity between the *ortho*- and the *para*-isocyanate groups with alcohols, which makes possible synthesis of isocyanurates and prepolymers with narrower molecular weight distribution than with diisocyanates, in which the isocyanate groups are equally reactive. At 40°C, the *para*-isocyanate group of TDI is about seven times more reactive than the *ortho* group. Furthermore, no matter which isocyanate group reacts first, the second group is less reactive than the first. Overall, after reaction of the *para*-isocyanate, the remaining *ortho* group is 20 times less reactive than a *para*-isocyanate on a second TDI. The difference in reactivity decreases as the temperature increases; at temperatures above 100°C, the *ortho*- and *para*-isocyanate groups have similar reactivities. Thus, for maximum selectivity a prepolymer should be prepared at a low temperature; of course, this means that the reaction is slow. Catalysts can be used, but the catalyst stays in the product and therefore sets a lower limit on the amount of catalyst in the final formulation.

Studies of the reaction of TDI with alcohols catalyzed with tertiary amines and with organotin compounds showed that the amines tended to equalize the reactivity of the two NCO groups [33]. In a study of the ratio of *para*-to-*ortho* urethane formation in the reaction of TDI with *n*-butanol in benzene with several catalysts, the lowest ratio (2.8) was obtained with $SnCl_4$, the highest ratio (9.9) with tin octanoate, DBTDL, and triisopentylphosphine. For the uncatalyzed reaction at 20°C the ratio was 11.5 [34].

Almost any polyhydroxy compound can be reacted with TDI to make prepolymers. Low molecular weight hydroxy-terminated polyesters or mixtures of diols and triols are commonly used. For safety, the levels of unreacted TDI in the prepolymer must be very low. Low levels of TDI can be assured by using an NCO/OH ratio below 2 : 1 and pushing the reaction to completion, but chain extension (caused by reaction of both NCO groups of some TDI molecules) increases the molecular weight of the product. An alternative process, used when low molecular weight prepolymers are needed, is to react the polyhydroxy compound, often trimethylolpropane (TMP), with a large excess of 2,4-TDI, then remove the excess TDI using a vacuum wiped-film evaporator. Very low levels of free TDI and minimal chain extension are attainable, yielding low molecular weight products suitable for high-solids coatings.



Idealized TDI prepolymer formation

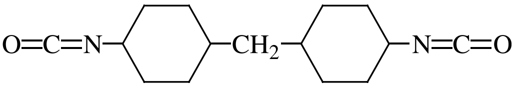
The isocyanurate derived from TDI made by trimerizing TDI (Section 12.1) has a lower toxic hazard than that of monomeric TDI. The trimerization reaction occurs exclusively with the *para*-isocyanate group.

12.3.2. Aliphatic Isocyanates

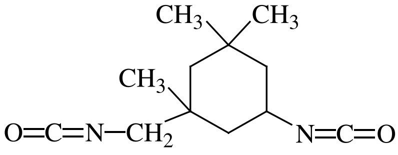
The principal aliphatic isocyanates used are 1,6-hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI), bis(4-isocyanatocyclohexyl)methane (H_{12} MDI), 1,3-xylylenediisocyanate (XDI), tetramethyl-*m*-xylidene diisocyanate (TMXDI), *m*-isopropenyl-α,α-dimethylbenzylisocyanate (TMI), and 2,2,5-trimethylhexane diisocyanate (TMHDI). Diisocyanates are usually converted to derivatives before use in coatings to increase functionality and reduce toxic hazard.

$O{=}C{=}N{-}(CH_2)_6{-}N{=}C{=}O$

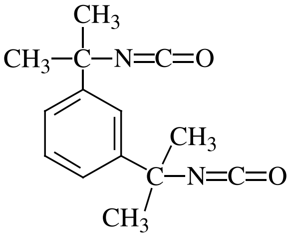
HDI



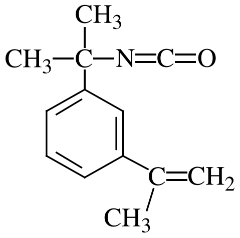
H_{12}MDI



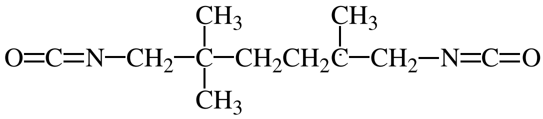
IPDI



TMXDI



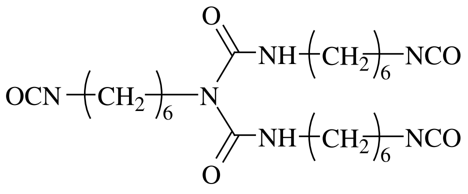
TMI



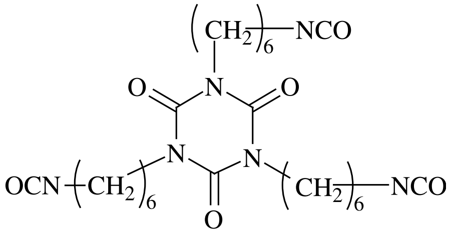
$$O{=}C{=}N{-}CH_2{-}\underset{CH_3}{\overset{CH_3}{C}}{-}CH_2CH_2\overset{CH_3}{C}{-}CH_2{-}N{=}C{=}O$$

TMHDI

HDI is especially hazardous and is handled on a large scale only in chemical plants. The first less hazardous derivative was a biuret, which can be made by reacting HDI with a small amount of water and removing the excess HDI. The structure of HDI biuret shown below is idealized; commercial products contain varying fractions of oligomeric biurets. (The presence of oligomeric biurets makes the average functionality higher than 3.) These polyfunctional isocyanates give coatings with good color retention and weather resistance. The viscosity of an early commercial product was about 11.5 Pa•s at 20°C. Grades with lower average molecular weights (and average functionalities nearer to 3) are available with viscosities as low as 1.4 Pa•s.



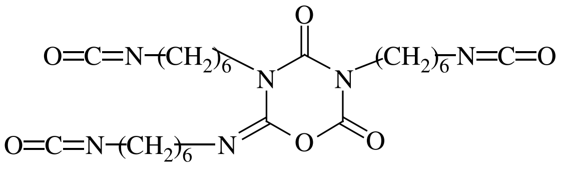
HDI biuret (and oligomers)



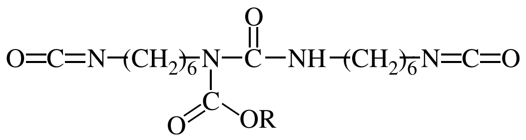
HDI isocyanurate (and oligomers)

HDI isocyanurates are used on a larger scale. The isocyanurate gives coatings with greater heat resistance and even better long-term exterior durability than does HDI biuret. Commercial products contain oligomeric material, and average functionality is over 3. Grades with lower oligomer content with viscosities as low as 1 Pa•s are available.

With ammonium fluoride as a catalyst, an isomeric trimer, an iminooxadiazenedione (called an unsymmetrical trimer) of HDI, is made as an approximately 50 : 50 mixture with HDI isocyanurate. It has the advantage that viscosity at the same oligomer content is lower than that of the corresponding HDI isocyanurate: 1 Pa•s versus 3 Pa•s [35]. A very low viscosity unsymmetrical trimer with a viscosity of 0.7 Pa•s has been made available, it is useful in very high-solids coatings and because of the low viscosity is easily incorporated in 2K waterborne urethane coatings [36].



Allophanate derivatives of HDI and IPDI are another type of polyfunctional isocyanate. They are made by reacting an alcohol or diol with excess isocyanate, then removing unreacted diisocyanate with a wiped film evaporator giving an isocyanate-terminated allophanate [37]. The properties can be varied by using different alcohols to make the starting urethane, to make the compounds with different R substituents shown in the structure. For example, the cetyl alcohol urethane from HDI yields an allophanate diisocyanate that is soluble in aliphatic hydrocarbons. Derivatives with higher functionality are made by reacting a glycol with excess diisocyanate.



$$O{=}C{=}N{-}(CH_2)_6{-}\underset{\substack{|\\ C(=O)OR}}{N}{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NH{-}(CH_2)_6{-}N{=}C{=}O$$

The uretdione dimer of HDI also has lower volatility with low viscosity and can be used for cross-linking in ambient cure coatings. Very low viscosity grades (<100 mPa•s) are reported to permit formulation of very low VOC coatings [38].

Commercial IPDI is a mixture of *Z* (*cis*) and *E* (*trans*) isomers in a 75 : 25 ratio. The isomers are difficult to separate. Isophorone diisocyanate has two different types of NCO groups. Studies performed under different conditions show that with DBTDL catalysis, the secondary NCO group of both *Z* and *E* isomers are more reactive than the primary NCO group [39–41]. The selectivity decreases with increasing temperature, and selectivity is greater with *sec*-butyl alcohol than with *n*-butyl alcohol [41]. DABCO [39] promotes selective reaction of the primary isocyanate group of IPDI in contrast to other amines [40] and DBTDL [41], where selectivity favors reaction with the secondary isocyanate groups. Selectivity decreases with increasing temperature [41]. High selectivity is particularly important in making IPDI prepolymers when low molecular weight and narrow distribution of molecular weight are desired. It was concluded that the optimal conditions for prepolymer synthesis based on IPDI are temperatures between 40 and 60°C using DBTDL catalyst.

Isocyanurate derivatives of IPDI analogous to the HDI isocyanurates discussed above are widely used cross-linkers. The rigidity of IPDI affords films with higher T_g. By blending IPDI and HDI isocyanurates, formulators can dial the T_g desired for a particular application.

Bis(4-isocyanatocyclohexyl)methane) ($H_{12}MDI$) is less volatile than HDI and IPDI and is sometimes used as a free diisocyanate in coatings to be applied by roll coating but not by spray coating. It is a mixture of stereoisomers; since both isocyanato groups are secondary, reactivity is lower than HDI or IPDI.

XDI, TMXDI, and TMI have aromatic rings, but give color retention and exterior durability equivalent to those of aliphatic isocyanates. The exterior durability of their urethanes probably results from the absence of isocyanate groups directly substituted on the aromatic ring, as well as from the absence of abstractable hydrogens on the carbons adjacent to nitrogen in the cases of TMXDI and TMI. Since the isocyanate group is on a tertiary carbon, the reactivity is lower than that of less sterically hindered aliphatic isocyanates. This difference can be offset by using higher catalyst levels and sterically accessible tin catalysts such as DMTDA instead of DBTDL. TMXDI is offered as a low molecular weight, essentially diisocyanate-free prepolymer with trimethylolpropane. TMI is used as a comonomer with acrylic esters to make 2000 to 4000 MW copolymers with 40 to 50 mole% TMI; thus, each molecule has several isocyanate groups [42].

12.4. TWO PACKAGE SOLVENTBORNE URETHANE COATINGS

The largest volume of urethane coatings comprises two package (2K) coatings that are mixed just before application. One package contains the polyol (or other coreactant), pigments, solvents, catalyst(s), and additives; the other contains the polyisocyanate and moisture-free solvents. Sometimes, the catalyst is in a separate third package so that the cure rate can be adjusted for variations in ambient conditions. While the major reaction is formation of urethane cross-links, some urea cross-links result from reaction of atmospheric water with the isocyanate. 2K urethane coatings can be formulated for ambient-temperature cure or baking coatings.

In many applications the components are mixed at the start of a work shift. Viscosity starts to increase as soon as they are mixed, but the coatings must remain sprayable for 4 hours or for 8 hours after mixing. They are said to have a 4- or 8-hour *pot life*. For factory application the pot life can be considerably shorter when special equipment is used to mix the components just before spraying. If a very fast cure rate at relatively low temperatures is needed, reactive coreactants and/or high catalyst levels are used, and the pot life is very short. Such formulations can be applied using special spray equipment in which the two packages are fed to a spray gun by separate proportioning pumps and mixed inside the gun just before they are sprayed or by impingement mixing as they are sprayed. Such spray equipment is expensive, and care is required to assure that the proper ratios are fed and thoroughly mixed.

An important variable in 2K polyisocyanate–polyol coatings is the NCO/OH ratio. The ratio is commonly called *indexing*, or *the index*. In ambient cure systems, it is often found that a ratio on the order of 1.1 : 1 gives better film performance than a 1 : 1 ratio. A probable reason is that part of the NCO reacts with water from solvent, pigment, or air to give urea cross-links. To the extent that this happens, two hydroxyls are unreacted for each water molecule; use of excess NCO minimizes residual unreacted hydroxyl groups. Solvent resistance is also improved. Since polyisocyanates are typically lower in viscosity than the polyol, excess NCO gives a lower VOC [4]. Some finishes (e.g., aircraft finishes) are formulated with NCO/OH ratios as high as 2 : 1. The resulting reduced hydroxyl concentration gives longer pot life. It is possible that the high mobility of water and the reactivity of amine groups resulting from the water–isocyanate reaction favor faster reaction rates at higher T_g values than are possible with only the hydroxyl–isocyanate reaction. Since the rate of reaction of isocyanates generally decreases in the order primary alcohols $>$ secondary alcohols $>$ 2-hydroxyethyl ether alcohols $>$ 2-hydroxypropyl ether alcohols, the required excess of NCO over OH tends to increase in that order.

Almost any hydroxy-functional coreactant can be used; hydroxy-terminated polyester and hydroxy-substituted acrylic resins are most common. In general terms, polyesters permit higher solids and give films with greater solvent resistance and better adhesion to metals. Acrylics provide faster dry, lower cost (since their equivalent weight can be made higher than that of polyesters, resulting in the need for less of the more expensive isocyanate), and better exterior durability, resulting from superior hydrolytic and photochemical stability.

Other resins are also used in 2K coatings. Alkyd resins have unreacted hydroxyl groups and their rate of dry can be accelerated by adding a polyisocyanate such as the isocyanurate trimer of IPDI just before application. Nitrocellulose (shipped wet with plasticizer instead of ethyl or isopropyl alcohol) is used in formulating cross-linking furniture lacquers with isocyanates. Bisphenol A (BPA) epoxy resins are also cross-linked with isocyanates through their hydroxyl groups. Although hydroxy-terminated polyethers are widely used in urethane foams, they have limited use in coatings, since the resulting coatings show high moisture vapor permeability, relatively poor exterior durability, and are soft as a result of the low T_g of the polyethers.

As cross-linking proceeds, the T_g of the film increases. If the T_g of a partially reacted system is near the temperature at which cross-linking must occur, the rate of urethane formation becomes mobility controlled and the cure rate is slowed. If the T_g of the fully reacted system is significantly above the cure temperature, the reaction virtually stops before the cross-linking reaction has gone to completion [43]. Since in many ambient cure coatings, one wants a coating with a T_g somewhat above the curing temperature, selection of a combination of polyisocyanate and polyol that provides an appropriate final T_g is critical. A polyisocyanate with relatively flexible aliphatic chains (such as HDI isocyanurate) can be used with a relatively high T_g acrylic or polyester. On the other hand, a polyisocyanate that yields relatively rigid cross-link segments [such as the TMP/α,α-tetramethylxylyl diisocyanate (TMXDI) prepolymer] requires a lower T_g acrylic or polyester. Mobility control of reactions is more likely to be encountered in ambient temperature cure coatings than in baked coatings. Another approach to balancing T_g is to use mixtures of IPDI and HDI isocyanurates [44].

With 2K coatings there is always a compromise between pot life and curing time (Section 2.3.2). Several formulating variables are available to increase pot life with little effect on cure time. Concentrations of reactive groups should be kept as low as possible, but this becomes more difficult as one formulates to increasingly higher solids. Using mixed polyol/moisture curing systems helps. Since isocyanate–alcohol reactions proceed most slowly in media with high levels of hydrogen-bond accepting groups, strong hydrogen-bond accepting solvents should be selected to the extent possible. After application, as the solvent evaporates, the medium becomes less hydrogen-bond accepting and the reaction rate increases accordingly. This strategy serves the purposes both of extending pot life and of promoting reactivity after application. Since solvents with greater hydrogen-bond accepting strength tend to have higher viscosities, solvents having intermediate hydrogen-bond accepting strength usually give a better compromise between solids and pot life [12].

Organotin catalysts are generally preferable to amine catalysts (Section 12.2.2) because reaction rates often depend on alcohol concentration to the one-half power with organotin catalysts and to the first power with amine catalysts. Since the effectiveness of tin catalysts is reduced by carboxylic acids, one can add a volatile acid such as acetic or formic acid to the formulation. The acid inhibits reaction during the pot life stage but evaporates during application so that the inhibiting effect disappears. Similarly, 2,4-pentadione increases pot life by chelating with tin compounds and evaporating after application (Section 12.2.2.1).

The availability of lower viscosity isocyanate cross-linkers (Section 12.3.2) makes possible the formulation of higher-solids 2K coatings. However, one must consider not just the viscosity of the cross-linker, but also that of the combination of polyol and cross-linker. In some cases, a lower viscosity cross-linker also has a lower equivalent weight; this means that the weight ratio of cross-linker to polyol must be reduced to maintain the same NCO/OH stoichiometric ratio [45]. Since the polyol often has a much higher viscosity, this reduced ratio can give a higher viscosity, despite the lower viscosity of the cross-linker. Higher solids can be obtained using a somewhat higher viscosity polyisocyanate with a higher equivalent weight.

Reactive diluents are useful in increasing solids. For example, polytrimethylene carbonate polyols have been recommended as reactive diluents for acrylic polyols in coatings cross-linked with HDI isocyanurate. Best results were obtained with relatively low molecular weight triols made by reacting trimethylene carbonate with TMP. VOC was reduced while increasing the film flexibility and maintaining hardness, weather resistance, and mechanical properties [46].

Imines permit formulation of 2K coatings with very high solids, longer pot life, and faster drying than with polyols [4]. They can be used alone or in combination with a hydroxy-functional polyester or acrylic resin [47].

Ketimines react directly with isocyanates to yield a variety of products, depending on the particular reactants and conditions. For example, isobutyl isocyanate reacts with the ketimine derived from methylamine and acetone in 3 hours at 60°C to yield isobutyl methyl urea and a cyclic unsaturated substituted urea [4,48].

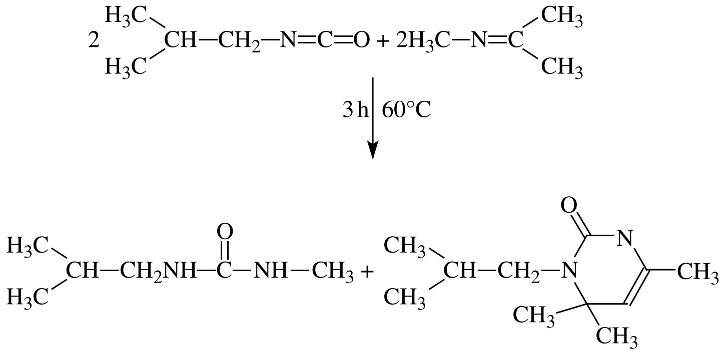
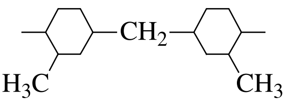
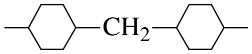
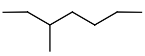


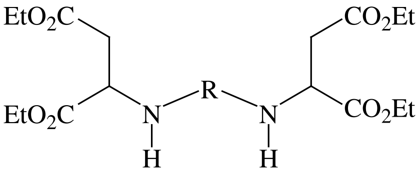
TABLE 12.2. Viscosities (100% Solids, mPa·s at 23°C) and Gel Times of Substituted Polyaspartic Acid Ethyl Esters

R	Viscosity	Gel Time
	1500	>24 h
	1200	2–3 h
	150	<5 min

Aldimines react analogously to ketimines with isocyanates to yield unsaturated substituted ureas [4]. Since aldimines are more stable than ketimines to hydrolysis, the fraction undergoing direct reaction with isocyanate in the presence of water is greater than that with ketimines.

Under conditions where imines can react directly with isocyanates or with water (Section 12.6), the ratio of the two reactions depends on the relative humidity, the time between application and cure, and the curing temperature [4]. The reaction with water releases amine to react with isocyanate and carbonyl compound, which volatilizes. In the direct reaction, carbonyl compound from the imine is not released, hence VOC emissions are lower. The direct reaction is catalyzed more than the water reactions by carboxylic acids, and water and tertiary amines reduce the rate of reaction. The imines have very low viscosities; for example, the bis(methyl isobutyl ketone) ketimine of ethylenediamine has a viscosity of 5 mPa•s and an equivalent weight of 112. Direct reaction is more favored with aldimines, especially above 60°C.

Hindered amines are also used for auto refinish clear coats. The coatings are called *2K urethane coatings*, although the cross-links are dominantly urea cross-links. Polyaspartic esters [3,4] are hindered amines that are used in high-solids coatings.



Plyaspartic esters (R is shown in Table 12.2)

As shown in Table 12.2, the gel time of polyisocyanate–polyaspartic ester combinations depends on the structure of the polyaspartic ester. The pot life of these combinations is increased by the addition of DBTDL [4]. On the other hand, carboxylic acids and water accelerate reaction rates. By proper selection of isocyanate and aspartate and adjustment of inhibitors and catalysts, it is possible to formulate very high solids 2K coatings with a reasonable pot life and fast curing.

12.4.1. 2K Urea Coatings

Polyurea coatings are those in which the final cross-linking reaction is between isocyanate and amine groups to form ureas. The term *2K urea coatings* is used in the maintenance field. Other applications of coatings based on isocyanates and amines—for example, some automotive refinish urethane clear coats—are called *2K urethane coatings* (Section 12.4). Moisture-curable urethanes cure by formation of urea bonds but are not called polyurea coatings.

The pot life of 2K urea coatings depends on the amine(s) and polyisocyanate(s) used. Primary aliphatic amines react too rapidly to be applied with any kind of equipment, aromatic amines can be applied with special equipment, and hindered amines can be used as 2K coatings. In applications such as roof coatings, floor coatings, traffic control paint, and thick-film sag-resistant maintenance coatings, rapid cure is very desirable (Section 33.1). This need has motivated development of equipment that makes it possible to spray apply coatings having very short pot lives (as short as 1 second). 2K urea coatings based on MDI–polyoxypropylene prepolymers with aromatic amines are used in maintenance coatings for which gloss and color retention are not critical. The coatings have the advantages that they cure rapidly even at freezing temperatures, have zero VOC, and have low temperature flexibility [49]. Roofs and floors can be walked on within 30 seconds after they are coated with such polyureas.

Another class of hindered amines is based on the addition of primary amines to polyacrylates such as TMP triacrylate and/or to BPA epoxy resins. A combination of a tertiary C_{10-12} alkylamine and *t*-octylamine, added to TMP triacrylate, followed by the addition of BPA epoxy resin, provide a hindered amine that is used with HDI isocyanurate in a 2K traffic marking paint [50]. The same hindered amine is used with HDI isocyanurate in maintenance top coats. The adhesion to properly prepared metal and concrete is such that no primer is required. The coatings cure even at temperatures as low as −18°C and provide high chemical resistance, which is superior to epoxy–polyamide coatings [49]. A hindered amine mixture based on amine adducts of BPA epoxy and TMP triacrylate was used in formulating 2K coatings with HDI isocyanurate in the other package. The coatings had adequate pot life, tack free time of 2.3 minutes at 25°C, adhesion to a variety of substrates, and good chemical resistance and exterior durability [51].

It is reported that the ureas formed can cyclize to hydantoins, losing alcohols. The resulting film shrinkage could weaken adhesion. To overcome this problem, aspartic ester–amides are recommended and used in 2K traffic marking paint with HDI isocyanurate [52].

12.5. BLOCKED ISOCYANATES

Blocked isocyanates are used as cross-linkers in baked coatings. The general idea is to react an isocyanate with a *blocking group* that prevents it from cross-linking at coating storage temperatures but that releases free isocyanate at bake temperatures. Blocked isocyanates are of major importance in cationic electrodeposition coatings, powder coatings, coatings for electrical wire, and increasingly, 1K automotive coatings. Common blocking agents include 2-ethylhexyl alcohol and 2-butoxyethanol in E-coats and ϵ-caprolactam, 2-butanone oxime [methyl ethyl ketone oxime (MEKO)], and uretdiones in powder coatings. For detailed discussion of these topics, see Sections 27.2 and 28.1.3, respectively.

A series of extensive review articles on blocked isocyanates may be found in Ref. [53]. Although *blocked isocyanate* is the most widely used term, *masked isocyanate* and *capped isocyanate* are sometimes used. The isocyanate group can be “blocked” through one of several methods.

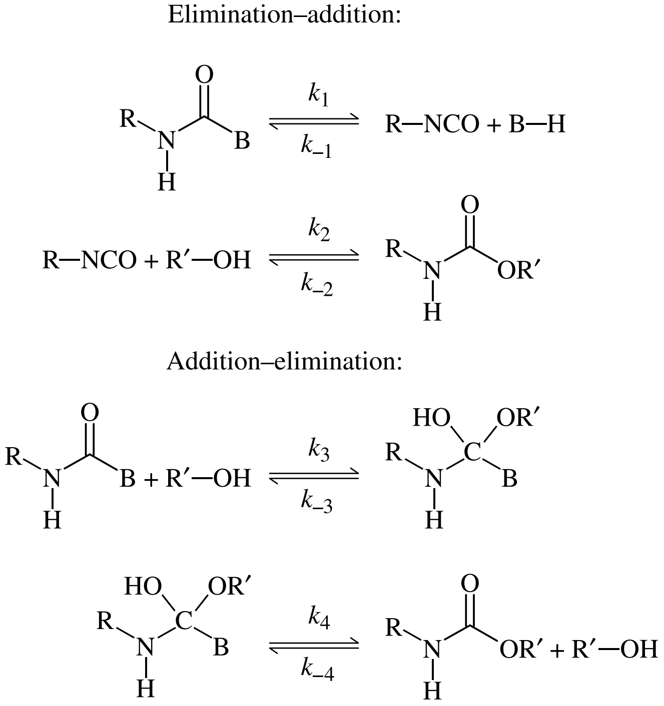
12.5.1. Principles of Blocking and Deblocking

There are two possible modes of reaction of blocked isocyanates with a hydroxyl group: (1) dissociation of the blocked isocyanate to blocking group and the isocyanate, which reacts with the hydroxyl (i.e., elimination–addition), and (2) addition of the alcohol to the blocked isocyanate to yield a tetrahedral intermediate followed by elimination of the blocking agent (i.e., addition–elimination). Both pathways are shown in Scheme 12.4, in which B—H represents the blocking group. Evidence has been presented for both pathways, with elimination–addition being favored by increasing temperature, in accordance with a consideration of the kinetic parameters E_a and A, as discussed in Section 2.3.2 and illustrated in Figure 2.6.

At storage temperatures the equilibrium is almost entirely on the side of the blocked isocyanate, but as temperature increases, the equilibrium shifts to the right, liberating isocyanate to cross-link with the co-reactant. The temperature at which deblocking is rapid depends on the blocking group. It also depends importantly on the relative reactivity and stability of the product of the reaction with the coreactant. Generally, if the final product is more stable than the blocked isocyanate, the reaction will proceed more rapidly and at a lower temperature than it will if the final product is less stable. The rate of cross-linking also depends on how rapidly the blocking agent evaporates from the film.

Kinetic studies of the reactions of blocked isocyanates are complicated by the fact that all, or almost all, of the reactions are reversible, and several side reactions are generally possible. Even the simplest case of heating a blocked isocyanates alone is complicated by possible side reactions of the isocyanates. At high temperatures, there are trimerization

Scheme 12.4



reactions of the isocyanate or reaction with the original blocked isocyanate to form, for example, an allophanate or biuret. These in turn can also thermally decompose through different kinetic pathways. When used with a polynucleophile, the liberated isocyanate can, in addition, react with the urethanes or ureas produced.

The curing schedule required for cross-linking of blocked polyisocyanates with polynucleophiles is dependent on many variables, among them the following:

- Structures of the isocyanate, blocking agent, and nucleophile
- Relative rate of reaction of the nucleophile with the isocyanate compared to the reverse reaction rate of the isocyanate with the blocking agent
- Rates of diffusion and evaporation of the blocking agent, and film thickness
- Polarity and hydrogen bonding potential of the reaction medium (solvents or coreactant)
- Concentrations of reactive groups
- Type and concentration of catalysts
- Extent of side reactions and whether they lead to cross-linking or termination
- Extent of cross-linking required to achieve optimum film properties

Typically, these variables have to be evaluated for each application. A combination that leads to a satisfactory cure for wire enamel in a few seconds at 265°C but may not be appropriate for an automotive clear coat cured in 20 minutes at 140°C.

In view of the many variables, comparisons of published *deblocking temperatures* for different blocked isocyanates must be made with care. One should be sure to compare data obtained by the same method. Furthermore, there is not a threshold temperature; rather, there is a determination of the temperature at which the analytical method used detects some extent of the deblocking and/or cross-linking reaction.

There are many different blocking agents, isocyanates, catalysts, catalyst concentrations, and potential cure temperatures, and times. Studying all of these variables and their interactions would take a prohibitive amount of time and effort by conventional approaches to formulations even with statistical experimental design techniques. As discussed in Chapter 34, such systems are potential candidates for high throughput experimental procedures carried out with combinatorial chemistry apparatus. See Ref. [54] for a discussion of the background of such experiments and their potential applicability to the coatings field. An example of such a study is given in Ref. [55]. In one set of experiments, four isocyanates, five blocking agents, and an acrylic polyol were evaluated with various catalysts at 12 temperatures from 80 to 200°C. With 3,5-dimethylpyrazole as a blocking agent, DBTDL gave the greatest catalytic effect (curing at 110°C) with all four isocyanates. With MEKO-blocked HDI isocyanurate, DBTDL and titanium(IV) 2-ethylhexanoate gave approximately equal results (curing at 140°C). Diethyl malonate–blocked HDI isocyanurate showed no catalysis (cure temperature 90°C). The 128 experiments required to obtain these results were completed in one day.

One needs to remember that reported deblocking temperatures frequently depend on the method of analysis, heating rate, and other variables. Different analytical techniques can give different deblocking temperatures for the same sample.

1. The most common methods for determining deblocking temperature follow some change in physical properties: for example, gel time, the time required for a mixture of

blocked isocyanate and coreactant to gel at a given temperature [56]. Another popular method is to determine the time required for a coating film to achieve solvent resistance sufficient to withstand 200 methyl ethyl ketone double rubs [57].

2. The IR spectra of isocyanates show a characteristic strong absorption band near 2250 cm^{-1}; deblocking temperatures have been reported as the temperature at which this absorption is first detected. The result depends on the rate at which the sample is heated; faster rates of heating give higher apparent deblocking temperatures. Fourier transform infrared spectroscopy (FTIR) has been used to determine reaction kinetics from a single dynamic temperature scan [58].

3. Use of FTIR in combination with dynamic mechanical analysis (DMA) is particularly effective in studying cure mechanisms by allowing the individual deblocking and cross-linking reactions to be observed during the curing process [59]. FTIR has also been used to determine the composition and rate of evolution of gases during cure; the data on blocking agent evolution can be used to calculate kinetic constants.

4. Isothermal thermogravimetric analysis (TGA) has been used to determine kinetic parameters for deblocking reactions [60]. The extent of reaction is followed by tracking weight loss due to the release of the blocking agent.

5. The changes in heat flow associated with deblocking as measured by differential scanning calorimetry (DSC) have been used to study the kinetics of the reaction [61].

6. The chemical species can be tracked directly using solid state NMR; solid state ^{13}C NMR can track the intensity of carbons within the blocking group, which become significantly more intense after the deblocking reaction [62].

7. Since the reaction of amines with oxime-blocked isocyanates is first order, rate constants for deblocking of blocked isocyanates can be determined by following the rate of reaction with amines [69].

8. The reaction of isocyanates with water leads to formation of CO_2; blocked isocyanates are heated in the presence of molecular sieves saturated with moisture, and the lowest temperature at which CO_2 is evolved is reported as the deblocking temperature [63].

Cross-linking may continue after 200 MEK double rubs has been reached, having little effect on MEK rub resistance but leading to further changes in the mechanical properties of films. Such further cross-linking can be followed by film properties, changes in dynamic mechanical analysis (DMA) results, and/or resistance to swelling by solvents. Evidence that a 200 MEK double rub test does not indicate full cure (or even give the same rank order of time to reach 200 double rubs as the time to reach full cure) is given in Ref. [5] by comparisons of these results with the measurement of cross-link density by DMA analysis.

Reaction rates and extents of reaction can be very dependent on volatilization of the blocking agent. Care must be taken in making measurements to ensure that the measurement conditions reflect the use conditions, including film thickness and the ability of the blocking agent to evaporate. When a sample of MEKO-blocked HDI isocyanurate was heated at 140°C while taking a time resolved series of IR spectra, the spectra showed that the NCO peak at 2250 cm^{-1} grew steadily. However, when the same blocked isocyanate was heated in a thin film but in a covered ATR cell, there was insignificant generation of isocyanate until after removal of the cover slide. Immediately the peak at 2250 cm^{-1} began to increase [64].

This inhibition of deblocking reactions has clear implications for studying blocked urethane systems in coatings. A related effect should be expected from increased film thickness. In this case, slow diffusion of the blocking group through the reactive medium could result in slower cure. Thus, analytical techniques used for tracking the deblocking kinetics in thin films should (1) allow for evaporation of the blocking group and (2) be of a film thickness comparable to that used in the final application. Not all systems that use blocked isocyanates require that the blocking group leave as it does in films. Studies related to shelf stability, adhesives, and thick section plastics require retention of the blocking group to predict field use performance.

In general, blocked aromatic isocyanates deblock at lower temperatures than blocked aliphatic isocyanates. This results from the π-conjugation of the aromatic ring with the isocyanate. Substitution of the aromatic ring with electron-withdrawing groups such as Cl, NO_2, and COOR increase deblocking rates, whereas electron donor groups such as alkyl groups decrease deblocking rates. There are also steric effects on deblocking rates. Blocked aliphatic isocyanates with the isocyanate group on a tertiary carbon (e.g., MEKO-blocked TMI) deblock at a lower temperatures [65]. MEKO blocked on the ortho position of TDI deblocks 3.2 times faster than the less sterically crowded para isomer at 110°C; MEKO-blocked TMI deblocks 7.9 times faster than less sterically crowded MEKO-blocked cyclohexyl isocyanate at 110°C; and bis(isopropylketoxime)-blocked TMI deblocks 5.5 times faster than MEKO-blocked TMI at 110°C [66].

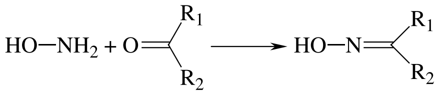
12.5.2. Blocking Groups

The structures of blocking groups have a major effect on deblocking temperatures and cure rates of coatings.

Many alcohols have been used as blocking agents; generally, they give high deblocking temperatures; but because of low reactivity, alcohol-blocked isocyanates have excellent stability in waterborne coatings. The stability is a major reason that 2-ethylhexyl alcohol was once used widely in electrodeposition primers (E-coats), where long-term tank stability is essential. The need to reduce curing temperatures for cationic E-coat primers has led to the use of monoethers of ethylene glycol such as 2-butoxyethyl alcohol [67].

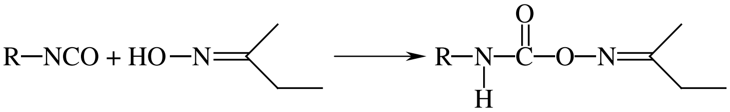
Phenol-blocked isocyanates deblock at lower temperatures than alcohol-blocked urethanes, in line with the slower rate of the forward reaction. Various alkyl phenols are also used. The blocking agent can be designed to have more than one function. For example, the reaction of 2-[(dimethylamino)methyl]phenol with HDI isocyanurate gives a blocked isocyanate that is also water-dispersible as its amine salt [68].

Oximes have been widely used due to their low deblocking temperatures compared to alcohols, phenols, and caprolactam. They have been the most favored of blocking groups for aliphatic polyisocyanates in solvent borne coatings and were the first to see use in automotive top coats. A variety of potential structures are available, since almost any aldehyde or ketone can be reacted with hydroxylamine to form the oxime.



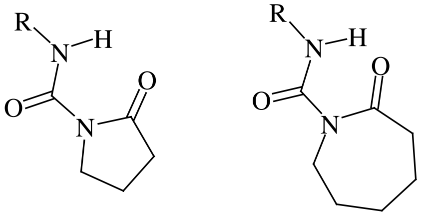
$$HO{-}NH_2 + O{=}C(R_1)(R_2) \longrightarrow HO{-}N{=}C(R_1)(R_2)$$

Among the advantages of the oxime groups is their high reactivity toward isocyanates, which allows the blocked products to be readily made without catalyst. The reaction rate of MEKO with cyclohexyl isocyanate was found to be between 50 and 75 times faster than octanol with the isocyanate [69]. However, the high reactivity of MEKO is disadvantageous with regard to the deblocking reaction, because it competes more effectively than the polyol reactant for the intermediate isocyanate, thereby slowing the forward reaction; there is also concern about possible toxic hazards of MEKO.



Introduction of an electron withdrawing group in the alpha position of an oxime group is reported to lower deblocking temperatures [70]. Oximes of alkyl esters of pyruvic acid–blocked isocyanates have lower deblocking temperatures than MEKO and do not yellow when overbaked. Coatings cured with these oximes have good acid resistance. The esters are said to be non-toxic.

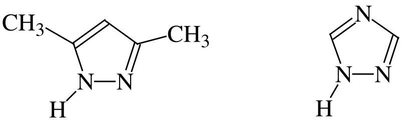
Caprolactam has been used widely as a blocking agent, particularly in powder coatings. It has a high deblocking temperature compared to oximes, and 2-pyrrolidone (also called pyrrolidinone) deblocks at even higher temperatures [71]. The bond angles in the seven-member strained ring of caprolactam may result in easier formation of a six-member ring between the urethane hydrogen and the carbonyl oxygen of the amide and possibly in a greater steric effect than with the five-member ring of pyrrolidone. The level of volatiles from blocked isocyanates can be quite substantial. In the case of IPDI monomer blocked with caprolactam, 50% of the adduct's mass will be lost through volatilization of the blocking group. Furthermore, caprolactam condenses in cooler parts of the oven, requiring extra maintenance.



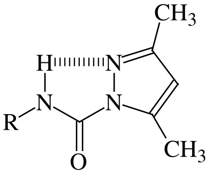
Acyl ureas from 2-pyrrolidone and caprolactam

Noncyclic acylureas are also used. Acetanilide-blocked HDI isocyanurate has been reported to have a deblocking temperature of 100°C, compared with the corresponding MEKO-blocked isocyanate deblocking temperature of 130°C [72]. Deblocking is promoted by having the carbonyl oxygen in a position to form an intermediate six-member ring with the proton on the nitrogen from the isocyanate.

Pyrazoles [73] and 1,2,4-triazoles [74] deblock at relatively low temperatures, which is probably facilitated by hydrogen-bonding, as illustrated below for 3,5-dimethylpyrazole. Consistent with this hypothesis, the deblocking reaction is enhanced by increasing basicity of pyrazoles. Hydrogen-bonding is expected to enhance elimination of the pyrazole by a cyclic proton transfer mechanism. The addition of DABCO interferes with this protonation. 3,5-Dimethylpyrazole and 1,2,4-triazole also have the advantages of less yellowing than oximes and have not been reported to have any toxic hazards. Furthermore, in contrast to phenol-blocked isocyanates, the cross-linking reactions are catalyzed by DBTL. It is suggested that the reaction proceeds by the elimination–addition pathway.



3,5-Dimethylpyrazole and 1,2,4-triazole



H-bonded 3,5-dimethylpyrazole-blocked isocyanate

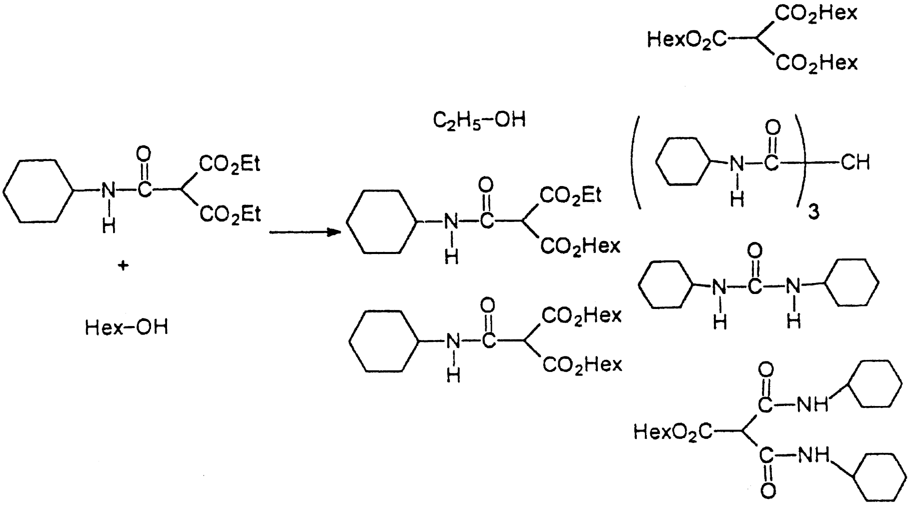
Secondary amines are useful blocking agents. However, primary amines are not. The urea from a primary amine and an isocyanate can cleave on either side of the central C═O group; cleavage to form the primary amine derived isocyanate releases a volatile, toxic monoisocyanate.

A study of a large number of hindered amines as blocking agents for powder coatings discloses that the most preferred amine is bis(2,2,6,6)-tetramethylpiperidinyl)amine, since it remains in the film to a large extent after baking and contributes to the UV stabilization of a coating [75]. It has been reported that highly hindered amines such as *t*-butylbenzylamine can be used as a blocking agent in coatings for plastics that cure at 120°C. In contrast, DMP used as a blocking agent required 135°C [76].

Any active methylene compound will react with an isocyanate by addition to the carbon of the active methylene group. By far the most useful active methylene compound for blocking is diethyl malonate (DEM). Although classified as blocked isocyanates, DEM-blocked isocyanates do not unblock in the usual way to give free isocyanate. Instead, a model compound study showed that reaction of DEM-blocked cyclohexyl isocyanate with *n*-hexyl alcohol yields primarily transesterification products, as well as products derived from cleavage of the CO—NH amide bond (plus a small amount of dicyclohexyl urea resulting from reaction of cyclohexyl amine and the small amount of cleavage to isocyanate) (Scheme 12.5) [77]. It was proposed that the enol form dissociated to give ketenes, which formed the various products (Scheme 12.6). Suppliers have recommended that formulations be based on a ratio of one blocked isocyanate to one coreactant group. However, there are potentially two cross-link sites for each isocyanate group, discounting side reactions.

There is a marked advantage in using a monoalcohol as part of the solvent in a diethyl malonate coating since this provides good package stability by providing excess monoalcohol for transesterification, as discussed in Section 2.3.2. Under storage conditions, the monoalcohol minimizes molecular weight buildup due to cross-linking, but when the alcohol evaporates after application, the cross-linking reaction proceeds rapidly. Package stability is also said to be improved by neutralizing the $NaOCH_3$ catalyst used in carrying out the blocking reaction with acids such as *p*-toluenesulfonic acid or 2-ethylhexyl acid phosphate [78].

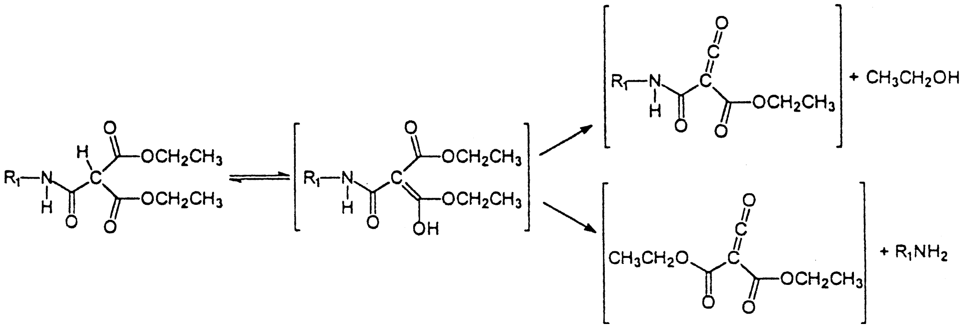
Scheme 12.5 *Products of diethyl malonate–blocked cyclohexyl isocyanate reacting with hexyl alcohol.*



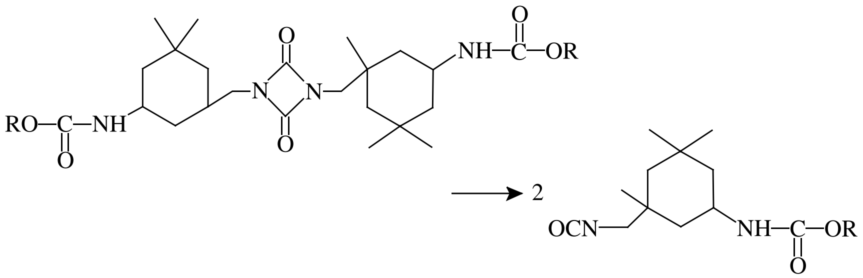
Although the cure temperatures are low, hydrolytic stability is adequate to use malonate-blocked isocyanates in 1K waterborne coatings [79]. The active hydrogen of DEM-blocked isocyanates also reacts with MF resins [80]. Clear coats for automobiles have been formulated with a combination of a hydroxy-functional acrylic resin, DEM-blocked HDI and IPDI trimers, and an MF resin [81]. Cross-linking results from reactions of the DEM-blocked isocyanate with hydroxyl groups, MF resin cross-linking of hydroxyl groups, and MF resin reaction with the malonic ester blocking groups.

There has been a trend to replace conventional blocked isocyanates in powder coatings with compounds that do not release a volatile blocking group on curing. Uretdione-blocked isocyanates are attractive because they do not generate volatile blocking groups. Because of their superior exterior durability, there is more interest in uretdiones from aliphatic isocyanates. When one attempts to make HDI uretdione, a major portion of the HDI is converted to isocyanurate. However, with IPDI it is possible to prepare the uretdione with only minor amounts of isocyanurate [82]. The free isocyanate groups on the uretdione must be reacted before use; reaction with polyols have been recommended for IPDI uretdione [83]. IPDI uretdione is at best only difunctional, so that

Scheme 12.6 *Proposed ketene formation of maleate-blocked isocyanate.*



cross-linking cannot be achieved with a difunctional coreactant. It can be reacted with a mixture of diols and triols to increase average functionality in the range 2.3 to 2.5 [82]. A mixture of IPDI and HDI can be dimerized; in the process some of the HDI is dimerized but some is trimerized; thus, the overall product has a functionality somewhat over 2, and the final films can be more flexible because of the hexamethylene groups [82].



A different approach to 1K urethane coatings is the use of encapsulated particles of isocyanates. These materials have been surface reacted so that they are insoluble in the rest of the vehicle at storage temperatures but dissolve in the coating during heating, releasing free isocyanate that reacts with a hydroxy-functional polymer. An approach to carrying out this idea is to make a fine particle size dispersion of isocyanate in water, in which surface isocyanate groups react with water to form a urea rich surface. The powder is filtered and dried, then dispersed in a coating [84]. Various methods have been used to make such particles. TDI isocyanurate dispersed in dioctyl phthalate with a small amount of 4,4′-diamino-3,3′-dimethyldicyclohexylamine added gives particles of about 10 μm that are used in plastisols [85]. TDI dimer dispersed in polypropylene glycol with a small amount of 2,5-dimethyl-2,5-hexanediamine gives a dispersion that is stable for over 3 months and cures at 120°C [86].

12.5.3. Catalysis of Blocked Isocyanate Coatings

Catalysts are usually included in blocked isocyanate formulations but commonly without consideration of what reaction or reactions they are involved in. Typically, the same catalysts that are used in unblocked 2K polyurethanes are used with the blocked systems, although at higher levels. As indicated earlier, many reactions are taking place and the catalyst can be involved in any one or more of these: the deblocking reaction, and/or the reaction of the free isocyanate with the other nucleophile, and/or an addition–elimination reaction, and/or side reactions.

Carlson et al. studied the effect of dibutyltin dilaurate (DBTL) on the deblocking of IPDI-based cross-linkers without a coreactant. In this case the DBTL showed no catalytic effect on the actual deblocking reaction but did, over a longer time, lead to a decrease in isocyanate concentration as a result of side reactions [87]. DBTL can catalyze the reaction of the unblocked isocyanate and a hydroxyl group and can be a mild allophanate catalyst.

A series of catalysts were studied in the reaction of MEKO-blocked HDI isocyanurate with a hydroxy-functional acrylic resin [88]. The films were intentionally undercured (20 minutes at 130°C) to emphasize the differences in catalytic activity. Several other blocked isocyanates were also tested, and the authors concluded that of the catalysts tested, bismuth tris(2-ethyl hexanoate), cobalt bis(2-ethyl hexanoate), and $Ti(AcAc)_4$ gave the most catalytic response.

A study of the catalytic effect of DBTDL on the deblocking temperatures of an IPDI isocyanurate/triol coating with a series of blocking agents used DMA to track the

TABLE 12.3. Minimum Temperatures (°C) for a Detectable Reaction of Blocked IPDI Isocyanurate with TMP Polyether Triol with and Without DBTDL Catalyst

Blocking Group	With DBTDL	Without DBTDL
Caprolactam	163	175
MEKO	137	156
1,2-Pyrazole	122	144
Diisopropylamine	115	136
3,5-Dimethylpyrazole	112	158

minimum temperatures at which cross-linking is detectable. As seen in Table 12.3, there were significant differences between the different blocking groups' response to catalysis [89]. In the same study, diethylmalonate showed the same temperature (104°C) with and without catalyst.

Catalysis of reactions of blocked isocyanate reactions with polyols in waterborne systems requires special considerations that have not been widely recognized except in cationic E-coats. It is well known that carboxylic acids inhibit catalysis by organotin compounds, but most waterborne systems include coreactants that are dispersed in water by amine salts of carboxylic acid groups. Blocked isocyanate anionic coatings are catalyzed to a lesser degree by DBTDL than the corresponding 2K solventborne coating and require higher curing temperature (or longer time) to reach the same extent of cross-linking [90]. The cure rate of such coatings was affected by the acid number of the coreactant coatings with higher acid number coreactants curing more slowly with the same level of catalyst. Another factor here is the hydrolytic stability of the catalyst. DBTDL is relatively easily hydrolyzed and hence is a questionable choice, although it is commonly reported as the catalyst.

12.6. MOISTURE-CURABLE URETHANE COATINGS

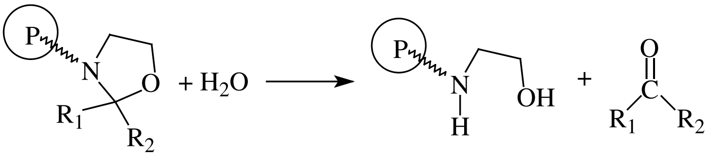
Moisture-curable urethane coatings cross-link by reaction of isocyanate resins with atmospheric water. Not only are they called *moisture-curable* but also commonly *moisture-cure* and occasionally, *hydrocure*, *moisture-hardening*, or *moisture-tempered.* They are one-package (1K) formulations that can cure at temperatures as low as 0°C. Such coatings are based mostly on isocyanate-terminated resins made from hydroxy-terminated polyesters or polyethers by reacting the terminal hydroxyl groups with excess polyisocyanate. To minimize the amount of unreacted diisocyanate, the resin is prepared utilizing an NCO/OH ratio that is significantly less than 2 : 1. Ratios higher that 2 : 1 are used with oligomeric MDI since the toxicity of MDI is low and lower viscosity resins can be obtained.

Almost any type of polyol can be used as the backbone of moisture-curable resins, although if functionality is too high, it becomes difficult to avoid gelation. Polyether polyols are widely used; the ether backbone is completely stable to hydrolysis; the resins tend to have low T_g, thereby enhancing flexibility; and they have relatively low costs. However, their exterior durability is relatively low. Polyester polyols are widely used, although the coatings may have poor saponification resistance. Depending on the components, resins with a broad range of T_g are available. Polycarbonate polyols give resins with hydrolytic stability superior to polyester polyols. Block copolymers of polyols and siloxane segments are prepared by reacting excess isocyanate with a combination of polyols and hydroxy-terminated siloxanes [91]. These resins cure by reaction of terminal isocyanate groups with water.

Hydrolytic resistance of coatings is affected by several variables, including cross-link density and free volume availability as well as the functional groups present. Model compound studies suggest that substituted ureas are somewhat more easily hydrolyzed under both neutral and acidic (pH 1.34) conditions than are analogous urethanes [92]. Ureas and urethanes from aliphatic isocyanates are somewhat more resistant to hydrolysis than those from aromatic isocyanates. Both urea and urethane groups are generally more stable to hydrolysis than are unhindered ester groups.

The coatings are stable when stored in the absence of water but cross-link after application by reaction of the isocyanates with water to form amines, which react with other isocyanates to form substituted urea cross-links. Cure rates depend on the water content of the air; at low temperatures, higher relative humidity is required than at higher temperatures, since relative humidity increases with decreasing temperature for the same water content. At high humidity and temperature, cure is rapid, but the carbon dioxide released by the reaction of isocyanate with water can be trapped as bubbles, especially in thick films. (See Ref. [93] for a discussion of the effects of temperature and humidity and other application considerations.)

Although the most common moisture-curable urethanes are based on the direct reaction of NCO groups and water, several other approaches are also used. Oxazolidines hydrolyze with water to yield free amine and hydroxyl groups: These in turn react with isocyanates to form the expected urea and urethane linkages. Difunctional oxazolidines yield higher functionality [94]. They are, in effect, *blocked amines*.



Other "blocked amine" reactants have been used in preparing moisture-curable systems. In general, such systems have the advantage of faster cure than obtained with isocyanate-terminated urethanes. When exposed to water, imines act as blocked amines because they hydrolyze to yield free amines, which react with an isocyanate. For example, a urethane from a polyester diol, polyester polyol, and IPDI with the diketimine from isophoronediamine and methyl isobutyl ketone (MIBK) is dry-to-sand in 30 minutes and through dry in 60 minutes [95]. Aldimines give more stable systems. For example, a moisture-curable coating is based on an MDI prepolymer and the aldimine from isobutyraldehyde and bis(4-aminocyclohexyl)methane [96]. Isocyanate-terminated urethane resins can be partially reacted with a hydroxy-functional oxazolidine. For example, a coating resin with excellent color and exterior durability is made from caprolactone polyester triol, tris(2-hydroxyethyl)isocyanurate, IPDI, and 2-hydroxyethyloxazolidine [97]. After application of such a system, moisture hydrolyzes the oxazolidine to an aminoalcohol that reacts more rapidly with isocyanate groups than water reacts.

The isocyanate of a moisture-curable urethane can be reacted with 3-aminopropyltriethoxysilane to give a resin with terminal triethoxysilyl groups that will also moisture cure. An advantage of the triethoxysilyl resin is that part of the solvent can be ethyl alcohol. The ethyl alcohol permits a reasonable pot life in the presence of water, such as comes into a coating from pigment surfaces. If free isocyanate groups are present, the coating is not stable in the presence of either ethyl alcohol or water. The trialkoxysilyl approach also avoids the formation of CO_2, which can lead to film imperfections, such as pinholing, in moisture-cure urethanes. (See Section16.2 for further discussion.)

12.7. WATERBORNE URETHANE COATINGS

12.7.1. Polyurethane Dispersions

Polyurethane dispersion resins are predominantly linear or lightly branched relatively high molecular weight polyurethane polymers dispersed in water. Such materials are latexes, but they are called *polyurethane dispersions* (PUDs). Since urethanes hydrogen-bond strongly with water, the particles are swollen with water, plasticizing the polymer, thereby permitting film formation with higher T_g polymers than is possible with acrylic latexes [98]. It is common practice for formulators to blend PUDs with less expensive azrylic latexes to upgrade film properties (Section 12.7.2).

PUDs are made with aliphatic diisocyanates, polyols, and a monomer designed to provide stability to the dispersion in water. To increase molecular weight they are chain extended after dispersion in water. The chain extension can be accomplished by allowing the terminal NCO groups to react with water or by adding a diamine to the initial dispersion that will react more rapidly than water with the isocyanate groups.

A variety of polyols are used. Polypropylene glycol has the advantage of imparting flexibility, hydrolytic stability, and low cost, but the films tend to have poor adhesion, poor exterior durability, and poor solvent resistance. Polytetramethylene glycol gives improved solvent resistance but at higher cost. Polyesters have the advantages of adhesion, toughness, abrasion resistance, and exterior durability and can be designed to give a wide variety of mechanical properties, but they suffer from limited hydrolytic stability. Polycarbonates provide hydrolytic stability, flexibility, and abrasion resistance but at higher cost.

2,2-Dimethylolpropionic acid (DMPA) is used as an ionic monomer precursor; the carboxylic acid groups are neutralized with a tertiary amine before dilution of the prepolymer with water to impart dispersibility. The hindered carboxylic acid group on DMPA is almost completely unreactive with isocyanates, so that the reaction is limited to the hydroxyl groups. Carboxylic acid groups also serve as sites for cross-linking by H-bonding as well as by covalent bonding. Polyglycol monoethers are used as nonionic monomers for stabilizing the dispersion. They give lower viscosity prepolymers; and the dispersions are more freeze–thaw stable as well as more stable to changes in pH and soluble ion concentration. However, films are more hydrophilic and exterior durability is poor.

One way to prepare PUDs is by the *prepolymer mixing process*. A polyol and DMPA are reacted with excess diisocyanate to form an isocyanate-terminated prepolymer. A tertiary amine is added, the solution is added to water, leading to a dispersion of polymer particles, and the polymer is chain extended by reacting with a diamine, such as hydrazine or ethylenediamine, giving a dispersion of a higher molecular weight polymer [99]. The dispersing step must be carried out in a short time at temperatures low enough so that the NCO groups do not react appreciably with water. The amine (or hydrazine) reacts much more rapidly than water. Aromatic isocyanates react with water too rapidly to be used in this process; generally, cycloaliphatic isocyanates such as IPDI are used. Monomeric HDI is not used since it is somewhat soluble in water, resulting in the formation of precipitates outside the dispersion particles. The final polymer contains carboxylic acid salts of the tertiary amine. Since the salts are very hydrophilic, they concentrate at the surface of the dispersed particles, stabilizing them against coalescence. Molecular weight is controlled by the original ratio of isocyanate to hydroxyl groups and by the ratio of extending diamine to terminal isocyanate groups. Frequently, the reaction is carried out with a solvent, *N*-methylpyrrolidone (NMP) most commonly, to dissolve DMPA and to reduce the viscosity for ease of dispersion.

Lower viscosity prepolymers for PUDs can be made using a *two-step process*. First a linear isocyanate-terminated polyurethane is made from a diisocyanate, a diol, and DMPA; in the second step the terminal isocyanate groups are reacted with a triol [100]. A variety of other techniques for making PUDs have been used [99].

PUDs with polyester backbones and DMPA are subject to hydrolysis, which can lead to breaking the polymer backbone and separation into two phases, especially at elevated temperatures [101]. The stability is lowest for PUDs not chain extended; as the amount of chain extension (with ethylenediamine) is increased, stability improves. The effect of using different chain extenders, including tri- and tetrafunctional amines, on polyester–DMPA PUD properties, including hydrolytic stability, has also been studied [102]. Hydrolytic stability, MEK rub resistance, and peel strength of films are higher using, for example, melamine as chain extender rather than ethylenediamine; viscosity is said to be unaffected by changing to trifunctional amine from difunctional amine extender.

One can incorporate a small amount of trifunctional isocyanate into an isocyanate-terminated polymer, resulting in some branching on dispersion in water. Also, one can chain extend with diethylene triamine to introduce branching or a low degree of cross-linking—low enough that the particles can still coalesce to a continuous film.

Cross-linkable polyurethane dispersions are also prepared. Diethanolamine or ethanolamine are added to the water in which the prepolymer is added, resulting in terminal hydroxy groups that can be cross-linked with MF resins or polyisocyanates. Polyunsaturated polyurethane dispersions (PUDs) are also being used (Section 15.7.2).

12.7.2. Acrylic–Polyurethane Dispersions

There have been three major approaches to preparing aqueous acrylic–urethane systems: (1) blending of PUDs and latexes (or water-reducible acrylic resins); (2) polymerizing vinyl monomers, such as acrylates, in PUDs to make hybrid acrylic–urethane resins; and (3) and cross-linking acrylic–urethane systems.

When combined aqueous polyurethane dispersions (PUDs) and acrylic latexes offer several potential advantages compared to each of the two separate types of polymers. In general terms, polyurethane based polymers offer superior abrasion resistance due to intermolecular hydrogen bonding. Acrylic resins have lower costs, due to both raw material cost and lower processing costs. Many latexes contain surfactants that can bloom to the surface of films reducing gloss, whereas PUDs can be made without surfactants. PUDs have a low minimum film formation temperature (MFFT) relative to their dry film T_g owing to the plasticizing effect of hydrogen bonding with water. Also, owing to hydrogen bonding of urethane groups, film properties are not as dependent on T_g as in acrylic latexes. Accordingly, low MFFT can be achieved without reducing hardness. For example, a paint made with an acid-functional acrylic latex and a PUD with a T_g of $-40°C$ has a longer open time, permitting rebrushing to assure hiding and lapping [103]. Coalescing solvents are required to permit film formation with latexes at low temperatures, whereas they are not required with PUDs. Films of PUDs alone have higher moisture vapor transmission than that of films from many acrylic latexes.

Although blends of PUDs with relatively inexpensive latexes can offer significant cost reductions and improvement in some properties, improvement of latex properties is not directly proportional to the ratio of the two products. For example, blending equal parts of an acrylic latex and a PUD gives films with a tensile strength of 2900 psi, compared to 2000 and 6400 psi for the individual films, respectively, corresponding to an average of 4200 psi. Similar nonlinear effects were observed with other mechanical and chemical properties. It is suggested that inhomogeneity caused by separate acrylic and urethane domains contributes to the less than expected improvement in properties. These areas may have excessive internal strains and/or incomplete coalescence, which leads to increased permeability and reduced cohesive strength [100].

Better film properties can be obtained by polymerizing the acrylate esters in the urethane. The earliest approach was to use the particles of the PUD as "seed" for polymerization of the acrylates. The effect of various reaction parameters on the rate of polymerization of MMA, BA, and a 50 : 50 mix of MMA and BA in an anionic polyester PUD, dissolved in *N*-methlpyrrolidone (NMP), has been reported [104].

To eliminate the NMP, another procedure for preparing hybrid polymers has been developed in which acrylic monomers are used as solvent. For example, a PUD, derived from poly(NPG adipate) diol, DMPA, and H_{12}MDI, is dissolved in BA, styrene, and 1,6-hexanediol diacrylate, neutralized with TEA, dispersed in water, chain extended with ethylenediamine, and then polymerized with AIBN [105].

12.7.2.1. Cross-Linked PUD–Acrylate Systems There are two types of cross-linked acrylic–urethane dispersions: (1) reaction of a functional group on one or both of a urethane and a vinyl resin that reacts with another functional group on the other resin; and (2) use of a separate cross-linker that can react with functional groups on both the urethane and the acrylic resin.

Several compositions and applications follow. A UV cure vehicle for wood coatings is prepared from a carboxy-functional polyol, adding glycidyl methacrylate (GMA) to react with COOH groups, adding DMPA and HDI, neutralizing with TEA and diisopropylethylamine, dispersing in water, chain extending with ethylenediamine, and adding a photoinitiator [106].

An autoxidizable coating is based on a water-reducible acrylic resin with a PUD made from a soy alkyd with HDI, neutralized with NH_4OH, and dispersed in water [107]. Hydrazine-terminated PUDs have been used with keto-functional latexes to make cross-linking systems. A study of cross-linking of blends of a keto-functional acrylic latex and hydrazine-terminated PUD has been published [108]. When the water evaporates from the film after application, cross-linking occurs by reaction of the hydrazine groups with keto groups to form hydrazone linkages.

External cross-linkers are used to react with functional groups on acrylic–PUDs. For example, a chip resistant automobile primer is formulated with an H_{12}MDI/HDI/polyester polyol PUD, a carboxy- and hydroxy-functional acrylic latex, 2-amino-2-methyl-propanol, and an MF resin [109].

Polyepoxides are used as cross-linkers. A top coat with exterior durability for application over stains on plastic composite surfaces is formulated with a urethane–acrylic hybrid PUD, an acrylic resin, and a methylpolysiloxane microemulsion. An aqueous aliphatic epoxy emulsion, which cross-links by reacting with COOH groups on the PUD, is added shorthly before application. The pot life of the combined system is over a week [110].

12.7.3. 2K Waterborne Urethanes

Since isocyanates react relatively readily with water, it was assumed for many years that they could not be used directly in waterborne coatings. By the late 1980s this assumption was in question and development of 2K waterborne coatings began. In the last few years, 2K waterborne systems have been adopted commercially on a large scale [111]. Bayer Corporation received a Presidential Green Award in 2000 for its work on these systems. Cross-linkers are polyisocyanates and to a lesser extent, polycarbodiimides and polyaziridines. See Ref. [112] for an extensive review of 2K urethane systems.

12.7.3.1. Components of Waterborne 2K Coatings Two types of polyisocyanate cross-linkers are used: conventional polyisocyanates and polyisocyanates that have been modified to be more hydrophilic. In general terms, hydrophilically modified isocyanates are easier to incorporate into a coating, but unmodified isocyanates are less expensive and give films that have better exterior durability. Modifying isocyanates so that they are more readily dispersible in water permits easier mixing of the two packages. Nonionic hydrophilically modified polyisocyanates made by reacting a fraction of the NCO groups on a polyisocyanate (such as HDI or IPDI isocyanurate) with a polyethylene glycol monoether are more easily stirred into an aqueous dispersion of a coreactant to form a heterogeneous dispersion, in which the polyisocyanate and coreactant are in separate dispersed particles [113]. It is critical that the adducts be non-crystalline. The ease of mixing and stability of the dispersions increases as the length or amount of the polyether modifier is increased [114]. Adequate water dispersibility without crystallization can be achieved using ethers with $n > 5$ but <10 [115]. Use of a polyester or polyether as a modifier for isocyanate overcomes the crystallization problem of polyethers and decreases the water sensitivity of final films. For example, reacting a polyethylene glycol monomethyl ether ($n = 7$) with ϵ-caprolactone gives a polyester or polyether that is used to modify HDI isocyanurate [116].

Water sensitivity of films is reduced by partially reacting a hydrophilically-modified polyisocyanate with an aminoalkyltrialkoxysilane. For example, HDI is reacted with the monomethyl ether of a polyethylene glycol ($n > 10$) and an amine-functional silane made by reacting diethyl maleate with 3-aminopropyltrimethoxysilane. Primers and top coats formulated with trialkoxysilylated isocyanate and water-reducible acrylic resins show substantial advantages in gloss retention and reduced blistering on water immersion than corresponding films without the silane [117].

PUDs with polyester backbones and DMPA have been widely used. However, they are subject to ester hydrolysis, or saponification at basic pH, which can lead to cleaving the polymer backbone and separation into two phases, especially at elevated temperatures. The hydrolysis is autocatalytic since carboxylic acids formed from ester hydrolysis catalyze the hydrolysis, as does DMPA. Chain extension with ethylenediamine improves stability, which supports acid catalysis. Polycarbonate diols are reported to be more resistant to hydrolysis than are polyester diols [118].

Hybrid PUDs containing hydroxy-functional acrylic–polyurethanes have been used [119], including their coreaction with a nonionic hydrophilically modified HDI isocyanurate [120].

Acrylic latexes have also been used in 2K waterborne urethane coatings. A statistical study of the effect of several variables on the performance of finishes for wood kitchen cabinets, based on hydroxy-functional acrylic latexes cross-linked with a nonionic hydrophilically modified polyisocyanate, has demonstrated that a high hydroxy content of the latex (hydroxyl number 52), small particle size of the latex, core–shell preparation of the latex, and low T_g (obtained by increasing level of coalescing solvent) enhanced performance [121].

An extensive study of the effect of carboxylic acid structure and level in acrylic latexes has been reported. It was shown that reaction of isocyanate groups with COOH groups derived from acrylic acid resulted in undesirable bubble formation to a greater extent than occurred with COOH groups derived from β-carboxyethyl acrylate. The latexes were made by emulsion polymerization of methyl methacrylate, butyl acrylate, and hydroxyethyl methacrylate, together with acrylic acid, methacrylic acid, or β-carboxyethyl acrylate, and neutralized with DMAE in 2K urethane coatings [122].

Isocyanates react with water as well as with the coreactant, which is usually hydroxy-functional. Although the rate constants of reaction with water are lower than with primary alcohols, the large excess of water means that a significant amount of the isocyanate will react with water. Since the reaction with water also gives cross-links (urea instead of urethane), the problem can be minimized by use of a large excess of isocyanate; this *indexing* is frequently a 2 : 1 or even higher isocyanate/hydroxyl ratio. However, urea linkages can lead to turbidity in films, due to the relatively low compatibility and crystallinity of urea compared to urethane groups in the polymer matrix, and the cost of the isocyanate is almost always higher than that of the polyol. Also, reaction with water leads to the evolution of CO_2, which may give foaming or bubbling of applied films. Hence, in most cases it is desirable to reduce the reaction with water so that indexing need be only a little greater than 1. The required excess of water is affected by the hydroxy-functionality, $\bar{f}_n$, of the coreactant.

Relative reaction rates of NCO with hydroxyl groups and water depend on the catalyst. $Zr(AcAc)_4$ (King Industries, ZrCAT) catalyst shows better selectivity than DBTDL [23,24]. See Section 12.2.2 for a further discussion of the effect of various catalysts on the relative rates of reaction of isocyanates with water and alcohols.

12.7.3.2. Mixing and Application Considerations

It is relatively easy to make 2K waterborne coatings with good properties in the laboratory; however, production use is more difficult. There are several potential problems. In some systems, it is difficult to assure that uniform stoichiometric ratios are obtained throughout the film. If reaction occurs to a significant extent before application, coalescence will be inhibited, and film properties may therefore, be poor. As with solventborne 2K coatings, waterborne 2K coatings can be expected to have limited pot life. In solventborne coatings, pot life can be determined by monitoring viscosity increases. In many 2K waterborne coatings, viscosity does not increase as reactions between NCO and OH take place, since they change the viscosity inside the aggregate particles but not the bulk viscosity. In fact, the generation of CO_2 by the reaction of isocyanate with water decreases the pH, leading to shrinking of the aggregate particles, which can result in viscosity reduction [123].

To minimize mixing problems, the two dispersions should start out with similar viscosities. Generally, it is desirable to use as low viscosity isocyanates as possible. The viscosity of HDI isocyanurate with a functionality of 3.3 is 1.7 Pa•s at 28°C, compared to 8.5 Pa•s for HDI biuret with the same functionality, making it easier to disperse the isocyanurate [124]. The viscosity of a combination of HDI uretdione and isocyanurate is lower than that of HDI isocyanurate by itself, which makes it easier to incorporate the combination into dispersions [125]. Very low viscosity HDI unsymmetrical trimer (0.7 Pa•s) has been recommended for use in 2K urethane coatings [36]. Use of a proprietary water-reducible acrylic resin with conventional HDI based isocyanates is reported to be satisfactory [126]. 4-Isocyanatomethyl-1,8-diisocyanatononane is reported to stir into water and aqueous systems more easily than other polyisocyanates [127]. The polyisocyanate component is sometimes diluted with solvent such as butyl acetate to reduce its viscosity. Solvents such as cyclic carbonates or lactones give smaller particle size and more uniform dispersions in water than those for butyl acetate [128]. Results also depend on the process used to mix the two packages together. High but not excessive shear is required to obtain relatively uniform particle size with an average diameter of about 150 nm [129].

In mixing two dispersions, one containing isocyanate, the other containing coreactant, the maximum physical stability of the dispersion will generally be reached with the smallest particle size. However, a smaller particle size requires high intensity agitation to break up the initial particles, which increases the possibility of contact of isocyanate groups with water. The probability of new particles being formed that contain both reactants also increases, resulting in non-uniform films, with some parts being high in isocyanate and others high in coreactant. In making dispersions of hydrophilically-modified polyisocyanates in dispersions of water-reducible acrylic resins, it has been shown that bimodal particle size distribution of small particles and larger particles form at low shear rates; at high shear rates there was a single broader small particle size distribution; with excess shearing, the particle size increased and distribution broadened [130].

Carrying out the high intensity mixing in line with application can minimize the problems. Spray equipment designed to provide in-line intensive mixing of the two components has been used to apply polyisocyanate 2K water-reducible coatings [131]. To assure proper mixing of 2K coatings, a specially designed jet mixer is recommended [132].

Performance can be affected by the rate of loss of water from films after application. If water is lost slowly, there will be a larger extent of reaction of isocyanate, with water requiring higher indexing to achieve full cross-linking of coreactant groups. Thicker films tend to increase the relative reaction with water by decreasing the rate of water loss through the film [133]. For ambient cure coatings, relative humidity affects the rate of water loss as well as surface cure. Above about 70% RH, gloss is reduced due to bubble formation caused by increased evolution of CO_2. FTIR ATR analysis of films of 2K waterborne urethane coatings shows that reaction of isocyanate with water to form urea groups increases near the surface as RH increases [134].

Baking coatings can generally be formulated with lower indexing than ambient cure coatings because of the faster removal of water from the films. A large fraction of the water evaporates during flash off and initial baking, reducing the extent of isocyanate reaction with water, thereby minimizing CO_2 evolution and permitting lower NCO/OH ratios. In one system, indexing of 1.3 to 1.8 for ambient cure coatings could be reduced to 1.1 to 1.3 for heat cure coatings [135].

12.8. HYDROXY-TERMINATED POLYURETHANES

Diisocyanates can be reacted with diols and triols at an N=C=O/OH ratio of less than 1 to make hydroxy-terminated polyurethanes, which can be cross-linked with MF resins or with other cross-linkers that react with hydroxyl groups. Urethane groups also cross-link with MF resins (Section 11.3.4). Compared to polyesters, hydrolytic stability is better and coatings provide the toughness and abrasion resistance associated with urethane coatings.

However, solids of equal molecular weight and viscosity are lower, due to intermolecular hydrogen bonding, and the residual urethane groups increase moisture absorption. Compared to hydroxy-functional acrylic resins, they offer the advantage of abrasion resistance and the possibility of using lower molecular weight resins. Whereas molecular weight reduction of acrylic resins made by conventional free radical–initiated polymerization is limited by the problem of ensuring that at least two hydroxyl groups are present on each oligomer molecule (Section 8.2.1), hydroxy-terminated polyurethanes have two (or more) terminal hydroxyl groups, even at very low molecular weight (as with polyesters). Furthermore, the urethane (carbamate) groups may participate in cross-linking with amino resins, in effect increasing functionality.

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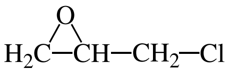
13

Epoxy and Phenolic Resins

Epoxy and phenolic resins are two other classes of step-growth resins important in coatings.

13.1. EPOXY RESINS

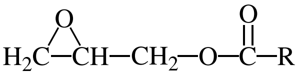
Terminology of epoxies can be confusing. Epoxy groups (also called *epoxides*) are three-membered cyclic ethers; in IUPAC and *Chemical Abstracts* nomenclature, they are called *oxiranes*. Most commercially important epoxy resins are derived from (chloromethyl) oxirane, more commonly known as *epichlorohydrin* (ECH). The resins generally contain oxiranylmethyl ethers or esters, usually called *glycidyl ethers* or *esters*. In addition to the uses discussed in this chapter, epoxy esters are discussed in Section 15.8 because of their close relationship to the chemistry of alkyds; acrylated epoxy resins are discussed in Section 29.2.4.


$H_2C(O)CH-CH_2-Cl$

Epichlorohydrin


$H_2C(O)CH-CH_2-OR$

Glycidyl ether


$H_2C(O)CH-CH_2-O-C(=O)-R$

Glycidyl ester

13.1.1. Bisphenol A Epoxy Resins

The first epoxy resins used in coatings, and still the largest volume, are bisphenol A (BPA) epoxies made by reacting BPA with ECH. Under basic conditions, the initial reaction

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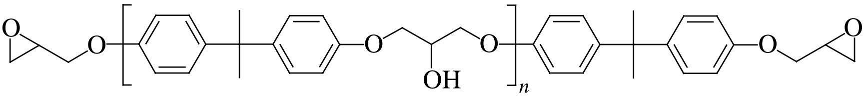
Organic Coatings: Science and Technology, Third Edition, by Zeno W. Wicks, Jr., Frank N. Jones,
S. Peter Pappas, and Douglas A. Wicks

is formation of a BPA anion (BPA^-), which attacks ECH and results in the formation of a new oxirane ring with elimination of chloride anion (Cl^-), as shown in Scheme 13.1.

The initial product is the monoglycidyl ether of BPA (MGEBPA). Analogous reaction of the phenolic group of MGEBPA with NaOH and ECH gives the diglycidyl ether of BPA (DGEBPA). The epoxy groups of MGEBPA and DGEBPA react with BPA^- to extend the chain, as shown for DGEBPA; these reactions introduce alcohol groups on the backbone. Continuation of these reactions results in linear polymers, since both the BPA and ECH are difunctional. Bisphenol A epoxy resins are made with excess ECH, so the end groups are glycidyl ethers. The polymers may be represented by the following general formula, where the molar ratio of ECH to BPA determines the average n value.



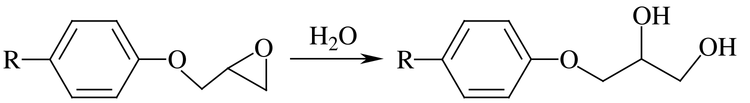
Bisphenol A epoxy resins

Molecular weight (MW) is controlled by the ratio of ECH to BPA. With a large excess of ECH, it is possible to make a resin that is dominantly DGEBPA, that is, where $n = 0$ in the general formula. The pure $n = 0$ compound is a crystalline solid, but the largest volume commercial grades are liquids with n values of 0.11 to 0.15 (called *standard liquid resin*). As the ratio of ECH to BPA is reduced, MW and the n value of the epoxy resin increase. Viscosity also increases with MW. Above an average n value of 1, the resins are amorphous solids with increasing T_g. Although the resins are said to have melting points, they do not melt in the sense that a crystalline solid does. Rather, under specified test conditions, the resins flow to some standard extent at the *melting point* (the term *softening point* is sometimes used). Commercially available higher MW resins are often designated as types 1001, 1004, 1007, and 1009. Table 13.1 gives average n values, epoxy equivalent weights (EEW), and melting points for commercial BPA epoxy resins [1]. EEW is also often called *weight per epoxide* (WPE). Different suppliers offer subtypes and quote significantly different ranges for EEW and WPE of the various types. As MW increases, EEW and average hydroxy functionality also increase. In some even higher MW ($n \geqslant 10$) epoxy resins, the amount of epoxy groups present is so small that the resins approach being just polyfunctional alcohols, commonly called *phenoxy resins.*

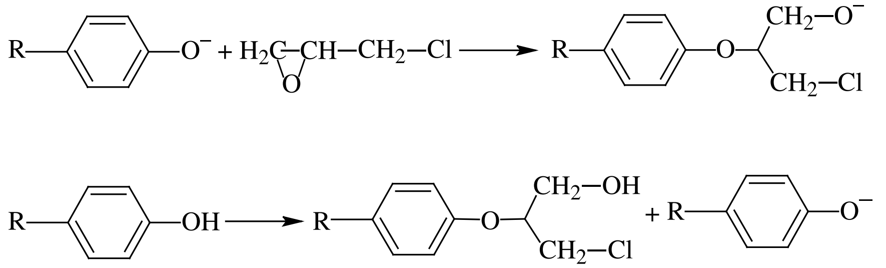
Although theoretically, there should be two epoxy groups on each molecule, a variety of other end groups are present to a small extent. To a minor degree, unreacted phenol and 1,2-chlorohydrin terminal groups are present; additional non-epoxy end groups result from side reactions. About 2% of the terminal groups are 1,2-glycol derivatives. These can result from hydrolytic side reactions of epoxy groups, and of chlorohydrin groups.

TABLE 13.1. Characterization of Commercial BPA Epoxy Resins

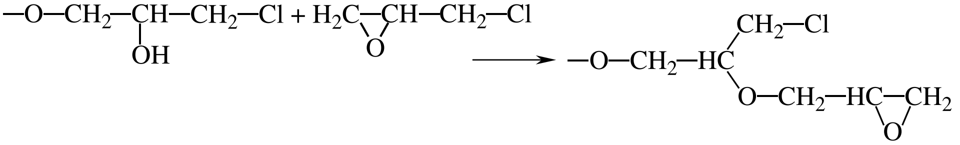
Resin	n Value	EEW	Melting Point (°C)
Standard liquid	0.13	182–192	Liquid
1001 Type	2	500–560	65–85
1004 Type	5.5	875–950	90–110
1007 Type	14.4	1600–2300	120–135
1009 Type	>16	2500–5500	130–160


(13.1)

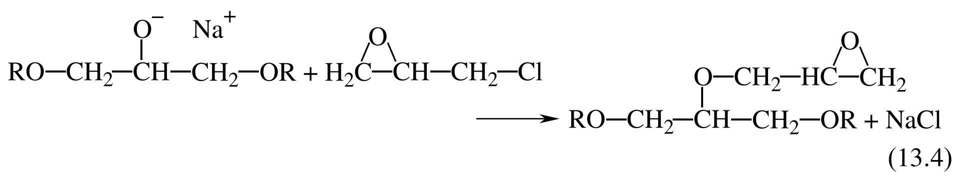
Another side reaction is ring opening by a phenoxide anion polymer end group with ECH at the less favored, more sterically hindered position: as shown in Eq. (13.2). The resulting 1,3-chlorohydrin derivative (after proton transfer) cannot ring close to give an oxirane and is relatively stable under the reaction conditions. This group is the main site of non-hydrolyzable chlorine that is commonly reported in specifications of commercial epoxy resins.


(13.2)

Instead of ring closing to give an epoxy group, the hydroxyl group of the 1,2-chlorhydrin can react with another ECH molecule to give an addition product:


(13.3)

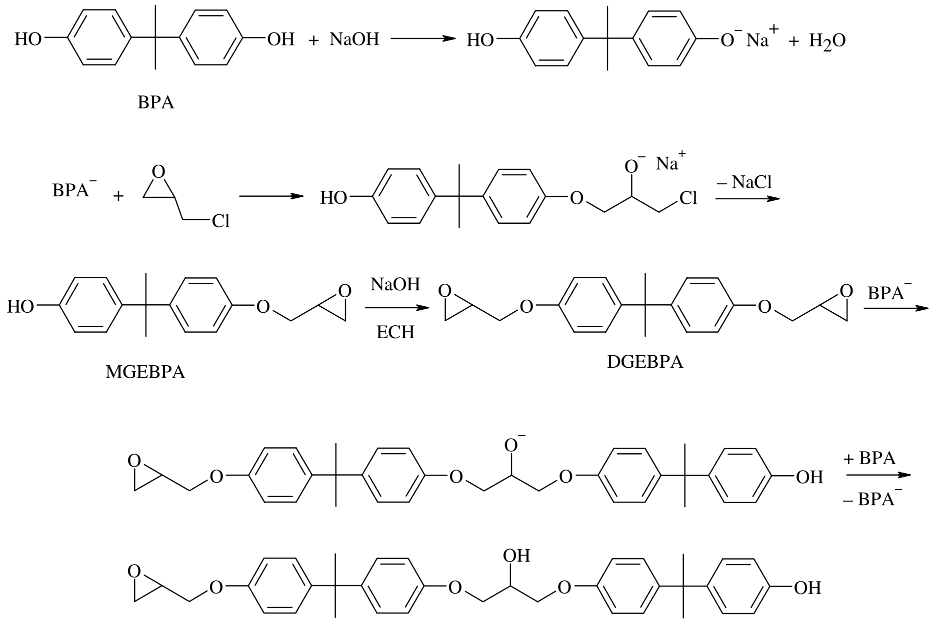
A hydroxyl group on the polymer backbone can also react with ECH to yield branched molecules with an epoxy functionality ($\bar{f}_n$) of 3:


(13.4)

If there were no side reactions, the epoxy $\bar{f}_n$ of BPA epoxy resins would be 2; however, the net effect of side reactions is that commercial BPA epoxy resins generally have an $\bar{f}_n$ value below 2, commonly about 1.9. In some cases, this lower $\bar{f}_n$ can have an important effect on film properties. The presence of terminal glycol groups can give lower viscosity resins since they result from chain termination, reducing MW. It has been shown that the presence of small controlled amounts of terminal glycol groups can have beneficial effects on adhesion [2].

The procedure shown in Scheme 13.1 for making BPA epoxy resins is called the *taffy process*. Stoichiometric amounts of NaOH are required, resulting in formation of a large amount of NaCl, which must be removed from the resin by washing with water. The washing step is not difficult for the standard liquid resin, due to its low viscosity.

Scheme 13.1



However, as the ratio of ECH to BPA is decreased, higher average MW products are produced, the reaction mixture becomes highly viscous, and water washing to remove NaCl becomes difficult. Also, as MW and viscosity increase, the probability of branching increases. The taffy process is now used only for liquid resins.

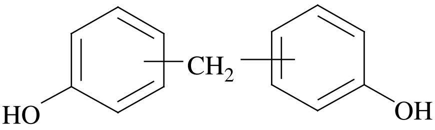
Higher MW epoxy resins are prepared by reacting the standard liquid epoxy resin ($n = 0.13$) with BPA in the presence of a catalyst such as ethyltriphenylphosphonium hydroxide. The catalyzed reaction of BPA with both epoxide groups of the standard resin results in a higher MW resin with BPA end groups, which react further with standard resin to give epoxide end groups. The average MW depends on the ratio of liquid resin to BPA. There can be variations in the resins obtained, depending on the catalyst used. This procedure for making epoxy resins is called the *advancement process* or *upgrade process*. The advancement process is carried out at higher temperature than the taffy process; hence, the viscosity is lower, agitation is better, and there is less branching. No NaCl is produced; therefore, the difficult salt removal step is unnecessary.

Development of advanced HPLC analytical techniques has permitted improvements in process development and control. Not only can the individual oligomers ($n = 0, 1, 2, 3$, etc.) be separated, but also oligomers in which one or both ends have 1,3-chlorohydrin or 1,2-dihydroxy groups can be separated [3] (Eqs. 13.1 and 13.2). Analysis of the products resulting when minor process changes are made in reaction conditions permits establishing process parameters to meet relatively narrow product specifications. Tight process control is particularly critical for epoxy resins to be used in electronic applications and powder coatings (Chapter 28). Resins made by the taffy process consist of oligomers with $n = 0, 1, 2, 3, 4, 5$, and so on, whereas resins made by the advancement process have largely even number n value oligomers, that is, $n = 0, 2, 4, 6$, and so on. The predominance of oligomers with even number n values in resins from the advancement process follows from starting with the diglycidyl ether of BPA. Roughly 10 wt% of odd n molecules result from the presence of about 10% of $n = 1$ resin in the liquid resin.

Bisphenol A epoxy resins perform especially well in coatings applications in which excellent adhesion, electrical properties, and corrosion resistance are required. A limitation is poor exterior durability, primarily resulting from direct absorption of UV radiation by the aromatic ether groups, which ultimately leads to photoxidative degradation. Lower MW resins require less VOC and give better chemical resistance when cross-linked with amines since the cross-link density of films is higher. However, when higher MW resins are used with cross-linkers that react with hydroxyl groups (e.g., phenolic or amino resins), chemical resistance is better. Cross-linked higher MW resins also give films that dry more rapidly and have improved corrosion resistance.

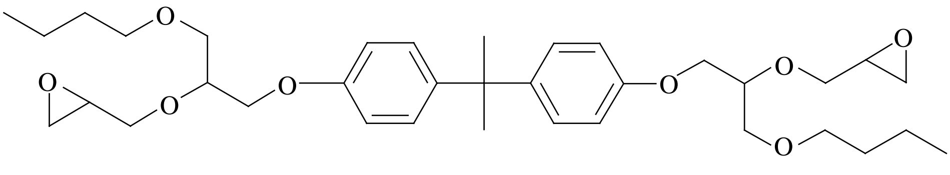
13.1.2. Other Epoxy Resins

A variety of other epoxy resins is available. Bisphenol F (BPF) epoxy resins (from reaction of ECH with BPF in place of BPA) have the advantage of lower viscosities at the same n value. Standard liquid BPA epoxies have viscosities on the order of 12 to 14 Pa•s at 25°C, whereas the viscosities of comparable BPF epoxies are 2.5 to 4.5 Pa•s. Solid BPF resins are seldom used.



BPF

Still lower viscosities can be obtained by reacting BPA epoxies with an alcohol, such as n-butyl alcohol, followed by reacting the resultant hydroxyl groups with ECH, using $(CH_3)_4NCl$ as catalyst [4]. A new epoxy resin is obtained, a major component of which is 2,2′-bis[p-(3-n-butoxy-2-glycidyloxypropyloxy)phenyl]propane. Viscosities on the order of 1 Pa•s are reported [5]. The effect of the butyl ether group is to lower the T_g and hence the viscosity. Cross-linked films are softer and more impact resistant than comparable films using BPA resins.

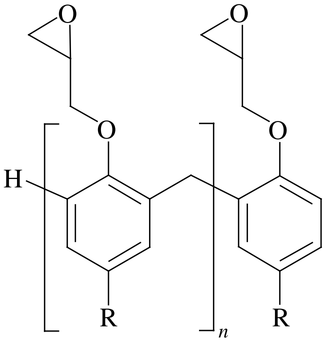


2,2′-bis[p-(3-n-butoxy-2-glycidyloxypropyloxy)phenyl]propane

Epoxy resins with lower viscosity than BPA epoxy resins can be made by substituting a flexible diol for BPA in the advancement process to make what might be called *copolymer epoxy resins*. Examples are advancement resins made from combinations of propylene or dipropylene glycol and BPA [6]. When cross-linked with phenolic resins, these resins form films that are more flexible than films from homopolymer BPA epoxy resins but still provide excellent adhesion. Lower T_g, lower viscosity, and more flexible epoxy resins can also be prepared from bisphenols with longer chain links between the two phenol rings, especially multiple 1,2-diether groups [7]. Experimental resins to demonstrate the idea were prepared by reacting a series of such bisphenols with DGEBPA, using ethyltriphenylphosphonium acetate/acetic acid in methyl alcohol as a catalyst. The polyglycidyl ether of castor oil is used with BPA to improve flexibility and water resistance.

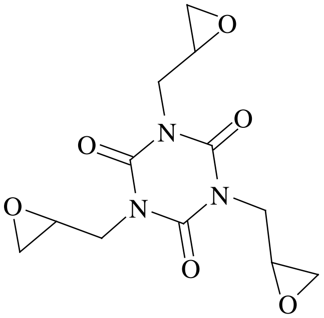
Hydrogenated BPA epoxy resins have lower T_g and lower viscosity than do BPA resins having the same n value. They also exhibit better exterior durability relative to both BPA and BPF resins, resulting from the absence of the UV absorbing aromatic ether groups. Brominated BPA epoxy resins are used in flame retardant coatings.

Epoxy resins are also prepared by reaction of ECH with novolac phenolic resins (Section 13.6.2). The resulting novolac epoxy resins are useful in applications in which more than two epoxy groups per molecule are desirable, especially in powder coatings where solid epoxy resins are needed. Epoxy resins derived from the reaction of *o*- or *p*-cresol–formaldehyde novolacs and ECH are available, with an epoxy $\bar{f}_n$ of 2.2 to 5.5. Other novolac epoxy resins are prepared from novolac resins made with phenol or bisphenol A. Epoxy resins with a functionality of 4 are obtained from tetraphenolethane. Cross-linked novolac epoxy resin coatings are more chemically resistant than BPA epoxy resins, due to the higher cross-linked density resulting from the higher functionality. A general structure of novolac epoxies is shown below.



Epoxy novolac resin

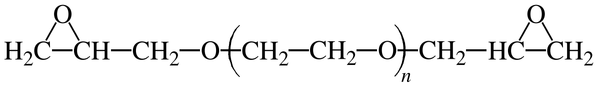
Triglycidylisocyanurate (TGIC) is a solid trifunctional epoxy cross-linker used in powder coatings. The presence of three functional groups gives higher cross-link density than that obtained with BPA epoxy resins, and photochemical stability of the cured coatings is superior. However, there is concern that use of TGIC may present toxic hazards.



Triglycidylisocyanurate

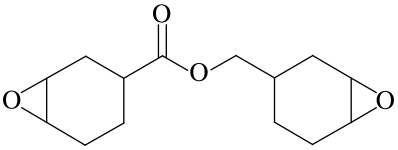
In order to reduce VOC, reactive diluents are being used. A coating formulated with the triglycidyl ether of TMP and a phenol–formaldehyde novolac resin showed better resistance to methylene chloride, acetic acid, and sulfuric acid than one formulated with a bisphenol F resin [8]. Neopentyl glycol, butanediol, and cyclohexanedimethanol diglycidyl ethers are also used. Monofunctional epoxies such as the glycidyl ether of *n*-butyl alcohol, *o*-cresol glycidyl ether, and the glycidyl ester of neodecanoic acid are used to make very high solids coatings. Being monofunctional, they reduce cross-link density, generally resulting in some loss of properties when used with BPA epoxy resins. They are more useful for reducing VOC of novolac epoxies, since novolacs have higher functionality as well as higher viscosity than BPA epoxies.

A variety of other aliphatic epoxy products is available. Epoxidized soy and linseed oils are used in making acrylate derivatives for UV cure resins (Section 29.2.4) and thermal cationic cure resins (Section 13.3.6). Others are made by the reaction of polyols, such as glycerol, sorbitol, and polyethylene or polypropylene glycols, with ECH and a base catalyst. Such aliphatic epoxies are used as reactive diluents to reduce viscosity and give films with better exterior durability.

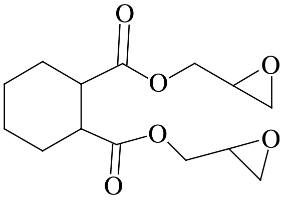


Polyethylene glycol diglycidyl ether

Also available are low MW cycloaliphatic diepoxy compounds such as 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexylcarboxylate (**1**), prepared by epoxidation of the corresponding alkenes, generally with peracetic acid. Another is diglycidyl 1,2-cyclohexanedicarboxylate (**2**). Such low MW epoxy derivatives are particularly useful as reactive diluents in cationic coatings (Sections 13.3.6 and 29.3.1). They can also be used as cross-linking agents for polyols (Section 13.3.3), carboxylic acids, and anhydrides (Section 13.3.2).

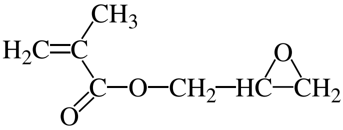


(**1**)



(**2**)

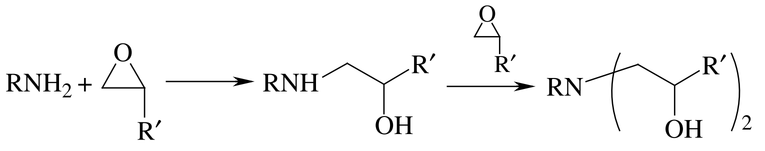
A widely used way to make epoxy-functional resins is by free radical polymerization of acrylic esters with glycidyl methacrylate (GMA) as a co-monomer. By varying co-monomers, GMA content, and MW, a range of materials can be made. Exterior durability and acid resistance can be excellent. GMA modified acrylic resins are used in clear coats for automobiles, among other applications.

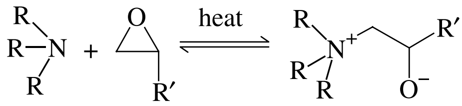


Glycidyl methacrylate (GMA)

13.2. EPOXY–AMINE SYSTEMS

Epoxy groups react at ambient temperatures with primary amines to form secondary amines and with secondary amines to form tertiary amines. Tertiary amines react at higher temperatures to form quaternary ammonium compounds.



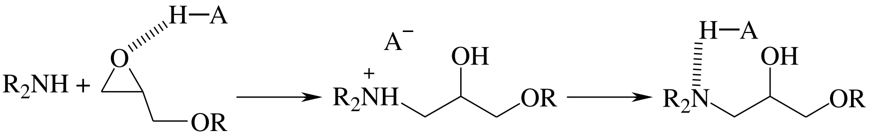


Reaction rates depend on epoxy and amine structure, concentration, catalysis, and media effects. Terminal epoxy groups such as glycidyl ethers and esters are more reactive than internal epoxy groups [e.g., cycloaliphatic diepoxide (**1**)], which are more sterically hindered.

Reactivity of amines tends to increase with base strength and decrease with steric crowding. The general order of reactivity, primary $>$ secondary $\gg$ tertiary amines, can be attributed to steric effects as well as to the absence of a transferable proton in the case of tertiary amines. Cycloaliphatic amines have reduced reactivity; the second reaction of such an amine is particularly slow. Aliphatic amines are more reactive than aromatic amines, which are less basic. The reaction is catalyzed by water, alcohols, tertiary amines, and weak acids (most notably by phenols), which promote ring opening by proton complexation with the epoxide oxygen. Strong acids are not effective catalysts for the reaction, since they protonate the amine in preference to the epoxide. Hydrogen-bond acceptor solvents tend to reduce reaction rates, probably by complexing with hydrogen donors in competition with the epoxy group.

Scheme 13.2 shows the attack on an epoxy group by the nonbonded electron pair of a secondary amine. Attack is primarily at the less sterically hindered terminal end of the epoxy group. Scheme 13.2 also shows catalysis by a weak acid (HA) by hydrogen complexation and hydrogen donation to the epoxide oxygen, which facilitates ring opening. The catalyst is regenerated by removing the proton from the amine nitrogen, which takes on a positive charge during the reaction. The conjugate base A^- could also participate in the catalysis by assisting removal of the amine proton during the ring-opening reaction. Based on this reasonable possibility, an explanation for the more effective catalysis by weak acids relative to strong acids noted earlier can be hypothesized. A strong acid (e.g., HCl) exists predominately as the amine salt ($R_2NH_2^+Cl^-$). Because of the large

Scheme 13.2



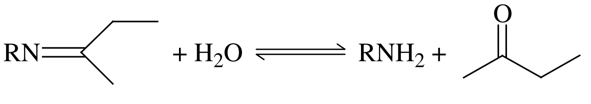
excess of amine reactant compared to the catalyst, even weaker acids such as phenols are also expected to exist largely as the corresponding salts ($R_2NH_2^+ArO^-$). This suggests that the proton donor in the reaction is the same amine ion in both cases. On the other hand, the proton acceptor, ArO^-, is a substantially stronger base than Cl^- because conjugate base strength increases as acid strength decreases. The proton acceptor ArO^- more effectively promotes the second reaction shown in Scheme 13.2. Although we are unaware of experimental evidence that directly supports this hypothesis in epoxy–amine reactions, the general importance of concerted weak acid–weak base catalysis is well established [9]. 2,4,6-[Tris(dimethylaminomethyl)]phenol, which has both phenolic and tertiary amine groups, is an important catalyst for epoxy–amine reactions.

Epoxy–amine reactivity is too high at ambient temperatures to allow sufficient storage stability of a coating containing polyamine and polyepoxide in the same package; thus, two package (2K) coatings are required. With many aliphatic amines, the pot life is limited to a few hours, and the coating generally takes about a week to cure at ambient temperature.

13.2.1. Pot Life and Cure Time Considerations

Epoxy–amine coatings are formulated to maximize pot life and minimize cure time. (See Section 2.3.2 for a discussion of kinetic limitations that prevent both long-term one-package stability and moderate cure temperatures and of ways to obviate these limitations.) Many factors must be considered, including reactive group concentrations; structural effects of amine, epoxy, and solvents on reaction rates; the equivalent and molecular weights; and the $\bar{f}_n$ of the reactants. As the MW of a BPA epoxy resin is increased, the number of equivalents per liter of epoxy groups decreases; therefore, the reaction rate is slower. Furthermore, as the MW increases, viscosity increases. Thus, to formulate to the same viscosity, the amount of solvent must be increased, which decreases the concentration of both the amine and epoxy groups and lengthens pot life. Unfortunately, the need to reduce VOC emissions forces formulation of higher solids coatings, which have shorter pot lives.

An approach to the important problem of lengthening pot life without reducing cure time is to use blocked amine cross-linkers. Ketones react with primary amines to give ketimines, which do not readily react with epoxy groups. However, ketimines hydrolyze with water to release free amine plus ketone: the reverse reaction of ketimine formation. Ketimine–epoxy moisture-curable coatings are stable in a moisture-free environment but cure after application and exposure to ambient moisture. Most commonly, methyl ethyl ketone (MEK) is used. The high volatility of MEK from thin coating films minimizes reverse reaction with amine.

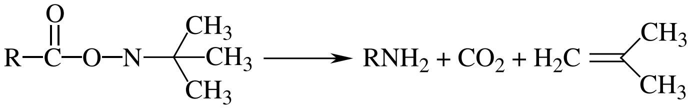


Ketimine MEK

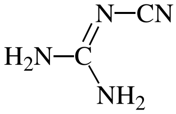
Ketimine–epoxy systems are stable indefinitely in the absence of water and should therefore permit formulation of one package coatings. Nevertheless, they are most commonly used in long pot life two package coatings, because of the difficulty of drying all of the components in a coating. Many epoxy–amine coatings are pigmented, and pigment surfaces have a layer of water on them before they are dispersed. The water remains in the coating and hydrolyzes the ketimine. Although removal of water from the surface of the pigment is possible, it adds to the cost. The amount of water is not high, usually less than 1% of the pigment weight, but the MW of water is so low that a little water will hydrolyze a larger amount of ketimine. Solvents also contain water, and use of anhydrous solvents would also increase costs. A further difficulty is that, cure rate depends on relative humidity as well as temperature.

An interesting approach to increasing storage stability of epoxy coatings sufficiently to permit formulation of one package coatings that can be cured at moderately elevated temperatures is to use a cross-linker that must undergo a phase change in order to react. A solid polyamide prepared from phthalic anhydride and diethylenetriamine [DETA; $H_2N(CH_2CH_2NH)_2H$] is an example [10]. When dispersed in an epoxy resin and heated above 100°C, the solid polyamide liquefies and reacts to form imides, releasing amine cross-linkers, including free DETA. Because the polyamide is a solid during storage, its reaction rate is not controlled by the kinetics of the reaction, so Arrhenius restrictions on package stability versus cure schedule (Section 2.3.2) do not apply.

Tertiary alcohol (e.g., *t*-butyl) urethanes are relatively unstable and may thermally decompose to give alkenes, carbon dioxide, and amines. Advantage is taken of this reaction by using *t*-butyl alcohol–blocked isocyanates as sources of amines to cross-link epoxy resins. It has been shown that reaction of an oligomer obtained from reaction of *t*-butyl alcohol–blocked IPDI with an epoxy resin liberates amine that reacts with epoxy groups to yield amine cross-links, typical of epoxy amine coatings, rather than urethane cross-links [11].

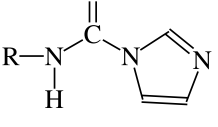


A commonly used cross-linker for epoxy powder coatings is dicyandiamide (DICY), a crystalline compound (mp 205°C) that also provides latency by insolubility. The complex reactions of epoxies with DICY have been the subject of numerous studies [12] but are not fully understood.



Dicyandiamide (DICY)

Dicyandiamide decomposes into soluble reactive products below its melting point, and cure temperatures can be reduced substantially by using as accelerators tertiary amines (e.g., benzyldimethylamine), imidazoles (e.g., 2-methylimidazole), or a substituted urea [e.g., *N*-3-(*p*-chlorophenyl)-*N*′,*N*′-dimethylurea] that releases free amine at elevated temperatures. Imidazole-blocked 1,5-naphthalene diisocyanate (an imidazole urea) has been patented for use as a blocked catalyst for epoxy–dicyandiamide coatings [13]. The blocked catalyst provides stability required for one package products.



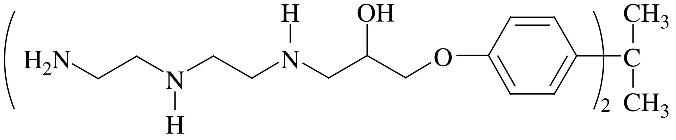
Imidazole urea

13.2.2. Toxicity and Stoichiometric Considerations

Factors other than reaction rates are involved in selecting amines. Many amines are toxic. Although they are easily handled safely in a chemical plant, toxic hazards can arise if relatively inexperienced, careless, or uninformed personnel mix and apply 2K epoxy coatings incorporating some amines. For example, diethylenetriamine (DETA) is an efficient cross-linker for epoxies, but the handling hazard is high. In general, toxic hazards are reduced by increasing MW and reducing water solubility. As MW increases, volatility decreases, which reduces the chances of inhaling dangerous amounts of amine. Also, as water solubility decreases and MW increases, permeability through body membranes such as skin decreases, generally reducing the toxic hazard. There are, of course, exceptions to these broad generalizations. Safety data sheets supplied by the manufacturer should always be read for safe handling recommendations.

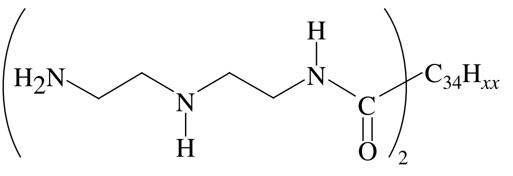
Other disadvantages of using low MW, highly functional amines are their low equivalent weights (EW) and viscosities. The EW of pure DETA is 21. If DETA were used with an epoxy resin with an EW of about 500, the stoichiometric weight ratio of the two components would be about 25 : 1. This disparate amount would reduce the probability of mixing stoichiometric amounts in two package coatings and increase the difficulty of uniform mixing.

One approach to designing amine cross-linkers with a higher EW and lower toxic hazard is to make *amine adducts*. Standard liquid BPA epoxy ($n = 0.13$) is reacted with an excess of a multifunctional amine such as DETA. The excess amine is removed by vacuum distillation, leaving the amine-terminated adduct, as shown in the idealized structure below. The low MW DETA is handled in the chemical factory only with proper precautions. Similar adducts are prepared using a variety of amines to provide adducts with a range of cure rates and pot lives.



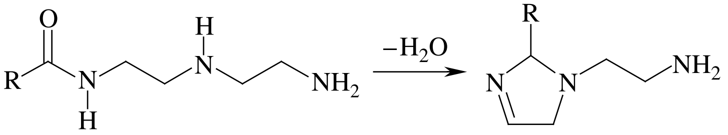
Epoxy amine adduct

Another approach is to react a multifunctional amine (e.g., DETA) with aliphatic mono- or dicarboxylic acids to form amine-terminated amides. Dimer fatty acids are widely used; they are complex mixtures, predominately C_{36} dicarboxylic acids, made by acid catalyzed dimerization of unsaturated C_{18} fatty acids from linseed or soy oil and tall oil fatty acids (Section 14.3.1). The reaction yields amine-functional polyamides. Terminology is confusing; amides derived from dimer acids are frequently called simply *polyamides*. The amide nitrogen groups do not react with epoxy groups; only the terminal amine groups do. (There are similar polyamides that are not amine-functional and not useful as cross-linkers for epoxy resins.) An example is made by reacting dimer acids with excess DETA. A mixture of products is obtained, including the simplest polyamide, shown below. The amine EW is the corresponding MW divided by the number of reactive NH groups (six in the polyamide shown). A range of polyfunctional amines is used in making polyamides, including DETA, triethylenetetramine (TETA), aminoethylpiperazine, and aromatic diamines such as *m*-phenylenediamine. The long aliphatic chains from the dimer acids improve flexibility, wetting, and adhesion as compared to use of an amine such as DETA.



Polyamide

In the preparation of polyamides using an amine such as DETA, the polyamide can react further by eliminating water and forming a terminal imidazoline group. The extent of this reaction varies, depending upon reaction conditions. The fraction of imidazoline affects solubility, compatibility, and pot life (and inversely reactivity). Imidazoline formation reduces average functionality and cross-link density of cured films [14,15]. Commercial grades of polyamides contain from 35 to more than 85% imidazoline, from which the formulator may choose in designing coatings for a particular application.



Imidazoline

A third approach is to react DETA with monocarboxylic acids. The products, frequently called *amidoamines*, are commonly used with a BPA epoxy. This, of course, increases the viscosity and the adducts are generally used with a high-boiling solvent such as benzyl alcohol. Compatibility with the cured film and its high boiling point result in part of the benzyl alcohol staying in the film.

Conventional amine curing agents are unsatisfactory when it is necessary to cure an epoxy coating at temperatures below 5°C—the cure rate is too slow. This problem has been addressed by using amine Mannich bases, prepared by reacting a methylolphenol with excess polyamine [16]. Although the functionality of the amine is reduced, the presence of the phenolic hydroxyl accelerates the epoxy–amine reaction.

13.2.3. Graininess and Blushing

BPA epoxy resins and polyamides are mutually soluble in the solvents used in epoxy–amine coatings, but most are not compatible in the absence of solvents. Thus, as solvent evaporates, phase separation can occur, resulting in a rough surface, called *graininess*. Graininess can be avoided by mixing the two packages 30 minutes to an hour prior to application. Partial reaction of the two components takes place during the waiting period. The elimination of graininess can be attributed to increased viscosity and/or the formation of reaction products that improve the compatibility of the mixture. When liquid standard resin is used, longer times are required after mixing to avoid phase separation. Proprietary amine cross-linkers are available that exhibit better compatibility, minimizing the problem [15].

Blushing or *scumming* is the appearance of a grayish, greasy deposit on the surface of films, usually accompanied by incomplete surface cure. Low-temperature high-humidity conditions increase the probability of blushing. Blushing decreases gloss, increases yellowing, gives poor recoatability, and may interfere with intercoat adhesion. Blushing is said to result from formation of relatively stable carbamate salts of some amine groups on exposure to carbon dioxide and water vapor in the atmosphere [17].

$$\mathrm{RNH_2 + CO_2 + H_2O \longrightarrow RNH{-}CO_2H \xrightarrow{RNH_2} RNH{-}CO_2^{-}\ H_3^{+}NR}$$

As with graininess, it is often possible to minimize blushing by mixing the epoxy and amine components one hour or so before application. During the waiting period, some of the most reactive amine groups (those most likely to form carbamates) react with epoxy groups, so when the film is applied after this waiting period, blushing is less likely to occur. If the waiting period is too long, viscosity increase is excessive. Amine adduct and Mannich base epoxy coatings show little, if any, blushing.

13.2.4. T_g Considerations

It is critical to select a combination of epoxy resin and amine cross-linker that will give a final T_g that permits relatively complete reaction of the amine and epoxy groups at the temperature encountered during application. As polymerization and cross-linking proceed, the T_g increases. As the T_g of a homogeneous network approaches the cure temperature T, $T - T_g$ and free volume decrease, and the reaction rate becomes limited by the mobility of the reactants rather than by their reactivity. If the T_g approaches a value of about 40 to 50°C above the reaction temperature, reaction essentially ceases and functional groups remain unreacted (Section 2.3.3). Unreacted functional groups cause adverse effects on mechanical properties and solvent resistance. If a coating that cures well when applied to an offshore oil rig in the Caribbean is applied to the support structure of an oil rig in the North Sea, where the water temperature even in summer does not exceed 4°C, adequate curing may not occur. A possible example of the effect of T_g is a report that after 7 days curing at 25°C, films from butyl ether–modified BPA epoxy resin (Section 13.1.2), cross-linked with an amine adduct, had better methyl alcohol resistance than films made with the same amine adduct and unmodified BPA epoxy resin [5]. There is no evident explanation for these results based on the chemical compositions. The superior methyl alcohol resistance may have resulted from a greater extent of reaction of the lower T_g butylated derivative before mobility limitation slowed the reaction.

13.2.5. Other Formulating Considerations

Epoxy coatings can be formulated for application under water to oil rigs, bridges, and so on. In such formulations it is essential that the polyamine be insoluble in water and that solubility of water in the polyamine is minimal. Water plasticizes epoxy–amine coatings, lowering the T_g.

Epoxy–amine coatings tend to exhibit limited solvent resistance and are particularly susceptible to attack by acidic solvents such as acetic acid. At least in part, this sensitivity results from diffusion of acetic acid into the film, followed by formation of acetate salts with amine groups. The hydrophilic salt groups increase the solubility of water in the film, increasing water permeability, which lowers T_g by plasticizing the film, making it more susceptible to damage. This situation is exacerbated when cross-link density is low. Bisphenol A epoxy resins have an $\bar{f}_n$ of about 1.9, so even with highly functional amine components, cross-link density is limited, especially if there is deviation from stoichiometry. Since the amines are usually polyfunctional, it is generally best to formulate with a small excess (about 10%) of amine cross-linker to assure that the epoxy groups are fully reacted. The problem can be alleviated by use of higher functionality epoxy resins such as novolac epoxies, which have $\bar{f}_n$ up to 5. With the higher functionality and more viscous novolac epoxies, care must be exercised in selection of an amine cross-linker to ensure adequate reaction. Sometimes, blends of BPA and novolac epoxy resins are used.

Addition of aminoethylaminopropyltrimethoxysilane to BPA epoxy–polyamide coatings improves heat resistance, decreases color change with heat, increases hardness, and increases solvent resistance as a result of the additional cross-linking [18].

Siloxane-modified epoxy resins are also reported to give superior coating properties. Formulation of a BPA epoxy resin modified by reaction with hydroxyl-terminated dimethylsiloxane, with a polyamide cross-linker, resulted in improved resistance to impact, mandrel bending, scratching, humidity, and NaOH. Due to the lower surface tension, films picked up much less dust [19].

Another factor to be considered when formulating epoxy–amine coatings is the effect of solvent composition on the coating. As noted earlier, hydrogen-bond acceptor solvents extend pot life. However, ketones and esters should be avoided, since they form ketimines or undergo aminolysis, respectively, especially with primary amines, at room temperature, which reduces the concentration of reactive amine groups. An exception is *t*-butyl acetate, in which case amine loss is essentially as slow as when xylene is used [20]. Another important advantage of *t*-butyl acetate is its negligible photochemical reactivity, resulting in its exemption from VOC regulations in the United States in 2005 and its absence on the HAP list.

Alcohols and water catalyze the reaction of amines with epoxy resins and can also react with epoxy groups, affecting the stability of the epoxy component package. Alcohols react very slowly with epoxy groups at room temperature. When the reactant is a monoalcohol, there is little change in viscosity. Formulators generally judge package stability by changes in viscosity, but in this case, there could be a change in epoxy functionality without a significant change in viscosity. To the extent that epoxy groups react with an alcohol, the potential for cross-linking is decreased. Since the $\bar{f}_n$ of BPA epoxy resins is somewhat less than 2, further loss of functionality could cause the final film to have inferior properties. Apparently, in many systems, there is no difficulty. For example, some epoxy resins are sold as solutions in glycol monoethers. However, in other cases, a decrease in epoxy content has been observed after storage over a period of several months.

A similar situation can arise with water. Again, reaction of an epoxy group with water consumes epoxy groups. In some cases, in which the epoxy package is pigmented with TiO_2, it has been shown that the epoxy content decreases with storage time, presumably as a result of the reaction of water from the surface of the TiO_2. This reaction, as well as that with alcohols, may be catalyzed by basic and/or acidic impurities or by alumina (basic) and silica (acidic), generally present as surface treatments on TiO_2. In most cases epoxy-package pigmented coatings have been used without problems. Apparently, the effects of both alcohols and water on package stability are system dependent. In view of such reports, it is recommended that package stability be checked periodically by epoxy group analysis rather than by relying solely on monitoring viscosity changes.

13.2.6. Waterborne Epoxy–Amine Systems

To reduce solvent content, waterborne epoxy–amine coatings have been widely investigated. One approach has been to make emulsions. Incorporation of emulsifying agents in either or both the amine and the epoxy package permits the addition of water during mixing. Application solids of a waterborne coating are lower than those of an organic solvent-soluble system, but the VOC content is lower, since a substantial fraction of the volatiles is water. Some loss of epoxy groups can be expected during the pot life of the mixed coating, due to the high water content. Proprietary "self-emulsifiable" epoxy resins and polyamides are available, which are made by reacting a surfactant with the epoxy resin or polyamide; properties approaching those of solventborne coatings can be achieved [21]. Properties equal to solventborne coatings have been disclosed for waterborne epoxy–amine coatings, derived from an advanced BPA epoxy resin emulsified with an epoxy-terminated surfactant together with a glycidyl ether of C_{8-14} alcohols and an amino-amide cross-linker [22].

Another approach to waterborne systems is to use salts of resins having primary amine groups. The amine groups of a concentrated solution of the resin in organic solvents are neutralized with hydrochloric acid. When the solution is diluted with water, polymer aggregates, swollen with solvent and water, are formed having the amine salt groups on the outer periphery of the aggregates suspended in a continuous water phase. The behavior is analogous to that of water-reducible resins discussed in Section 8.3. When an organic solution of epoxy resin is mixed into the system, it goes inside the resin aggregates. The epoxy groups are thus kept separate from the amine hydrochloride groups, permitting a pot life of several days. After the coating is applied, the water and solvent evaporate, leaving the amine hydrochloride and epoxy groups in the same phase. They react to yield a chlorohydrin and a free primary amine. Then the amine can react twice with two additional epoxy groups. Since BPA epoxy resins have less than two epoxy groups per molecule and about one in three of these groups will be converted to chlorohydrins, it is desirable to use at least some novolac epoxy with an $\bar{f}_n$ up to 5. Then when a third of the groups are converted to chlorohydrins, there is still an average of more than two epoxy groups per molecule to cross-link with amine groups.

A novel approach is to use weakly acidic solvents, such as nitroalkanes [23,24]. Nitroalkanes form salts of amines: as shown in the equation below; the salt groups stabilize epoxy–amine emulsions and allow the system to be reduced with water. Following application, the nitroalkane solvent evaporates, shifting the acid–base equilibrium to the free amine, that is, to the left in the equation. Thus, the amine–nitroalkane combination functions as a transient emulsifying agent that stabilizes the emulsion during storage and yet is not present to affect the final film properties adversely. Conversion of amine groups to salts prolongs the pot life of the mixed composition, since polar salt groups are oriented outward into the water phase while the epoxy groups are in the interior of the emulsion particles.

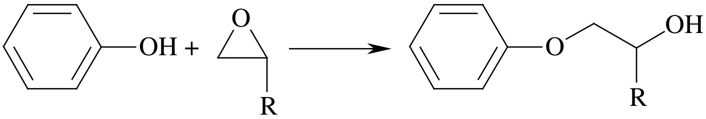
$$R{-}NH_2 + R_2CH{-}NO_2 \rightleftharpoons R_2C{=}NO_2^{-}\ H_3\overset{+}{N}{-}R$$

Resins used in automotive primers applied by cathodic electrodeposition are prepared by the reaction of epoxy and amine resins. The use of aqueous dispersions of carboxylate salts of such resins is discussed in Section 27.2.

13.3. OTHER CROSS-LINKING AGENTS FOR EPOXY RESINS

13.3.1. Phenols

Epoxy resins, including BPA and novolac epoxies, can be cross-linked with phenolic resins; both resole and novolac phenolic resins, discussed in Sections 13.6.1 and 13.6.2, respectively, can be used. The reaction with phenols occurs predominantly at the less hindered CH_2 site of unsymmetrical epoxides (e.g., glycidyl derivatives): The reaction is acid catalyzed; pTSA and phosphoric acids are commonly used.



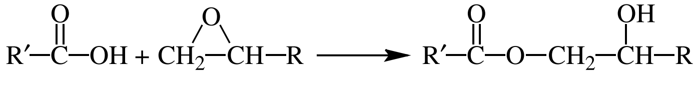
The phenolic hydroxyl groups of both resole and novolac phenolics react with epoxy groups. In addition, the methylol groups of the resole phenolics undergo self-condensation and probably also react with hydroxyl groups on the epoxy resin. Thus, cross-link density is higher with resole phenolics. There is also a reaction with the hydroxy groups formed by the reaction with phenols. The coatings require baking, and package stability is relatively limited. Package stability is enhanced with etherified resole resins. Increased solids and high functionality are reported using butoxymethylolated BPA as the phenolic resin [5]. For other examples, see Section 13.6.3.

Unpigmented epoxy–phenolic coatings are used as linings for beverage cans and for some types of food cans. Concern has been raised because of the possible endocrine disruption by free bisphenol A, an estrogen mimic. Studies are under way to determine whether trace amounts of BPA are extracted in food or beverage cans from BPA epoxy containing can linings [25]. Pigmented epoxy–phenolic coatings are used as high performance primers. In both cases, the major advantages are adhesion to metals, even in the presence of water, and complete resistance to hydrolysis. In both of these applications, neither the discoloration that occurs on baking nor poor exterior durability is important.

Waterborne epoxy–phenolic emulsion coatings have been developed. Since conventional surfactants remain in the final film and detract from water resistance, water-soluble amine salts of methacrylic acid copolymers have been recommended [26]. For example, an amine salt of a copolymer of 40 : 20 : 20 : 20 methacrylic acid/methyl methacrylate/ethyl acrylate/styrene was shown to be an effective emulsifying agent. A further approach to waterborne epoxy–phenolic coatings is to prepare carboxylic acid–functional derivatives [27]. For example, a polyalkylidene phenol can be reacted with a BPA epoxy resin and then with formaldehyde and a haloacetic acid. The product has carboxylic acid, epoxy, and methylol groups. Aqueous dispersions are prepared using a tertiary amine.

13.3.2. Carboxylic Acids and Anhydrides

Carboxylic acids are effective cross-linkers for epoxy coatings. Reference [28] provides a review of the patent literature. The reaction of a carboxylic acid and an epoxy group yields a hydroxy ester. Ring opening occurs predominantly at the less hindered CH_2 carbon, although reaction at the more hindered CH—R site is significant.



$$\text{R}'\!-\!\overset{\overset{\displaystyle\text{O}}{\|}}{\text{C}}\!-\!\text{OH} + \overset{\text{O}}{\overbrace{\text{CH}_2\!-\!\text{CH}}}\!-\!\text{R} \longrightarrow \text{R}'\!-\!\overset{\overset{\displaystyle\text{O}}{\|}}{\text{C}}\!-\!\text{O}\!-\!\text{CH}_2\!-\!\overset{\overset{\displaystyle\text{OH}}{|}}{\text{CH}}\!-\!\text{R} \qquad (13.5)$$

The reaction has been shown to be second order in carboxylic acid. Most likely, one of the acid groups functions by nucleophilic attack at the CH_2 group, whereas the other functions as an electrophile and assists ring opening by complexation with the epoxy oxygen (Scheme 13.2). The second-order dependence of reaction rate on acid concentration also results in a rapidly decreasing rate with conversion, exacerbating the difficulty of achieving high conversions:

$$\text{rate} = k[\text{epoxy}][\text{RCOOH}]^2$$

The third-order dependence of the reaction rate (first order in epoxy and second order in carboxylic acid) also results in a small Arrhenius *A* value owing to the high molecular ordering of the epoxide and two carboxylic acid groups required in the transition state, reducing reactivity at all temperatures. Glycidyl methacrylate copolymers and cycloaliphatic epoxides such as 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexylcarboxylate (**1**) and diglycidyl 1,2-cyclohexanedicarboxylate (**2**) react more rapidly than BPA epoxies. Tertiary amines catalyze the reaction of carboxylic acids with epoxies. Triphenylphosphine is also reported to be a particularly effective catalyst. With triphenylphosphine catalysis and an excess of epoxy groups to carboxylic acid groups, coatings can be formulated that cross-link at 25°C [29].

An extensive study of catalysis selection on curing temperature and film properties in triglycidylisocyanurate/carboxylic acid–functional polyesters for potential use in powder coatings has been published [30]. Benzyltrimethylammonium chloride was found to give the best combination of catalyst effects: fastest cure at 120°C, slowest cure at 80 to 90°C, and least yellowing on overbake. The slow cure at 80 to 90° is indicative of stability during extrusion. The results in actual powder coatings will be of interest.

Latent amine catalysts have been designed for powder coatings formulated with BPA epoxy resins and carboxylic acid–functional polyesters [31]. The catalysts are crystalline solid amic acids (e.g., the amic acid derived from the reaction of 3-methylphthalic anhydride and *N*, *N*-dimethylaminopropylamine). The amic acids are zwitterions, in which the tertiary amine is protonated, minimizing both their solubility in the powder coating and their catalytic activity. On heating, the amic acid melts and undergoes intramolecular cyclization to an imide with the elimination of water and deprotonation of the tertiary amine, which catalyzes the carboxylic acid–epoxy reaction.

Hydroxyl groups compete with carboxylic acid groups in reactions with epoxides. When carboxylic acids are used as cross-linking agents, part of the cross-links result from the reaction of epoxies with hydroxyl groups originally present on the epoxy resin or generated in the epoxy–carboxylic acid reaction. Esterification of carboxylic acid groups with hydroxyls may also occur.

Carboxylic acid–functional acrylics can be cross-linked with BPA epoxy resins, as well as with acrylic copolymers, having pendant epoxy groups derived from glycidyl methacrylate (GMA) as a co-monomer [28]. Self cross-linking acrylics can be made by incorporating both (meth)acrylic acid and GMA in the same polymer. Although the reaction rate of epoxy groups with carboxylic acid groups at storage temperatures is slow, it is not zero. When self cross-linking resins are made, the time of storage stability starts when the resin is made. On the other hand, when the functional groups are on two different resins, the time of storage stability does not start until the resins are mixed to make the liquid coating.

A waterborne epoxy coating cross-linked with carboxylic acid groups has been reported to give films with a combination of flexibility, hardness, solvent resistance, and light color [32]. The cross-linker was prepared by reacting 2 mol of trimellitic anhydride (TMA) with 1 mol of ethylene glycol to give a combination of 60% ethylene glycol bis(anhydromellitate) and 11% unreacted TMA, the balance being oligomers. Aqueous dispersions of a BPA epoxy resin were reacted with aqueous solutions of the cross-linker which were stable and in which the anhydride groups hydrolyzed to acids.

Cyclic anhydrides are also used as cross-linkers for epoxy resins. (See Ref. [28] for a review of the patent literature.) Anhydrides react initially with the epoxy resin hydroxyl groups, yielding esters and carboxylic acids. The resulting carboxylic acid groups then react with epoxy groups. This reaction generates a new hydroxyl group, and so on. Epoxy groups can also react directly with anhydrides. Tertiary amines are generally used as catalysts; they probably function primarily by reacting with the epoxy to form a transient zwitterion, which then reacts with the anhydride.

13.3.3. Hydroxyl Groups

Hydroxy-functional resins are not sufficiently reactive with BPA epoxy resins to be useful as cross-linkers, although when BPA epoxies react with resole phenolic resins, carboxylic acids, and anhydrides, reaction also occurs with hydroxyl groups. However, with proper catalysis, cycloaliphatic epoxies serve as cross-linking agents for polyols for films baked at 120°C. This reactivity has been used to formulate waterborne coatings based on caprolactone polyols and 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexylcarboxylate (**1**) with diethylammonium triflate as a blocked catalyst [33]. The active catalyst, triflic acid, is sufficiently strong that it is not consumed by direct addition to epoxide groups. (See a related discussion in Section 13.3.6.)

BPA epoxy resins can be cross-linked by reactions of their hydroxyl groups. Both MF and UF amino resins are used; cross-linking occurs mainly between the activated ether groups of the MF or UF resin and the hydroxyl groups of the epoxy resin by transetherification (Chapter 11). Generally, amine salts or esters of pTSA or another sulfonic acid are used as latent catalysts.

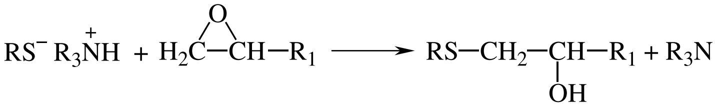
BPA epoxy resin emulsions in water have been cationically polymerized by perchloric acid. The product is higher MW polyols, although some epoxy groups remain. Coatings are formulated with MF resins to yield cross-linked films. The resins have the advantage that the amount of free BPA and $n = 0$ BPA epoxy resin is much lower than when conventional epoxy resins are used, such as in can linings [34].

Polyisocyanates also cross-link the hydroxyl groups of epoxy resins. Blocked isocyanates are generally preferred because they permit one-package stability (Section 12.5).

13.3.4. Mercaptans

Mercaptans (thiols, RSH) react with epoxies to yield sulfides. The reaction is strongly catalyzed by tertiary amines, which convert the mercaptan into the more highly reactive mercaptide anion RS^-. Following addition of RS^-, the intermediate alkoxide anion is protonated by the ammonium cation, thereby regenerating the catalyst, as shown.

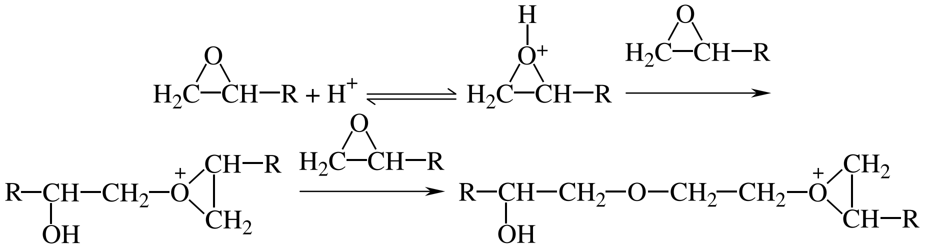
$$RS{-}H + R_3N \rightleftharpoons RS^- R_3\overset{+}{N}H$$



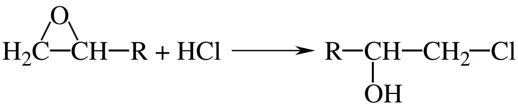
Reactivity of the mercaptide anion is sufficient for ambient temperature cure 2K coatings. Polysulfide rubbers are low MW mercaptan-terminated polymers; they have been used to cross-link with BPA epoxy resins in primers for aircraft. The unpleasant odor of mercaptans is a drawback for some applications.

13.3.5. Homopolymerization

Epoxy groups undergo homopolymerization to polyethers in the presence of tertiary amines, Lewis acids, and very strong protic acids (super acids). Acid precursors are most commonly used as initiators. There are two types: blocked or latent acids that undergo thermal decomposition to give the free acid and photoinitiators that release acid on exposure to UV. UV curable epoxy coatings are discussed in Section 29.3.1. The following equation shows initiation and the first step of polymerization:



Suitable super acids are trifluoromethylsulfonic acid (triflic acid; F_3CSO_3H), hexafluoroantimonic acid ($HSbF_6$), hexafluoroarsenic acid ($HAsF_6$), hexafluorophosphoric acid (HPF_6), and boron trifluoride (BF_3) etherate. Since strong acids have weak conjugate bases, the corresponding counter ions are nonnucleophilic. Only super acids are effective for homopolymerization of epoxies. Relatively strong acids such as HCl and pTSA are ineffective because the conjugate bases of such acids are nucleophilic enough to add to the protonated epoxy group, preventing addition of a second epoxy group, as in the homopolymerization reaction. The result is addition to form a chlorohydrin (or a sulfonate ester) rather than polymerization.



Homopolymerization can also be used for thermosetting coatings. α,α-Dimethylbenzylpyridinium hexafluoroantimonate is a blocked catalyst that permits curing at 120°C of a GMA copolymer using 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexylcarboxylate (**1**) as a reactive diluent while retaining adequate pot life [35]. Cycloaliphatic epoxides such as **1** have been used along with polyols in thermal cationic cure coatings (Section 13.3.3); part of the cross-linking is from homopolymerization and part from reaction with hydroxyl groups [36]. Epoxidized linseed oil can be added to increase impact resistance.

13.4. WATER-REDUCIBLE EPOXY ACRYLIC GRAFT COPOLYMERS

A large scale use of epoxy resins is to make water-dispersible acrylic graft copolymers [37,38]. One way to prepare such graft copolymers is to react an acrylic copolymer derived from ethyl acrylate, styrene, and methacrylic acid with a BPA epoxy resin in a glycol ether solvent under conditions where only a fraction of the carboxyl groups react. A phenolic resin or Class I MF resin is added as a cross-linker, the acid groups are neutralized with an amine, and the system is diluted with water. The result is a dispersion that is used as a spray applied coating for the interior linings of two piece beverage cans.

A second method is to polymerize ethyl acrylate, styrene, and methacrylic acid using benzoyl peroxide as initiator in the presence of a BPA epoxy resin in a glycol ether solvent. The reaction is carried out at about 130°C, at which both benzoyloxy and phenyl radicals are generated. These radicals can initiate polymerization as well as abstract hydrogens from the epoxy resin [39]. Abstraction of a hydrogen results in a free radical on the epoxy resin backbone, which serves as an initiating site for polymerization of the vinyl co-monomers. Thus, a graft copolymer is formed with acrylic–styrene side chains substituted with carboxylic acid groups (from the methacrylic acid). The product is a mixture of epoxy–acrylic graft copolymer, nongrafted acrylic copolymer, and unreacted epoxy resin. The complex resin mixture is mixed with amine, cross-linker, and water as above to form a dispersion. Since the water-solubilizing groups are attached by C—C bonds rather than by ester groups, as in the first method, the resins are resistant to hydrolysis during storage. Sometimes, a latex is blended with epoxy–acrylic dispersions to reduce cost.

13.5. EPOXY RESIN PHOSPHATE ESTERS

Phosphoric acid reacts with BPA epoxy resins to generate phosphate esters. Complex reactions occur; the predominant product is the monophosphoric acid ester of the primary alcohol, but other products are also present [30]. Most epoxy groups are hydrolyzed during the reaction to give the corresponding diols.

Low MW *epoxy phosphates* are used as adhesion promoters. Higher MW epoxy resins can also be modified by reacting with minor amounts of aqueous phosphoric acid. Their use in epoxy–phenolic formulations gives coatings with better adhesion and flexibility, without the need for a phosphoric acid catalyst, than those with corresponding unmodified epoxy–phenolic coatings [40].

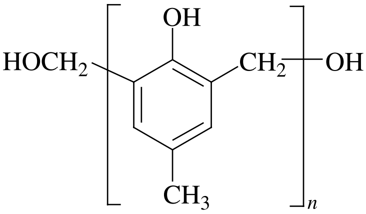
13.6. PHENOLIC RESINS

Although their importance has waned, phenolic resins still have significant uses. Phenolics are made by reaction of formaldehyde with phenol and substituted phenols. The products depend on the phenol(s) used, the stoichiometric ratio of phenol to formaldehyde, and the pH during the reaction. Phenolic resins are divided into two broad classes: *resole phenolics*, which are made using alkaline catalysts and high ratios of formaldehyde to phenol, and *novolac phenolics*, which are made using acid catalysts and low ratios of formaldehyde to phenol. Phenolic resins are used on a large scale in plastics and adhesives applications. (See Ref. [41] for details of the chemistry and the wide range of applications.)

13.6.1. Resole Phenolic Resins

Under alkaline conditions, the initial reaction product of phenol and formaldehyde is a mixture of ortho and para methylolated phenols. The methylolated phenols are more reactive with formaldehyde than the unsubstituted phenol, resulting in the rapid formation of 2,4-dimethylolphenol and subsequently, 2,4,6-trimethylolphenol; the latter is the predominant product, with a large excess of formaldehyde and a relatively short reaction time. With lower ratios (but still a molar excess) of formaldehyde to phenol and longer reaction times, formation of higher MW resole phenolic resins is favored. Polymerization occurs primarily by a methylol group on one phenol reacting at the ortho or para position of another phenol to form a methylene bridge connecting the two phenols. Dibenzyl ether bridges connecting two phenols also form by reaction of two methylol groups with each other. With excess formaldehyde, methylol groups are present on the terminal phenol groups of resole resins. Although not shown in the general structure, some of the aromatic rings have three substituents.

Such phenol-based resole resins cross-link on heating and are used in adhesive and plastics applications. However, they are not suitable for coatings applications, primarily because their cross-link density is higher than appropriate for any coating. Furthermore, the package stability of the resins is limited. Resole phenolics useful in coatings applications are made from monosubstituted phenols and mixtures of monosubstituted phenols with phenol. The use of substituted phenols reduces the potential cross-link density. There are two broad categories of such resins: (1) those that are soluble in alcohol and other low MW oxygenated solvents, commonly called *alcohol-soluble heat-reactive phenolics*, and (2) those that are soluble in vegetable oils and are called *oil-soluble heat-reactive phenolics*.



Resole phenolic resin (from *p*-cresol) (idealized structure)

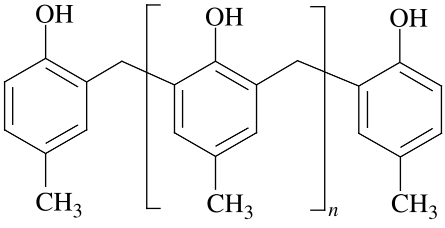
Alcohol-soluble heat-reactive resole resins are prepared by reacting phenol, *o*- or *p*-cresol, and formaldehyde in the presence of a base catalyst at less than 60°C while removing water under vacuum. The catalyst is neutralized, alcohol is added, and the salt resulting from catalyst neutralization is removed by filtration. Potential cross-link density is controlled by the ratio of phenol to cresol; MW is controlled by the ratio of formaldehyde to phenols and by reaction time.

Such resole phenolic resins are used in interior can coatings and tank linings. They require baking using an acid catalyst to cure in short times. To enhance flexibility and adhesion, they are commonly blended with low MW poly(vinyl butyral) as a plasticizer. The films are resistant to swelling by oils, such as encountered in canned fish, and are completely resistant to hydrolysis. These resins and other heat-reactive phenolics discolor during baking due to quinone methide formation, which restricts their use to applications for which development of a yellow-brown color is permissible. These resins are also blended with epoxy resins in thermosetting coatings for applications such as primers and can coatings (Section 13.3.1). The absence of hydrolyzable bonds and generally excellent adhesion properties are their chief advantages.

Oil-soluble heat-reactive phenolics are prepared by reacting a para-substituted phenol (e.g., *p*-phenylphenol, *p*-*t*-butylphenol, or *p*-nonylphenol) with somewhat less than 2 mol of formaldehyde per mole of substituted phenol. The resulting resole phenolics are cast from the reactor after neutralization of the catalyst. The resulting resole phenolics are solid, linear resins with terminal methylol groups. The most common use for such resins is to make varnishes with linseed oil and/or tung oil. However, since varnishes have, in large measure, been replaced by other vehicles, the consumption of these resins has declined markedly.

13.6.2. Novolac Phenolic Resins

Novolac phenolics of interest for coatings are made with acid catalysts and *o*- or *p*-substituted phenols. MW is controlled by the molar ratio of phenol and formaldehyde, which is always greater than 1. In contrast to resole phenolics, the terminal phenol groups are not metholylated, as shown in the idealized structure.



Novolac phenolic resin

Three types of novolac resins are used in coatings:

1. Alcohol-soluble nonheat-reactive low MW phenolics are derived from *o*- or *p*-cresol. An important use for these resins is in the preparation of novolac epoxy resins by reaction with epichlorohydrin (Section 13.1.2).

2. Oil-soluble nonheat-reactive novolac phenolic resins are made using a low ratio of formaldehyde, an acid catalyst, and a substituted phenol (e.g., *p*-phenylphenol, *p*-*t*-butylphenol, or *p*-nonylphenol). They are used together with drying oils, particularly tung oil or tung–linseed oil mixtures, to make varnishes. Such varnishes are still used to a small extent as marine spar varnish, for which their reputation for durability maintains their position in the do-it-yourself marine yacht market. The durability of phenolic varnishes may well result, at least in part, from the antioxidant activity of the phenolic groups. (See Section 5.2.2 for a discussion of phenolic antioxidants.)

3. Rosin-modified phenolic resins are the principal type of modified phenolics still in use. Their use in coatings is limited to low cost varnishes. The largest volume use is in printing inks. For inks, the phenolic resin is prepared in the presence of rosin esters and/or zinc or calcium salts of rosin. The structures of the reaction products, which are

high melting hydrocarbon-soluble resins, are not completely known. An important example of their use is in publication gravure inks such as those used in mail-order catalogs and some magazines. They are also used, to a degree, in heat-set letterpress printing inks for magazine and paperback book applications.

13.6.3. Ether Derivatives of Phenolic Resins

The package stability of alcohol-soluble resole resins and their compatibility with epoxy resins can be improved by partial conversion of the methylol groups to ethers. The ether groups undergo exchange reactions with hydroxyl groups in the presence of acid catalysts. Allyl ethers have been used for many years to cross-link epoxy resins in interior can coatings.

Low MW *n*- and isobutyl ethers are also used for cross-linking epoxy resins and other hydroxy-substituted resins, primarily by etherification and transetherification reactions [42]. A typical resin has an average of 2.2 aromatic rings per molecule. Due to its low average MW (ca. 320) the resin has a moderate viscosity, as supplied in butyl alcohol solution. The reactive groups in the resins are primarily butoxymethyl groups, but there are also benzyloxy groups and some free methylol groups. Furthermore, the phenol groups can react with epoxy groups. Acid catalysts such as phosphoric or sulfonic acids are generally used. Blocked acids may be utilized to extend shelf life.

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14

Drying Oils

Among the oldest binders for paints are *drying oils*, which are liquid vegetable or fish oils that react with oxygen to form solid films. They have been used since prehistoric times. Leonardo da Vinci, Rembrandt van Rijn, and most other famous painters used drying oils. In the nineteenth and early twentieth centuries, binders of most paints were drying oils. Their use has decreased; however, they still have applications. Most important, they are raw materials for other binders, such as alkyd, epoxy ester, and uralkyd resins (Chapter 15). These resins can be considered to be synthetic drying oils; an understanding of drying oil chemistry is a necessary foundation for understanding them, which is presented herein; general references are also provided for more specific details.

14.1. COMPOSITION OF NATURAL OILS

Naturally occurring oils are *triglycerides*, triesters of glycerol and fatty acids. Some triglycerides are drying oils, but many are not. The reactivity of drying oils with oxygen results from the presence of 1,4-dienes ($—CH{=}CHCH_2CH{=}CH—$), which comprise diallylic methylene groups, or 1,3-conjugated double bonds. Esters of many different fatty acids occur in nature. Fatty acids with 18 carbon atoms are most common; those found in oils that are most important in coatings are provided below. The letters c and t represent *cis* and *trans* orientation, corresponding to *zusammen* and *entgegen*, respectively; the numbers designate the position of the first

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Organic Coatings: Science and Technology, Third Edition, by Zeno W. Wicks, Jr., Frank N. Jones,
S. Peter Pappas, and Douglas A. Wicks

carbon of the double bond.

$CH_3(CH_2)_{16}COOH$
Stearic acid

$CH_3(CH_2)_{14}COOH$
Palmitic acid

$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$ (9c)
Oleic acid

$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$ (9c 12c)
Linoleic acid

$CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$ (9c 12c 15c)
Linolenic acid

$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_2CH{=}CH(CH_2)_3COOH$ (5c 9c 12c)
Pinolenic acid

$CH_3(CH_2)_5CH(OH)CH_2CH{=}CH(CH_2)_7COOH$
Ricinoleic acid

$CH_3(CH_2)_3CH{=}CHCH{=}CHCH{=}CH(CH_2)_7COOH$ (9t 11c 13t)
α-Eleostearic acid

The oils are mixtures of mixed triglycerides with different fatty acids distributed among the triglyceride molecules. Separation of the tens or hundreds of different triglyceride molecules present in an oil borders on the impossible. Therefore, oils are characterized by high performance liquid chromatography (HPLC) or gas chromatography (GC) of the methyl esters obtained by transesterification [1]. Typical fatty acid contents of some oils are given in Table 14.1. Compositions of the oils vary, sometimes quite widely, with variations in plant strain, climate, soil, and other growth conditions. Differences in sunflower oils are especially large, as illustrated in Table 14.1 for sunflower oils from Minnesota and Texas. In general, oils derived from seeds grown in colder climates have lower freezing points, due to higher levels of unsaturation.

Included in Table 14.1 are *tall oil fatty acids* (TOFA). The word *tall* is the Swedish word for *pine*. Tall oil fatty acids are obtained as a by-product of the sulfate pulping process for making paper. Oils present in the trees are saponified to soaps in the process. Tall oil fatty acids are obtained by acidification, followed by fractional distillation to separate the fatty acids from rosin acids and other by-products also present. These important fatty acids have a range of compositions, especially between acids of North American and European origin, as shown. They are often chemically modified to give conjugated bonds (Section 14.3.3).

Animal oils and fats are also triglycerides, but the only animal oils used to any degree in coatings are refined fish oils. They contain triglycerides of a wide spectrum of highly unsaturated fatty acids, including C_{18} to C_{26} fatty acids having up to five nonconjugated double bonds each separated by single methylene groups.

TABLE 14.1. Typical Fatty Acid Compositions of Selected Oils

	Fatty Acid				
Oil	Saturated[a]	Oleic	Linoleic	Linolenic	Other
Linseed	10	22	16	52	
Safflower	11	13	75	1	
Soybean	15	25	51	9	
Sunflower, MN	13	26	61	trace	
Sunflower, TX	11	51	38	trace	
Tung	5	8	43	80[b]	—
Tall oil fatty acids[c]	8	46	41[d]	3	2[e]
Tall oil fatty acids[f]	2.5	30	45	1	14[g]
Castor	3	7	3		87[h]
Coconut	91	7	2		

[a] Saturated fatty acids are mainly mixtures of stearic (C_{18}) and palmitic (C_{16}) acids; coconut oil also contains C_8, C_{10}, C_{12}, and C_{14} saturated fatty acids.
[b] α-Eleostearic acid.
[c] North American origin.
[d] Linoleic plus geometric and conjugated isomers.
[e] Rosin.
[f] European origin.
[g] Pinolenic acid.
[h] Ricinoleic acid.

14.2. AUTOXIDATION AND CROSS-LINKING

Drying, semi-drying, and non-drying oils are often defined based on their *iodine value*, that is, grams of iodine required to saturate the double bonds of 100 g of an oil. Some authors classify oils as follows: drying oils, iodine value greater than 140; semi-drying oils, iodine value 125 to 140; and non-drying oils, iodine value less than 125 [2]. Although iodine values can serve as satisfactory quality control specifications, they are not useful and can be misleading in defining a drying oil or for predicting reactivity.

14.2.1. Nonconjugated Drying Oils

A useful empirical relationship is that nonconjugated oils are drying oils if their *drying index* is greater than 70 [3]. The drying index is calculated as follows:

$$\text{drying index} = (\%\text{linoleic acid}) + 2(\%\text{linolenic acid})$$

Using this formula with the data from Table 14.1, the drying index of linseed oil is 120, so it is a drying oil; the drying index of soybean oil is 69, so it is a semi-drying oil. Linoleic and linolenic acids have one and two diallylic methylene groups ($\text{—CH=CHCH}_2\text{CH=CH—}$) per molecule, respectively, which are the active groups for initiating drying. Accordingly, drying is related more specifically to the average number of diallylic groups per molecule. If this number is greater than about 2.2, the oil is a drying oil; if it is moderately below 2.2, the oil is a semi-drying oil; there is no sharp dividing line between semi-drying oils and non-drying oils. These statements apply to synthetic drying oils as well as to natural oils. Since diallylic groups are the sites for cross-linking, it is convenient to relate the average number of such groups per molecule to the number average functionality $\bar{f}_n$ of the triglyceride or synthetic drying oil.

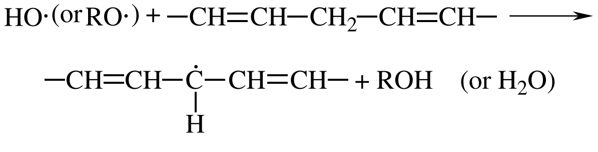
The diallylic methylene groups, activated by their allylic relationship to two double bonds, are much more reactive than methylene groups allylic to only one double bond, as reflected by the relative rates of autoxidation of synthetic triolein (glyceryl trioleate), trilinolein, and trilinolenein, which are 1 : 120 : 330, respectively [4]. The number of diallylic groups ($\bar{f}_{\mathrm{n}}$) of the three triglycerides are 0, 3, and 6, respectively; the theoretical iodine values are 86, 173, and 262. The autoxidation rates are more closely related to the number of diallylic groups between double bonds, $\bar{f}_{\mathrm{n}}$, than to iodine values, which are proportional to the average number of double bonds per molecule. Based on the data in Table 14.1, the $\bar{f}_{\mathrm{n}}$ of the linseed oil is 3.6; it is a drying oil. The $\bar{f}_{\mathrm{n}}$ of soybean oil is 2.07; it is a semi-drying oil. The higher the $\bar{f}_{\mathrm{n}}$ of a drying oil, the more rapidly a solvent-resistant cross-linked film forms on exposure to air.

The reactions taking place during drying are complex. Early studies of the chemistry of drying were done without benefit of modern analytical instrumentation, which has recently been brought to bear on this complex problem [5–7]. Cross-linked films form from linseed oil in the following stages: (1) an induction period during which naturally present antioxidants (mainly tocopherols) are consumed, (2) a period of rapid oxygen uptake with a weight gain of about 10% (FTIR shows an increase in hydroperoxides and appearance of conjugated dienes during this stage), and (3) a complex sequence of autocatalytic reactions in which hydroperoxides are consumed and cross-linked film is formed. In one study, steps 1, 2, and 3 were far along in 4, 10, and 50 hours, respectively, when catalyzed by a *drier* (Section 14.2.2) [5]. Cleavage reactions to form low molecular weight by-products also occur during the later stages of film formation. Slow continuing cleavage and cross-linking reactions through the lifetime of the film lead to embrittlement, discoloration, and formation of volatile by-products. Oils with significant quantities of fatty acids having three double bonds, such as linolenic acid, discolor to a particularly marked degree.

The following scheme illustrates some of the many reactions that occur during cross-linking. Initially, naturally present hydroperoxides decompose to form free radicals.

$$\mathrm{ROOH} \longrightarrow \mathrm{RO}\cdot + \mathrm{HO}\cdot$$

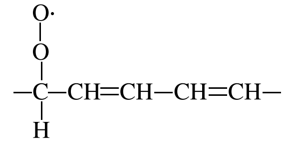
At first, these highly reactive free radicals react mainly with the naturally present antioxidant. But as the antioxidant is consumed, the free radicals react with other compounds. The diallylic methylene hydrogens are particularly susceptible to abstraction, yielding the resonance-stabilized free radical (**1**):



$$\mathrm{HO\cdot(or\,RO\cdot)} + \mathrm{-CH{=}CH{-}CH_2{-}CH{=}CH-} \longrightarrow$$
$$\mathrm{-CH{=}CH{-}}\underset{\displaystyle\mathrm{H}}{\dot{\mathrm{C}}}\mathrm{{-}CH{=}CH-} + \mathrm{ROH}\quad(\mathrm{or}\ \mathrm{H_2O})$$

(**1**)

Free radical **1**, in which the free electron is delocalized with high electron density on the terminal carbons, reacts with oxygen to give predominantly a conjugated peroxy free radical such as **2**:



$$-\underset{\mathrm{H}}{\underset{|}{\overset{\mathrm{O}\cdot}{\overset{|}{\overset{\mathrm{O}}{\overset{|}{\mathrm{C}}}}}}}-\mathrm{CH{=}CH{-}CH{=}CH}-$$

(**2**)

The peroxy free radicals can abstract hydrogens from other diallylic methylene groups to form additional hydroperoxides and generate free radicals such as **1**. Thus, a chain reaction is established, resulting in autoxidation. At least part of the cross-linking occurs by radical–radical combination reactions forming C—C, ether, and peroxide bonds. These reactions correspond to termination by combination reactions in free-radical chain-growth polymerization (Section 2.2.1).

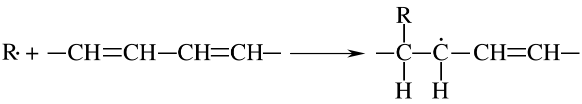
$$\mathrm{R}\cdot + \mathrm{R}\cdot \longrightarrow \mathrm{R{-}R}$$

$$\mathrm{RO}\cdot + \mathrm{R}\cdot \longrightarrow \mathrm{R{-}O{-}R}$$

$$\mathrm{RO}\cdot + \mathrm{RO}\cdot \longrightarrow \mathrm{RO{-}OR}$$

Cross-linking reactions

Reactions analogous to the addition step in chain-growth polymerization could also produce cross-links. For example, free radicals may add to conjugated double bonds, either initially present or formed from oxidation of diallylic groups, as in intermediate **2**, to give **3**.



$$\mathrm{R}\cdot + -\mathrm{CH{=}CH{-}CH{=}CH}- \longrightarrow -\underset{\mathrm{H}}{\underset{|}{\overset{\mathrm{R}}{\overset{|}{\mathrm{C}}}}}-\underset{\mathrm{H}}{\underset{|}{\dot{\mathrm{C}}}}-\mathrm{CH{=}CH}-$$

(**3**)

Such addition reactions could yield C—C or C—O linkages, depending on the structure of R·. Subsequently, free radical **3** can add oxygen to form a peroxy free radical, abstract a hydrogen from a diallylic methylene group, combine with another free radical, or add to a conjugated double bond system.

Studies of the catalyzed reactions of ethyl linoleate with oxygen (Section 14.2.2) by ^{1}H and ^{13}C NMR indicated that the predominant cross-linking reactions were those that formed ether and peroxy cross-links [6,7]. Mass spectroscopic studies showed that only about 5% of the cross-links were new C—C bonds [6]. However, Fourier transform infrared spectroscopy (FTIR) and FT Raman analysis of drying linseed oil lead to the conclusion that only C—O—C and C—C bonds were formed [8], which illustrates the difficulty of analyzing products in these systems. Substantial levels of epoxy groups were detected in the reaction mixture, rising to a maximum in about 5 days and virtually disappearing in 100 days [8]. It is suggested that epoxy groups may react with carboxyl groups from oxidation of aldehydes to form ester cross-links.

Rearrangement and cleavage of hydroperoxides to aldehydes and ketones, among other products, lead to low molecular weight by-products. It has also been shown that low MW carboxylic acids are released from linseed oil films as they age [9]. The characteristic odor of oil and alkyd paints during drying is attributable to such volatile by-products, as well as to the odor of organic solvents.

Undesirable odor has been a factor motivating replacement of oil and alkyds in paints with latex, particularly for interior applications. The reactions leading to these odors have been studied extensively in connection with flavor changes of vegetable cooking oils [10]. Aldehydes have been shown to be major by-products from the catalyzed autoxidation of methyl oleate, linoleate, and linolenate, as well as from curing of drying oil-modified alkyd resins [5,11]. It has also been shown that C_9 acid esters remain in the nonvolatile reaction mixture [11]. It has been proposed that formation of aldehydes, ketones, and carboxylic acids in the aging of films of linseed oil result from photoxidation [12].

Dried films, especially of oils with three double bonds, yellow with aging. The yellow color bleaches significantly when exposed to light; hence, yellowing is most severe when films are covered, such as by a picture hanging on a wall. The reactions leading to color are complex and are not fully understood. Yellowing has been shown to result from incorporation of nitrogen compounds and is increased markedly by exposure to ammonia. It has been proposed that ammonia reacts with 1,4-diketones formed in autoxidation to yield pyrroles, which oxidize to yield highly colored products [13]. A review of the causes of yellowing concludes that previous suggestions do not correspond to expectations from the mechanisms of drying of oils. The authors also show that yellowing of poppy seed oil is almost as severe as that of linseed oil, yet poppy seed oil contains very few fatty acids with three double bonds. It was proposed that yellowing results from contaminants in the oils but specific contaminants were not identified [14].

14.2.2. Catalysis of Autoxidation and Cross-Linking

The rates at which uncatalyzed nonconjugated drying oils dry are slow. Many years ago, it was found that metal salts (*driers*) catalyze drying. The most widely used driers are oil-soluble cobalt, manganese, lead, zirconium, and calcium salts of 2-ethylhexanoic acid or naphthenic acids. Salts of other metals, including rare earths, are also used. Despite many studies, there is not agreement as to the mechanisms by which driers work.

Cobalt and manganese salts, called *top driers* or *surface driers*, primarily catalyze drying at the film surface. Lead and zirconium salts catalyze drying throughout the film and are called *through driers*. Calcium salts show little, if any, activity alone, but reduce the amount of other driers needed. The surface-drying catalysis by cobalt is reported to accelerate the reaction of oxygen with methylene groups to form hydroperoxides; whereas manganese salts are reported, primarily, to accelerate decomposition of hydroperoxides to free radicals [15].

$$\mathrm{Co^{2+} + ROOH \longrightarrow RO\cdot + OH^- + Co^{3+}}$$

$$\mathrm{Co^{3+} + ROOH \longrightarrow ROO\cdot + H^+ + Co^{2+}}$$

Catalyzed decomposition of hydroperoxides

The net result is formation of water and free radicals. Note that cobalt cycles between the two oxidation states. The activity of through driers has not been adequately explained.

Combinations of metal salts are almost always used. Mixtures of lead with cobalt and/or manganese are particularly effective, but as a result of toxicity control regulations, lead driers can no longer be used in consumer paints sold in interstate commerce in the United States. Combinations of cobalt and/or manganese with zirconium, frequently including calcium, are commonly used. Zirconium may inhibit the deactivation of cobalt by carboxylic acids. A cobalt–zirconium combination is said to be particularly effective. Cobalt is said to primarily catalyze oxidation rather than polymerization, whereas a 1 : 3 Co–Zr complex increased both oxidation and polymerization. Zirconium was reported to be more effective than lead [16]. In a study of driers for high-solids alkyds, a combination of cobalt and neodymium salts with bipyridyl was found to be most suitable [17]. 1,10-Phenanthroline is also used to accelerate the activity of cobalt and manganese driers.

It has been reported that cobalt and cobalt salts may be carcinogenic and genotoxic. Model compound studies were carried out to find replacements. A tetranuclear cluster $[Mn_4O_2(\text{2-ethylhexanoate})_6(\text{bipyridine})_2]$ and a complex of manganese acetylacetonate/2,2′-bipyridine were found to be very effective [18,19].

Calcium does not undergo redox reactions; it has been suggested that it may promote drying by adsorbing preferentially on pigment surfaces, minimizing the adsorption of active driers. The amounts of driers needed are system specific. Their use should be kept to the minimum possible level, since they not only catalyze drying, but also catalyze the reactions that cause postdrying embrittlement, discoloration, and cleavage.

Skinning occurs when coatings prepared from drying oils or oxidizing alkyds are exposed to the atmosphere, especially when driers have been added. To control antiskinning, additives are required. (Antiskinning additives and a comparison of their effectiveness are reviewed in Ref. [20].) The most effective antiskinning agent was found to be methyl ethyl ketone oxime (MEKO). MEKO forms a complex with cobalt ions, $[Co(MEKO)_{1-8}]^{3+}$. The complex is in equilibrium with the components so that while it is present it reduces the effectiveness of the cobalt, but when paint is applied, the MEKO evaporates relatively rapidly, reversing the equilibrium releasing the cobalt. The MEKO is added to the coating just before filling into containers. In some cases a small amount of a solution of MEKO is added after the containers are filled and just before they are sealed, to prevent skinning during storage. Addition of 0.2% of MEKO prevents skinning for more than 250 days. In one study, MEKO increased the dust-free time of an alkyd coating to 2 hours from 1 hour 45 minutes, but reduced the fully dried time from 4 hours 45 minutes to 4 hours. The initial effect results from the time for the MEKO to evaporate completely. The fast full drying may result from faster permeation of oxygen in the earlier stages after application while MEKO is inhibiting surface cure.

14.2.3. Conjugated Drying Oils

Oils containing conjugated double bonds, such as tung oil, dry more rapidly than any nonconjugated drying oil. Drying of the ethyl ester of conjugated linoleic acid has been studied. Higher oligomers were formed than under comparable conditions with the nonconjugated ethyl linoleate. It was found that the initial cross-links were peroxide links, which, over time, became ether cross-links [21]. In general, the water and alkali resistance of films derived from conjugated oils are superior, presumably because more of the cross-links are stable ether bonds. However, since the α-eleostearic acid in tung oil has three double bonds, with baking and aging, discoloration is severe.

14.3. SYNTHETIC AND MODIFIED DRYING OILS

Several types of chemical modification of drying oils are in use. In addition to those discussed here, drying oil-modified alkyds, epoxy esters, and uralkyds are discussed in Chapter 15.

14.3.1. Heat-Bodied Oils, Blown Oils, and Dimer Acids

Both nonconjugated and conjugated drying oils can be thermally polymerized by heating under an inert atmosphere to form *bodied oils*. Bodied oils have higher viscosities and are used in oil paints to improve application and performance characteristics. Process temperatures may be as high as 300 to 320°C for nonconjugated oils and 225 to 240°C for conjugated oils, although the reactions occur at an appreciable rate at somewhat lower temperatures. At least in part, bodying may result from thermal decomposition of hydroperoxides, always present in natural oils, to yield free radicals, resulting in a limited degree of cross-linking. It has also been shown that thermal rearrangement to conjugated systems occurs followed by Diels–Alder reactions, which lead to formation of dimers [22]. Since tung oil has a high concentration of conjugated double bonds, it undergoes thermal polymerization more rapidly than nonconjugated oils (e.g., linseed oil). Unless one is careful to control the heating of tung oil, the polymerization will lead to gelation.

Viscosity can also be increased by passing air through drying oils at relatively moderate temperatures, 140 to 150°C, to produce *blown oils*. Presumably, reactions similar to those involved in cross-linking cause autoxidative oligomerization of the oil. The effects of temperature on blowing have been investigated. It is reported that the blown oils are shear thinning [23].

Polyunsaturated acids dimerize or oligomerize by heat treatment; the reactions are acid catalyzed. For example, the doubly unsaturated fatty acids of TOFA can be dimerized or oligomerized followed by removal of the residual monobasic acids by distillation. Under the high reaction temperatures, some decarboxylation occurs. Decarboxylation can be minimized by heating under pressure in the presence of a small percentage of water and activated clay. The products obtained are called *dimer acids*. They are predominantly C_{36} dicarboxylic acids, with small fractions of monocarboxylic acid and some C_{54} tricarboxylic acids. For some uses it is desirable to eliminate residual double bonds by hydrogenation. Dimer acids are used to make polyesters (Section 10.1.2) and polyamides (Section 13.2.2).

14.3.2. Varnishes

The drying rate of drying oils can be increased by dissolving a solid resin in the oil and diluting with a hydrocarbon solvent. Such a solution is called a *varnish*. The solid resin serves to increase the T_g of the solvent-free film so that film hardness is achieved more rapidly. The rate of cross-linking does not increase, so the time required for the film to become solvent resistant is not shortened. Any high melting thermoplastic resin soluble in drying oil will serve the purpose. The higher the "melt point" of the resin, the greater the effect on drying time. Naturally occurring resins such as congo, copal, damar, and kauri resins, synthetic resins such as ester gum (glyceryl esters of rosin), phenolic resins (Section 13.6), and coumarone–indene resins have been used.

In varnish manufacture, the drying oil (usually linseed oil, tung oil, or mixtures of the two) and the resin are cooked together to high temperature to obtain a homogeneous solution of the proper viscosity. The varnish is then thinned with hydrocarbon solvents to application viscosity. During cooking, some dimerization or oligomerization of the drying oil occurs; in some cases, reaction between the oil and resin has been demonstrated. Varnishes were widely used in the nineteenth and early twentieth centuries, but have been mostly replaced by a variety of other products, especially alkyds, epoxy esters, and uralkyds. The term *varnish* has come to be used more generally for transparent coatings, even though few of them today are varnishes in the original meaning of the word.

14.3.3. Synthetic Conjugated Oils

Tung oil dries rapidly but is expensive; and its films discolor rapidly due to the presence of three double bonds. These shortcomings led to efforts to synthesize conjugated oils, especially those containing esters of fatty acids with two conjugated double bonds. One approach is to dehydrate castor oil using acid catalysis. A major component (87%) of the fatty acid content of castor oil triglycerides is ricinoleic acid, 12-hydroxy-(*Z*)-9-octadecenoic acid, which dehydrates to mixed geometric isomers of 9,11-conjugated and 9,12-non-conjugated fatty acid esters. *Dehydrated castor oil* dries relatively rapidly at room temperature, but on further exposure to air, the surface becomes tacky. This *after tack* has been attributed to the presence of various geometric isomers formed during dehydration. Dehydrated castor oil and its fatty acids are used primarily to prepare alkyds and epoxy esters for baking coatings, in which after tack does not occur.

Non-conjugated oils can be partially isomerized to conjugated oils by heating with a variety of catalysts, mainly alkaline hydroxides. A similar process can be used to partially conjugate double bonds of TOFAs. Synthesis of conjugated fatty acids by treatment of oils at high temperature with aqueous alkali hydroxides accomplishes isomerization and saponification simultaneously [24]. The principal use of such conjugated oils and fatty acids has been to make alkyds and epoxy esters.

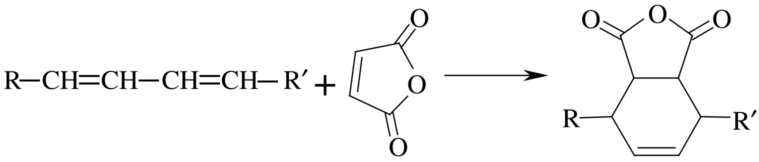
14.3.4. Esters of Higher Functionality Polyols

When oil-derived fatty acids are reacted with polyols having more than three hydroxyl groups per molecule, the number of cross-linking sites per molecule increases relative to the corresponding natural triglyceride oil. Whereas soybean oil is a semi-drying oil since $\bar{f}_n$ is 2.07, the pentaerythritol (PE) tetraester of soybean fatty acids has an $\bar{f}_n$ value of 2.76 and is a drying oil. The PE ester of linseed fatty acids has an $\bar{f}_n$ value of about 5 and gives dry, solvent-resistant films more rapidly than does linseed oil. Still faster drying rates can be achieved with still higher functionality polyols, such as di- and tripentaerythritol. Alkyds, epoxy esters, and uralkyds (Chapter 15) made with fatty acids from such oils as soybean and linseed oils can be considered as higher functionality synthetic drying oils.

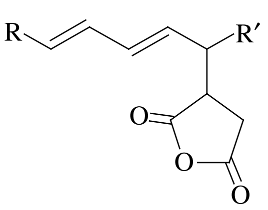
14.3.5. Maleated Oils

Both conjugated and nonconjugated oils react with maleic anhydride to form adducts. Conjugated oils such as dehydrated castor oil react at moderate temperatures by a

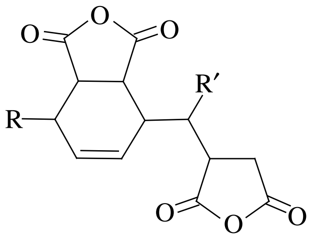
Diels–Alder reaction:



Non-conjugated oils such as soybean and linseed oils require higher temperatures (>100°C) and form a variety of adduct structures. Model compound studies using methyl linoleate demonstrate that maleic anhydride undergoes an ene reaction to give succinyl anhydride adducts. The ene reaction results in conjugated bonds, as shown in general structure (**4**); subsequent Diels–Alder reaction with a second maleic anhydride gives a dianhydride, as shown in general structure (**5**) [25].



(**4**)



(**5**)

The products of these reactions, termed *maleated oils*, or sometimes, *maleinized oils*, react with polyols to give moderate molecular weight derivatives that dry faster than unmodified drying oils. For example, maleated soybean oil esterified with glycerol dries at a rate comparable to that of a bodied linseed oil with a similar viscosity.

Maleated linseed oil can be made water-reducible by hydrolysis with aqueous ammonia to convert the anhydride groups to the ammonium salts of the diacid. Such products have not found significant commercial use, but the process is used to make water-reducible alkyds and epoxy esters (Sections 15.3 and 15.8).

14.3.6. Vinyl-Modified Oils

Both conjugated and non-conjugated drying oils react in the presence of a free radical initiator with such unsaturated monomers as styrene, vinyltoluene, and acrylic esters. High degrees of chain transfer result in the formation of a variety of products: for example, low molecular weight polymers of the monomer or mixture of monomers, short-chain graft copolymers, and dimerized drying oil molecules. The reaction of drying oils with such monomers is not commercially important, but the same principle is used to make modified alkyds (Section 15.6). Linseed oil modified with cyclopentadiene has found fairly sizable commercial use. This product is made by heating a mixture of linseed oil and dicyclopentadiene above 170°C, at which monomeric cyclopentadiene is liberated at an appreciable rate by the reverse Diels–Alder reaction. The product is inexpensive and dries faster than linseed oil. However, its odor and dark color limit its applications.

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15

Alkyd Resins

Although no longer the largest volume vehicles in coatings, alkyds are still of major importance. In 2002, \$410 million worth of alkyds were used in U.S. coatings [1]. Alkyds are prepared from polyols, dibasic acids, and fatty acids. They are polyesters, but in the coatings field the term *polyester* is reserved for "oil-free polyesters" (i.e., those free of fatty acids), discussed in Chapter 10. The term *alkyd* is derived from *alc*ohol and ac*id*. Alkyds tend to be lower in cost than most other vehicles and tend to give coatings that exhibit fewer film defects during application (Chapter 24). However, the durability of alkyd films, especially outdoors, tends to be poorer than that of films from acrylics, polyesters, and polyurethanes, although better than that of BPA epoxies.

There are many types of alkyds. One classification is into *oxidizing* and *nonoxidizing* types. Oxidizing alkyds cross-link by the same mechanism as drying oils, as discussed in Chapter 14. Nonoxidizing alkyds are used as polymeric plasticizers or as hydroxy-functional resins, which are cross-linked by melamine–formaldehyde (MF), or urea–formaldehyde (UF) resins or by isocyanate cross-linkers. A second classification is based on the ratio of monobasic fatty acids to dibasic acids utilized in their preparation, which was adapted from the terminology used to classify varnishes. Varnishes with high ratios of oil to resin were called *long oil varnishes*; those with a lower ratio, *medium oil* varnishes; and those with an even lower ratio, *short oil varnishes*. The oil length of an alkyd is calculated by dividing the amount of "oil" in the final alkyd by the total weight of the weight of all ingredients minus water evolved in reaction, expressed as a percentage. The amount of oil is defined as the triglyceride equivalent to the amount of fatty acids in the alkyd. The 1.04 factor in the second equation converts the weight of fatty

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Organic Coatings: Science and Technology, Third Edition, by Zeno W. Wicks, Jr., Frank N. Jones,
S. Peter Pappas, and Douglas A. Wicks

acids to the corresponding weight of triglyceride oil:

$$\text{oil length} = \frac{\text{weight of ``oil''}}{\text{weight of all ingredients} - \text{water evolved}} \times 100$$

$$\text{oil length} = \frac{1.04 \times \text{weight of fatty acids}}{\text{weight of all ingredients} - \text{water evolved}} \times 100$$

Alkyds with oil lengths greater than 60 are *long oil alkyds*, those with oil lengths from 40 to 60 are *medium oil alkyds*, and those with oil lengths less than 40 are *short oil alkyds*. There is some variation in the literature in the dividing lines between these classes.

Another classification is *unmodified* or *modified alkyds*. Modified alkyds contain other monomers in addition to polyols, polybasic acids, and fatty acids. Examples are *styrenated alkyds* (Section 15.6) and *silicone alkyds* (Section 16.1.2).

15.1. OXIDIZING ALKYDS

Oxidizing alkyds can be considered as synthetic drying oils. They are polyesters of one or more polyols, one or more dibasic acids, and fatty acids from one or more drying or semidrying oils. The most commonly used polyol is glycerol, the most commonly used dibasic acid is phthalic anhydride (PA), and a widely used oil is soybean oil. Let us consider a simple idealized example of the alkyd prepared from 1 mol of PA, 2 mol of glycerol, and 4 mol of soybean fatty acids. Using the fatty acid composition data for soybean oil from Table 14.1, we can calculate that this alkyd would have an $\bar{f}_n$ of 2.76 [i.e., it would have an average of 2.76 activated diallylic groups ($-CH{=}CHCH_2CH{=}CH-$) per molecule (see Sections 14.2.1 and 14.3.4 for a discussion of $\bar{f}_n$)] and therefore would dry to a solid film. The alkyd would form a solvent resistant film in about the same time as a pentaerythritol (PE) ester of soybean fatty acids (Section 14.3.4) since they have the same $\bar{f}_n$. However, the alkyd would form a tack-free film faster because the rigid aromatic rings from PA increase the T_g of the film.

If the mole ratio of PA to glycerol were 2 : 3, corresponding to an equivalent ratio of 4 : 9, 5 mol of soybean fatty acid could be esterified to yield an alkyd with an $\bar{f}_n$ of 3.45. This alkyd would cross-link more rapidly than the 1 : 2 : 4 mole ratio alkyd and would also form tack-free films even faster because the ratio of aromatic rings to long aliphatic chains would be 2 : 5 instead of 1 : 4. As the ratio of PA to glycerol is increased further, the average functionality for autoxidation increases and the T_g after solvent evaporation increases because of the increasing ratio of aromatic to long aliphatic chains. For both reasons, films dry faster.

A theoretical alkyd prepared from 1 mol each of glycerol, PA, and fatty acid would have an oil length of about 60. However, if one were to try to prepare such an alkyd, the resin would gel prior to complete reaction. Gelation would result from reaction of a sufficient number of trifunctional glycerol molecules with three difunctional PA molecules to form cross-linked polymer molecules, swollen with partially reacted components. Gelation can be avoided by using a sufficient excess of glycerol to reduce the extent of cross-linking. When the reaction is carried to near completion with excess glycerol, there are few unreacted carboxylic acid groups, but many unreacted hydroxyl groups.

Alkyds are manufactured in batch step-growth polymerization processes (Section 15.5), usually at temperatures above 200°C. It is often desired to adjust monomer compositions and process conditions so that the polymer is approaching gelation at the end of the process, but if it gels in the kettle, a very expensive cleanup job is required. There have been many attempts, none fully successful, to calculate the ratios of functional groups and the extent of reaction that can be reached without encountering gelation. The problem is complex. The reactivity of the hydroxyl groups can be different; for example, glycerol contains both primary and secondary alcohol groups. Under esterification conditions, polyol molecules can self-condense to form ethers and in some cases can dehydrate to form volatile aldehydes (Section 15.5.2). Reactivity of the carboxylic acids also varies. The rate of formation of the first ester from a cyclic anhydride is more rapid than formation of the second ester. Aliphatic acids esterify more rapidly than aromatic acids. Polyunsaturated fatty acids and their esters can dimerize or oligomerize to form cross-links. Of the many papers in the field, that by Blackinton recognizes the complexities best [2]. In addition to the foregoing complexities, particular emphasis is placed on the extent of formation of cyclic compounds by intramolecular esterification reactions.

In practice, alkyd resin formulators have found that the **mole** ratio of dibasic acid to polyol should be less than 1 to avoid gelation. How much less than 1 depends on many variables. Composition variables are discussed in Sections 15.1.1 through 15.1.3; the effect of variables in reaction conditions is discussed in Section 15.5.

For medium oil alkyds, the ratio of dibasic acid to polyol is not generally changed much relative to alkyds with an oil length of about 60, but the fatty acid content is reduced to the extent desired. This results in a larger excess of hydroxyl groups in the final alkyd. It is commonly said that as the oil length of an oxidizing alkyd is reduced below 60, the drying time decreases to a minimum at an oil length of about 50. However, this conventional wisdom must be viewed cautiously. The ratio of aromatic rings to aliphatic chains continues to increase, increasing T_g after the solvent evaporates from the film tending to shorten the time to form a tack-free film. However, at the same molecular weight (MW), the number of fatty acid ester groups per molecule decreases as the oil length decreases below 60, since more hydroxyl groups are left unesterified. Therefore, the time required to achieve sufficient cross-linking for solvent resistance increases.

Long oil alkyds are soluble in aliphatic hydrocarbon solvents. As the oil length decreases, mixtures of aliphatic and aromatic solvents are required, and oil lengths below about 50 require aromatic or oxygenated solvents, which are more expensive than aliphatics. The viscosity of solutions of long oil alkyds, especially of those with oil lengths below 65, is higher in aliphatic than in aromatic solvents; in medium oil alkyds, which require mixtures of aliphatic and aromatic solvents, viscosity decreases as the proportion of aromatic solvents increases. In former days, and to some extent still, it was considered desirable to use a solvent mixture that gave the highest possible viscosity; then at application viscosity, the solids were lower and the raw material cost per unit volume was less. Accordingly, alkyds were designed to have high dilutability with aliphatic solvents. This was false economy, but it was a common practice and is still being practiced to some extent. Increasingly, the emphasis is on reducing VOC, so the question becomes how to design alkyds with low solvent requirements rather than high dilutability potential. Furthermore, the aromatic solvents are on the HAP list. High-solids alkyds are discussed in Section 15.2.

15.1.1. Monobasic Acid Selection

Drying alkyds can be made with fatty acids from semi-drying oils, since the $\bar{f}_n$ can be well above 2.2. For alkyds made by the monoglyceride process (Section 15.5.1), soybean oil is used in the largest volume. Soybean oil is economical and supplies are dependable because it is a large scale agricultural commodity; alkyd production takes only a few percent of the world supply. For alkyds made by the fatty acid process (Section 15.5.1), tall oil fatty acids (TOFA) are, at times, more economical than soybean fatty acids. Both soybean oil and TOFA contain roughly 40 to 60% linoleic acid and significant amounts of linolenic acid (Table 14.1). White coatings containing linolenic acid esters gradually turn yellow. Premium cost "nonyellowing" alkyds are made with safflower or sunflower oils, which are high in linoleic acid but contain very little linolenic acid.

Applications in which fast oxidative drying and high cross-link density are important require alkyds made with drying oils. The rate of oxidative cross-linking is affected by the functionality of the drying oils used. At the same oil length and MW, the time required to achieve a specific degree of cross-linking decreases as the average number of diallylic groups ($\bar{f}_n$) increases. Linseed long oil alkyds therefore cross-link more rapidly than soybean long oil alkyds. The effect is especially large in very long oil alkyds and less noticeable in alkyds with oil lengths around 60, where $\bar{f}_n$ is very high even with soybean oil, and the effect of further increase in functionality by using linseed oil is small. Because of the large fraction of esters of fatty acids with three double bonds in linseed alkyds, their color and color retention is poorer than that of soybean alkyds. Tung oil–based alkyds, because of the high proportion of esters with three conjugated double bonds, dry still faster. Tung oil alkyds also exhibit a high degree of yellowing. Dehydrated castor alkyds have fairly good color retention, since they contain only a small proportion of esters of fatty acids with three double bonds; they are used primarily in baking coatings.

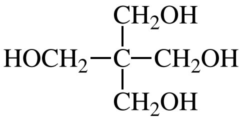
As discussed in Section 14.3.1, drying oils and drying oil fatty acids undergo dimerization at elevated temperatures. Dimerization occurs concurrently with esterification during alkyd synthesis; it generates difunctional acids, increasing the mole ratio of dibasic acids to polyol. The rate of dimerization is faster with drying oils having a higher average number of diallylic groups per molecule and with those having conjugated double bonds. Thus, the MW, and therefore the viscosity, of an alkyd made with the same ratio of reactants depend on the fatty acid composition. The higher the degree of unsaturation, the higher the viscosity, due to the greater extent of dimerization. Linseed alkyds have higher viscosities than soybean alkyds made with the same monomer ratios under the same conditions. The effect is particularly marked with tung oil. It is difficult to prepare straight tung alkyds because of the risk of gelation; commonly, mixed linseed-tung alkyds are made when high oxidative cross-linking functionality is desired.

A critical factor involved in the choice of fatty acid is cost. Drying oils are agricultural products and hence tend to be volatile in price. By far the major market for vegetable oils is for foods. Depending on relative prices, one drying oil is often substituted for another in certain alkyds. By adjusting for functionality differences, substitutions can frequently be made without significant changes in properties.

Benzoic acid is also used, especially to esterify some of the excess hydroxyl groups remaining in the preparation of medium oil alkyds. The benzoic acid increases the ratio of aromatic to aliphatic chains in the alkyd, thus contributing to a higher T_g of the solvent-free alkyd and more rapid formation of a tack-free film. At the same time, the reduction in the free hydroxyl content may somewhat reduce the water sensitivity of the dried films. Rosin can also be used in the same fashion. Although rosin is not an aromatic acid, its polynuclear ring structures are rigid enough to increase T_g. If the critical requirement in drying is rapid development of solvent resistance, such benzoic acid and rosin modifications do not serve the purpose; they only reduce tack-free time. Frequently, benzoic acid–modified alkyds are called *chain-stopped alkyds*. The implication of the terminology is that the benzoic acid stops chain growth. This is not the case; the benzoic acid simply esterifies hydroxyl groups that would not have been esterified if the benzoic acid were absent. The effect on degree of polymerization is negligible.

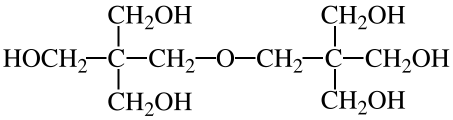
15.1.2. Polyol Selection

Glycerol is the most widely used polyol because it is present in naturally occurring oils from which alkyds are commonly synthesized (Section 15.5.1). The next most widely used polyol is pentaerythritol (PE). To avoid gelation, the tetrafunctionality of PE must be taken into account when replacing glycerol with PE. If the substitution is made on a mole basis rather than an equivalent basis, chances for gelation are minimized. As mentioned earlier, the ratio of moles of dibasic acid to polyol should be less than 1, and generally, a slightly lower mole ratio is required with PE than with glycerol. At the same mole ratio of dibasic acid to polyol, more moles of fatty acid can be esterified with PE. Hence, in long oil alkyds, the average functionality for cross-linking is higher, and the time to reach a given degree of solvent resistance is shorter for a PE alkyd than for a glycerol alkyd. Because of this difference, one must be careful in comparing oil lengths of glycerol and PE alkyds.



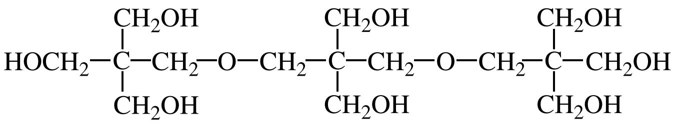
$$HOCH_2-\overset{\displaystyle CH_2OH}{\underset{\displaystyle CH_2OH}{C}}-CH_2OH$$

Pentaerythritol



$$HOCH_2-\overset{\displaystyle CH_2OH}{\underset{\displaystyle CH_2OH}{C}}-CH_2-O-CH_2-\overset{\displaystyle CH_2OH}{\underset{\displaystyle CH_2OH}{C}}-CH_2OH$$

Dipentaerythritol



$$HOCH_2-\overset{\displaystyle CH_2OH}{\underset{\displaystyle CH_2OH}{C}}-CH_2-O-CH_2-\overset{\displaystyle CH_2OH}{\underset{\displaystyle CH_2OH}{C}}-CH_2-O-CH_2-\overset{\displaystyle CH_2OH}{\underset{\displaystyle CH_2OH}{C}}-CH_2OH$$

Tripentaerythritol

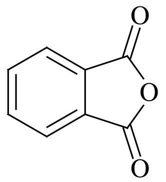
When PE is synthesized, di- and tripentaerythritol are by-products, and commercial PE contains some of these higher polyols. Consequently, care must be exercised in changing sources of PE, since the amount of the higher polyols may differ. Because of the very high functionality, diPE and triPE ($F = 6$ and 8, respectively) are useful in making fast drying low MW alkyds (Section 15.2).

Styrene and allyl alcohol can copolymerize to form a high-functionality polyol for alkyds. For example, it can be used in combination with PE to make long-oil alkyds with relatively low viscosities and good hardness and humidity resistance [3].

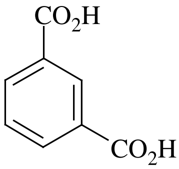
To reduce cost, it is sometimes desirable to use mixtures of PE and ethylene or propylene glycol. A 1 : 1 mole ratio of tetra- and difunctional polyols gives an average functionality of 3, corresponding to glycerol. The corresponding alkyds can be expected to be similar, but not identical. Trimethylolpropane (TMP) is useful, but the rate of esterification is slower than with glycerol. Although all of TMP's alcohol groups are primary, they are somewhat sterically hindered by the neopentyl structure [4]. Trimethylolpropane however, gives a narrower MW distribution, which provides alkyds with a somewhat lower viscosity than the comparable glycerol-based alkyd. A kinetic study demonstrated that esterification of one or two of the hydroxyl groups of TMP has little effect on the rate constant for esterification of the third hydroxyl group [5]. It can be speculated that PE behaves similarly.

15.1.3. Dibasic Acid Selection

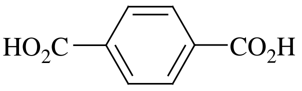
Dibasic acids used to prepare alkyds are usually aromatic. Their rigid aromatic rings increase the T_g of the resin. Cycloaliphatic anhydrides, such as hexahydrophthalic anhydride, are also used. Although they are not as rigid as aromatic rings, the cycloaliphatic rings also increase T_g.



Phthalic anhydride
(PA)



Isophthalic acid
(IPA)



Terephthalic acid
(TPA)

By far the most widely used dibasic acid is PA. It has the advantage that the first esterification reaction proceeds rapidly by opening the anhydride ring. The amount of water evolved is lower, which also reduces reaction time. The relatively low melting point (the pure compound melts at 131°C) is desirable, since the crystals melt and dissolve readily in the reaction mixture. In large scale manufacturing, molten PA is used, which reduces packaging, shipping, and handling costs.

The next most widely used dibasic acid is isophthalic acid (IPA). As discussed in Section 10.1.2, esters of IPA are more resistant to hydrolysis than are those of PA in the pH range 4 to 8, the most important range for exterior durability. On the other hand, under alkaline conditions, esters of phthalic acid are more resistant to hydrolysis than isophthalic esters. The raw material cost for IPA is not particularly different from PA (even after adjusting for the extra mole of water that is lost), but the manufacturing cost is higher. The high melting point of IPA (330°C) leads to problems getting it to dissolve in the reaction mixture so that it can react. High temperatures are required for longer times than with PA; hence more dimerization of fatty acids occurs with TPA, resulting in higher viscosity. The longer time at higher temperature also leads to greater extents of side reactions of the polyol components, which are discussed in Section 15.6.2 [6]. Thus, when substituting IPA for PA, one must use a lower mole ratio of IPA to polyol in order to make an alkyd of similar viscosity.

Terephthalic acid is not useful in making alkyds because it dissolves very slowly even at the highest feasible process temperatures. However, it can be used by transesterification of its esters. Most notable is the use of recycled poly(ethylene terephthalate) (PET) in the synthesis of alkyds. In a typical process [7], PE, a small amount of ethylene glycol, part of the soy fatty acids, and dibutyltin oxide catalyst are heated until molten recycled PET is added and the temperature raised to 240°C until the viscosity and acid number meet specifications. Properties of films from this resin and a comparable standard alkyd were essentially equal. Dimethyl terephthalate is also used.

15.2. HIGH-SOLIDS OXIDIZING ALKYDS

The need to minimize VOC emissions has led to efforts to increase the solids content of alkyd resin coatings. Since xylene is on the HAP list, its use is being reduced. Some increase in solids can be realized by a change of solvents. Aliphatic (and to a somewhat lesser degree, aromatic) hydrocarbon solvents promote intermolecular hydrogen bonding, especially between carboxylic acids, but also between hydroxyl groups, thereby increasing viscosity. Use of at least some hydrogen-bond acceptor solvent, such as a ketone or an ester, or hydrogen-bond acceptor-donor solvent such as an alcohol, gives a significant reduction in viscosity at equal solids.

An approach to increasing solids is to decrease the MW, which is easily accomplished by decreasing the dibasic acid/polyol ratio and going to longer oil length alkyds. However, making a significant reduction in VOC by this route results in an alkyd with lower functionality for cross-linking and a lower ratio of aromatic to aliphatic chains. Both changes increase the time for drying. The effect of longer oil length on functionality can be minimized by using drying oils with higher average functionality. Use of oils containing linolenic or α-eleostearic acid is limited by their tendency to discolor. One can use safflower oil, which has a higher linoleic acid content, and less linolenic acid than soybean oil. Proprietary fatty acids with 78% linoleic acid are commercially available. Increasing the concentration of driers (Section 14.2.2) accelerates drying, but also accelerates yellowing and embrittlement.

Solids can be increased by making resins with narrower MW distributions. For example, one can add a transesterification catalyst near the end of the alkyd cook; this gives a more uniform MW and a lower viscosity product. To study the effect of distribution, model alkyds with very narrow MW distribution were synthesized by using dicyclohexylcarbodiimide, which allows low temperature esterification [4]. With the same ratio of reactants, the $\bar{M}_n$ and polydispersity were lower than for conventional alkyd control. These differences resulted from less dimerization through reactions of the double bond systems of the fatty acids and avoidance of self-etherification of polyol in low temperature preparation. It was found that the solids could be 2 to 10% higher than with the conventionally prepared alkyd of the same raw material composition. The model alkyds dried more rapidly, but their film properties, especially impact resistance, were inferior to those obtained with control resins with the usual broad MW distribution [4]. Conventionally prepared TMP alkyds had lower MWs and viscosities than the glycerol alkyds. This difference may result from less self-etherification of TMP than with glycerol.

High-solids alkyds for baking applications have been made using tripentaerythritol. The high functionality obtained using this polyol ($F = 8$) gives alkyds that cross-link as rapidly as shorter oil length higher viscosity glycerol alkyds [8]. However, for air dry applications, the lower aromatic/aliphatic ratio lengthens the tack-free time.

Another approach to high-solids alkyds is to use *reactive diluents* in place of part of the solvent. The idea is to have a component of lower MW and much lower viscosity than the alkyd resin, which reacts with the alkyd during drying, so it is not part of the VOC emissions. Use of reactive diluents in alkyd coatings is reviewed in Ref. [9]. The authors give a list of key properties of a reactive diluent: low viscosity, good compatibility with alkyds, low volatility (bp $> 300^{\circ}C$), nontoxic, low color, economic replacement of solvent, and of course, ability to participate in oxidative cure.

Mixed acrylic and drying oil fatty acid amides of hexa(aminomethoxymethyl)melamine are used [10,11]. Such reactive diluents contain high functionalities of $>NCH_2NHCOCH{=}CH_2$ and $>NCH_2NHCOC_{17}H_x$ moieties and promote fast drying. A combination of 2,7-octadienyl maleate and fumarate and 2-(2,7-octadienyloxy)succinate has been reported to be a particularly effective reactive diluent [9]. Use of a reactive diluent prepared by reacting drying oil fatty acids with excess dipentaerythritol and then with isophorone diisocyanate has been patented [12]. Epoxidized soybean oil can be used as a reactive diluent for high-solids alkyds using a combination of cobalt and neodymium driers [13].

Using optimized resins and in some cases, reactive diluents, good quality air dry and baking alkyd coatings can be formulated with VOC levels of 280 to $350\,g\,L^{-1}$ of coating. A $250\,g\,L^{-1}$ level is attainable only with some sacrifice of application and film properties; still lower limits of permissible VOC are projected. Lower VOC targets can possibly be achieved using exempt solvents (18.9.1).

15.3. WATER-REDUCIBLE ALKYDS

As with almost all other resin classes, work has been done to make alkyd resins for coatings that can be reduced with water. One approach that has been studied more extensively in Europe than in the United States is the use of alkyd emulsions [14,15]. (See Section 26.3 for further discussion.) The emulsions are stabilized with surfactants and can be prepared with little, if any, volatile solvent. Solid alkyds can be emulsified in hot water with emulsifying agents. Pigmented coatings formulated with alkyd emulsions lose dry time on storage because of absorption of cobalt drier on pigment surfaces and precipitation of cobalt hydroxide. Possible solutions to the problem are to use a combination of cobalt neodecanoate and 2,2′-bipyridyl [16] or to emulsify the driers and the alkyd separately and mix the emulsions so the alkyd and the drier are in separate phases [17].

It is common to add a few percent of an alkyd–surfactant blend to latex paints to improve adhesion to chalky surfaces (Section 32.1) and in some cases, to improve adhesion to metals (see Section 33.1.3). It is important to use alkyds that are as resistant as possible to hydrolysis. Hybrid alkyd–acrylic latexes have been prepared by dissolving an oxidizing alkyd in the monomers used in emulsion polymerization, yielding a latex with an alkyd grafted on the acrylic polymer [18,19]. Hybrid alkyd–acrylic latexes have been prepared by emulsion polymerization. Hydroperoxidized sunflower oil was used as the initiator to polymerize a combination of sunflower oil, a long oil alkyd, and ethyl methacrylate. Films formed from the latex gave the fast dry expected from a latex followed by autoxidation to give cross-linked films [20].

Another approach to hydrolytically stable waterborne alkyds is to make dispersions with an alkyd core and an acrylic shell. They are made by polymerizing unsaturated fatty acids with acrylic monomers, including acrylic acid, then reacting the product with a hydroxy-terminated alkyd resin and neutralizing with NH_4OH. The acrylic shell reduces contact between the alkyd and the water, increasing hydrolytic stability. To increase the hydrolytic stability further, it is recommended to use at least some polyol with secondary hydroxyl groups [21]. Such dispersions can be essentially solvent-free.

Yet another approach is to make alkyds with an acid number in the range 35 to 50 using secondary alcohols or ether alcohols as solvents. The acid groups are neutralized with ammonia or an amine. The resulting solution can be diluted with water to form a dispersion of solvent swollen aggregates in water. Such resins are analogous to the water-reducible acrylics discussed in Section 8.3, and their behavior during water dilution is similar. Note that the use of primary alcohol solvents must be avoided because they can more readily transesterify with the alkyd during resin production and storage, leading to reduction in MW and $\bar{f}_n$ [22].

Hydrolytic instability can be a problem with water-reducible alkyds. If the carboxylic acid groups are half esters of phthalic or trimellitic acid, the hydrolytic stability will be poor and probably inadequate for paints that require a shelf life of more than a few months. Due to the anchimeric effect of the neighboring carboxylic acid group, such esters are relatively easily hydrolyzed. As hydrolysis occurs, the solubilizing acid salt is detached from the resin molecules, and the aqueous dispersion loses stability. A more satisfactory way to introduce free carboxylic acid groups is by reacting a completed alkyd with maleic anhydride. Part of the maleic anhydride adds to the unsaturated fatty acid esters as discussed in Section 14.3.5. The anhydride groups are then hydrolyzed with amine and water to give the desired carboxylate salt groups, which are attached to resin molecules with C—C bonds and cannot be hydrolyzed off. There is still a hydrolytic stability problem with the alkyd backbone, but hydrolysis does not result in destabilization of the dispersion. Similarly, acrylated fatty acids can be used to synthesize water-reducible alkyds with improved hydrolytic stability [23].

After the film is applied, the water, solvent, and amine evaporate, and the film cross-links by autoxidation. Since there are a fairly large number of residual carboxylic acid groups left in the cross-linked binder, the water resistance, and particularly the alkali resistance of the films are reduced but are still satisfactory for some applications [24]. *Early water resistance* can be a problem if, for example, a freshly painted surface is rained on before all the amine has evaporated from the film. Commonly, ammonia is used as the neutralizing amine because it is assumed that ammonia volatilizes faster than any other amine. This assumption is not necessarily so; if the T_g of the alkyd film is sufficiently high before all of the amine has volatilized, loss of amine becomes controlled by diffusion rate. The rate of diffusion of amine through the carboxylic acid–functional film is affected by the base strength of the amine. A less basic amine, such as morpholine, may leave the film before ammonia even though its volatility is considerably lower.

Superior resistance to hydrolysis during storage can be achieved by reacting the hydroxyl groups of an alkyd with isophorone diisocyanate and dimethylolpropionic acid to form an aqueous polyurethane dispersion [25]. (See Section 15.7.2 for further discussion of autoxidizable polyurethane dispersions.)

15.4. NONOXIDIZING ALKYDS

Certain low MW short–medium and short oil alkyds are compatible with such polymers as nitrocellulose and thermoplastic polyacrylates. Therefore, such alkyds can be used as plasticizers for these polymers. They have the advantage over monomeric plasticizers (e.g., dibutyl or dioctyl phthalate) that they do not volatilize appreciably when films are baked. It is generally not desirable to use oxidizing alkyds, which would cross-link and lead to embrittlement of the films, especially on exterior exposure. Therefore, non-drying oil fatty acids (or oils) are used in the preparation of alkyds for such applications. For exterior acrylic lacquers, pelargonic acid (n-$C_8H_{17}COOH$) alkyds combine excellent resistance to photodegradation with good compatibility with thermoplastic acrylic resins. An interesting sidelight on terminology is that these pelargonic alkyds have been called polyesters rather than alkyds because the word *polyester* connotes higher quality than the word *alkyd*. Castor oil–derived alkyds are particularly appropriate plasticizers for nitrocellulose lacquers for interior applications, since the hydroxyl groups on the ricinoleic acid promote compatibility.

All alkyds, particularly short-medium oil and short oil alkyds, are made with a large excess of hydroxyl groups, to avoid gelation. These hydroxyl groups can be cross-linked with MF resins or with polyisocyanates. In some cases, relatively small amounts of MF resin are used to supplement the cross-linking during baking of medium oil oxidizing alkyds. To achieve compatibility, butylated MF resins are used. Such coatings provide somewhat better durability and faster curing than those provided by alkyd resins alone, with little increase in cost. The important advantage of the relative freedom from film defects common to alkyd coatings can be retained (Chapter 24). However, the high levels of unsaturation remaining in the cured films impart a tendency to discoloration on overbake or exterior exposure and cause loss of gloss and embrittlement on exterior exposure. These difficulties can be reduced by using non-drying oils with minimal levels of unsaturated fatty acids. Coconut oil has been widely used; its performance can be further enhanced by hydrogenation of the small amount of unsaturated acids present in it.

Since isophthalic (IPA) esters are more stable to hydrolysis in the pH range 4 to 8, than phthalate esters, the highest performance exterior alkyd–MF enamels use nonoxidizing IPA alkyds. For many applications, alkyd–MF coatings have been replaced with acrylic–MF or polyester–MF coatings to improve the overall balance of film properties.

Polyamide-modified alkyd resins are used as thixotropic agents to increase the low shear viscosity of alkyd paints. For example, high-solids thixotropic alkyds based on polyamides made with aromatic diamines have been developed that give superior performance in high-solids alkyd coatings [26].

15.5. SYNTHETIC PROCEDURES FOR ALKYD RESINS

Various synthetic procedures, each with many variables, are used to produce alkyd resins; the general reference and Refs. [27] and [28] provide useful reviews of manufacturing procedures. Alkyds can be made directly from oils or by using free fatty acids as raw materials.

15.5.1. Synthesis from Oils or Fatty Acids

15.5.1.1. Monoglyceride Process In the case of glycerol alkyds, it would be absurd to first saponify an oil to obtain fatty acids and glycerol, and then esterify the same groups in a different combination. Rather, the oil is first reacted with sufficient glycerol to give the total desired glycerol content, including the glycerol in the oil. Since PA is not soluble in the oil but is soluble in the glycerol, transesterification of oil with glycerol must be carried out as a separate step before the PA is added; otherwise, glycerol phthalate gel particles would form early in the process. This two-stage procedure is often called the *monoglyceride process*. The transesterification reaction is run at 230 to 250°C in the presence of a catalyst; many catalysts have been used. Before the strict regulation of lead in coatings, litharge (PbO) was widely used; the residual transesterification catalyst also acted as a drier. Examples of catalysts now used in the United States are tetraisopropyltitanate, lithium hydroxide, and lithium ricinoleate. The reaction is run under an inert atmosphere such as CO_2 or N_2 to minimize discoloration and dimerization of drying oils.

Although the process is called the monoglyceride process, the transesterification reaction actually results in a mixture of unreacted glycerol, monoglycerides, diglycerides, and unconverted drying oil. The composition depends on the ratio of glycerol to oil and on catalyst, time, and temperature. In general, the reaction is not taken to equilibrium. At some relatively arbitrary point, PA is added, beginning the second stage. The viscosity and properties of the alkyd can be affected by the extent of reaction before the PA addition. Although many tests have been devised to evaluate the extent of transesterification, none is very general because the starting ratio of glycerol to oil varies over a considerable range, depending on the oil length of the alkyd being made. (In calculating the mole ratio of dibasic acid to polyol, the glycerol already esterified in the oil must also be counted.) A useful empirical test is to follow the solubility of molten PA in the reaction mixture. This test has the advantage that it is directly related to a major requirement that must be met. In the first stage, it is common to transesterify the oil with less expensive pentaerythritol to obtain mixed partial esters. The second stage, esterification of the "monoglyceride" with PA, is carried out at a temperature of 220 to 255°C.

15.5.1.2. Fatty Acid Process It is often desirable to base an alkyd on a polyol (e.g., PE) other than glycerol. In this case, fatty acids must be used instead of oils, and the process can be performed in a single step with reduced time in the reactor. Any drying, semi-drying, or non-drying oil can be saponified to yield fatty acids, but the cost of separating fatty acids from the reaction mixture increases the cost of the alkyd. A more economical alternative is to use tall oil fatty acids (TOFA), which have the advantage that they are produced as fatty acids. TOFA compositions are roughly similar to those of soybean fatty acids (Table 14.1). Specially refined tall oils with higher linoleic acid content are available, as are other grades that have been treated with alkaline catalysts to isomerize the double bonds partially to conjugated structures. Generally, when fatty acids are used, the polyol, fatty acids, and dibasic acid are all added at the start of the reaction, and the esterification of both aliphatic and aromatic acids is carried out simultaneously in the range 220 to 255°C.

15.5.2. Process Variations

Esterification is a reversible reaction; therefore, an important factor affecting the rate of esterification is the rate of removal of water from the reactor. Most alkyds are produced using a reflux solvent such as xylene to promote the removal of water by azeotroping. Since the reaction is run at a temperature far above the boiling point of xylene, less than 5% xylene is used. The amount is dependent on the reactor and is set empirically such that there is enough to reflux vigorously but not so much as to cause flooding of the condenser. Some of the xylene is distilled off along with the water; water is separated and xylene is returned to the reactor. Methyl isobutyl ketone (MIBK) has also reported as a

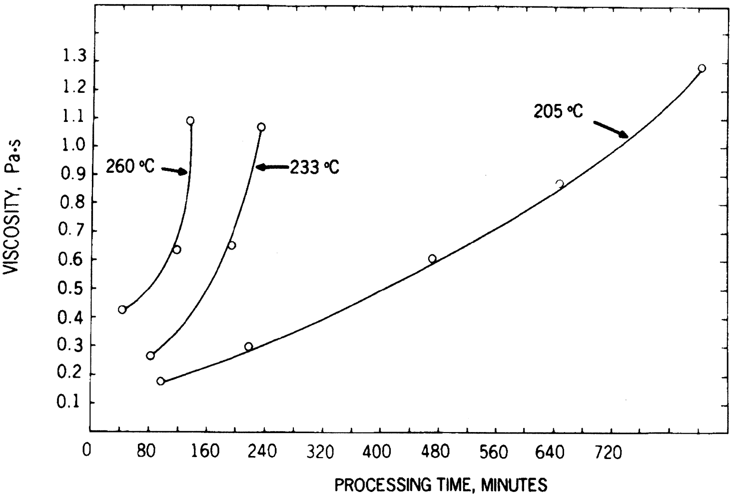


Figure 15.1. Effect of temperature and time on viscosity. (Adapted from Ref. [28], with permission.)

reflux solvent; it reduces the viscosity more than xylene. The presence of solvent is desirable for other reasons: Vapor serves as an inert atmosphere, reducing the amount of inert gas needed, and the solvent serves to avoid accumulation of sublimed solid monomers, mainly PA, in the reflux condenser.

Reaction time is affected by reaction temperature. Figure 15.1 shows the relation among temperature, time, and viscosity in preparing an alkyd. Figure 15.2 shows the relationship of the variables with acid number (i.e., milligrams of KOH required to titrate the acid in 1 g

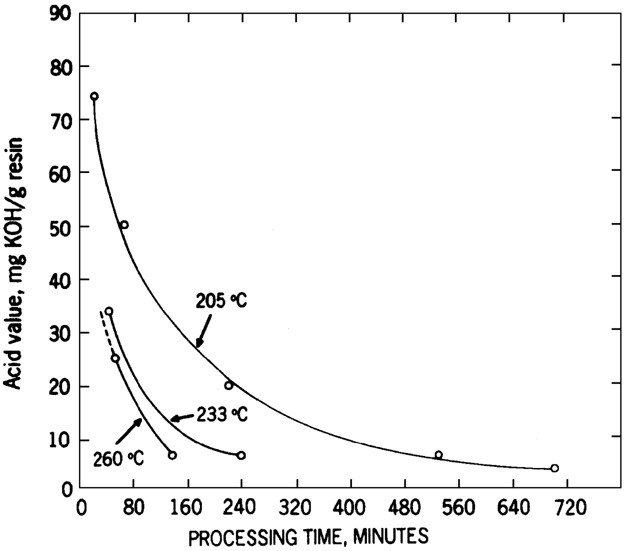


Figure 15.2. Effect of temperature and processing time on the acid value of a typical medium oil linseed alkyd. (Adapted from Ref. [28], with permission.)

of resin solids). There are economic advantages to short reaction times. Operating costs are reduced, and the shorter times permit more batches of alkyd to be produced in a year, increasing capacity without capital investment in more reactors. Therefore, it is desirable to operate at as high a temperature as possible without risking gelation.

A critical aspect of alkyd synthesis is deciding when the reaction is completed. Disappearance of carboxylic acid is followed by titration, and increase in MW is followed by viscosity. Determination of acid number and viscosity both take some time. Meanwhile, in the reactor, the reaction is continuing. After it is decided that the extent of reaction is sufficient, the reaction mixture must be "dropped" into a larger tank containing solvent. When a 40,000-L batch of alkyd is being made, a significant time is required to get the resin out of the reactor into the reducing tank; meanwhile, the reaction is continuing. The decision to start dropping the batch must be made so that the acid number and viscosity of the batch will be right after the continuing reaction that occurs between the time of sampling, determination of acid number and viscosity, and discharging of the reactor. The time for these determinations becomes the rate controlling step in production. If they control tests can be done rapidly enough, the reaction can be carried out at 240°C or even higher without overshooting the target acid number and viscosity. On the other hand, if the tests are done slowly, it may be necessary to run the reaction at only 220°C, which may require 2 hours or more of additional reaction time (Figures 15.1 and 15.2). Automatic titration instruments permit rapid determination of acid number, so the usual limit on time required is viscosity determination. While attempts have been made to use the viscosity of the resin at the reaction temperature to monitor change in the MW, the dependence of viscosity on MW at that high temperature is not sensitive enough to be very useful. The viscosity must be determined on a solution at some lower standard temperature. Since viscosity depends strongly on solution concentration and temperature, these variables must be carefully controlled.

In alkyd production, viscosity is commonly determined using Gardner bubble tubes, as discussed in Section 3.3.4. The cook is continued until the viscosity is high enough so that by the time the resin batch is dropped into the solvent and the batch cooled, its viscosity will be what is called for in the specification. This means starting to discharge the reactor when the test sample is at some lower viscosity. It is not possible to generalize how large this difference should be; it depends on the specific alkyd composition, the temperature at which the reaction is being run, the time required to do the determination, the time required to empty the reactor, and so on. Viscosities can be determined more rapidly using a cone and plate viscometer (Section 3.3.2) than with bubble tubes; the very small sample required for a cone and plate viscometer can be cooled and equilibrated at the measurement temperature more quickly.

Many variables affect the acid number and viscosity of alkyds. One is the ratio of reactants: The closer the ratio of moles of dibasic acid to polyol approaches 1, the higher the MW of the backbone of the resin, but also the greater the likelihood of gelation. A useful rule of thumb for a starting point is to use a mole ratio of 0.95. The final ratio is determined by adjustments such that the combination of acid number and solution viscosity come out at the desired levels. The greater the ratio of hydroxyl groups to carboxylic acid groups, the faster the acid groups are reduced to a low level. The degree of completion of the reaction is an important factor controlling the viscosity, as is the acid number. It is usually desirable to have a low acid number, typically in the range 5 to 10.

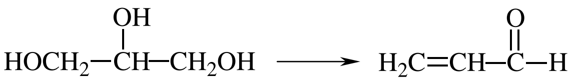
The composition of the fatty acids is a major factor affecting the viscosity, and compositions of an oil or grade of TOFA can be expected to vary somewhat from lot to lot.

Dimerization and oligomerization of the unsaturated fatty acids occur in the same temperature range at which the esterification is carried out (Section 14.3.1). Fatty acids with conjugated double bonds dimerize more rapidly than those with nonconjugated bonds, and dimerization rates increase with the level of unsaturation. At the same ratio of phthalic to polyol to fatty acids, alkyds of the same acid number and solution concentration will increase in viscosity in the order soybean < linseed < tung.

Some volatilization of polyol, PA, and fatty acids out of the reactor will occur depending on the design of the reactor, the rate of reflux of the azeotroping solvent, the rate of inert gas flow, and the reaction temperature, among other variables; the amount and ratio of these losses affect the viscosity at the standard acid number. The exact ratio of reactants must be established in the reactor that is used for synthesis. Since gelation can occur if the ratio of dibasic acid to polyol is too high, it is better not to put all of the PA into the reactor in the beginning. If the viscosity is too low when the acid number is getting down near the standard, more PA can easily be added. The amount of PA held back can be reduced as experience is gained cooking a particular alkyd in a particular reactor.

Side reactions can affect the viscosity–acid number relationship. Glycerol and other polyols form ethers to some degree during the reaction. Glycerol can also form toxic acrolein by successive dehydrations.

$$\mathrm{HOCH_2{-}\overset{\overset{\displaystyle OH}{|}}{C}H{-}CH_2OH \longrightarrow HOCH_2{-}\overset{\overset{\displaystyle OH}{|}}{C}H{-}CH_2OCH_2{-}\overset{\overset{\displaystyle OH}{|}}{C}H{-}CH_2OH}$$



$$\mathrm{HOCH_2{-}\overset{\overset{\displaystyle OH}{|}}{C}H{-}CH_2OH \longrightarrow H_2C{=}CH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H}$$

When these reactions occur, the mole ratio of dibasic acid to polyol increases and the number of hydroxyl groups decreases; therefore, at the same acid number, the MW will be higher. Excessively high viscosity and even gelation can result. Ether formation is catalyzed by strong protonic acids; therefore, it is desirable to avoid them as catalysts for the esterification. Monobutyltin oxide has been used as an esterification catalyst; presumably, it does not significantly catalyze ether formation. As noted earlier, PE and TMP seem less vulnerable than glycerol to undesirable side reactions such as ether formation, and glycerol is the only polyol that can decompose to form acrolein. A hydroxyl group on one end of a growing polyester chain can react with a carboxylic acid group on another end of the same molecule, leading to ring formation. Transesterification of chain linkages can have the same result. Since cyclization reactions reduce chain length, their net effect is to reduce viscosity.

Many alkyd resins have broad, uneven MW distributions (Figure 2.3). Kumanotani has shown that even modest changes in reaction conditions can cause large differences in MW distribution, which can have significant effects on final film properties [29]. In many alkyds, very small gel particles, microgels, are formed. Kumanotani has shown that these microgels play an important role in giving greater strength properties to final films. Process changes that may make the alkyd more uniform may be undesirable. For example, allowing glycerolysis to approach equilibrium before addition of PA and using transesterification catalysts in the final stages of esterification both favor narrower MW distributions and lower viscosities, but films made from the more uniform alkyds may exhibit inferior mechanical properties.

15.6. MODIFIED ALKYDS

Oxidizing alkyds can be modified by reaction with vinyl monomers. The most widely used monomers are styrene, vinyltoluene, and methyl methacrylate, but essentially any vinyl monomer can be reacted in the presence of an alkyd to give a modified alkyd. Methyl methacrylate imparts better heat and weather resistance than styrene but at higher cost.

In making styrenated alkyds, an oxidizing alkyd is prepared in the usual way; then styrene and a free radical initiator such as benzoyl peroxide are added. The resulting free radical chain process leads to a variety of reactions, including formation of low MW homopolymer of styrene, grafting of polystyrene onto the alkyd, and dimerization of alkyd molecules. The reaction is generally carried out at about 130°C, which favors decomposition of benzoyl peroxide to form phenyl free radicals; phenyl radicals have a greater tendency to abstract hydrogen, which favors grafting. After the reaction is complete, the resin is diluted with solvent. The ratio of alkyd to styrene can be varied over a wide range; commonly 50% alkyd and 50% styrene is used. The ratio of aromatic rings to aliphatic chains is greatly increased, and as a result, the T_g of styrenated alkyds is higher and the tack-free time is shorter. Styrenated alkyds give a "dry" film in 1 hour or less versus 4 to 6 hours for the counterpart non-styrenated alkyd. However, the average functionality for oxidative cross-linking is reduced, not just by dilution with styrene, but also because the free radical reactions involved in the styrenation consume some activated methylene groups. As a result, the time required to develop solvent resistance is longer than for the counterpart alkyd. The fast drying and low cost make styrenated alkyds very attractive for some applications, but in other cases, the longer time required for cross-linking is more critical, in which case styrenated alkyds are not appropriate.

Styrenated alkyd vehicles are often used for air dry primers. One must be careful to apply the top coat almost immediately, or not until after the film has had ample time to cross-link. During the intermediate time interval, application of the top coat is likely to cause nonuniform swelling of the primer, leading to what is called *lifting* of the primer. The result of lifting is the development of wrinkled areas in the surface of the dried film. End users who are accustomed to using alkyd primers, which do not give a hard film until a significant degree of cross-linking has occurred, are particularly likely to encounter problems of lifting if they switch to styrenated alkyd primers.

Acrylate-functional alkyds are reported to dry more rapidly than the corresponding unmodified resin. For example, the carboxylic acid groups on an alkyd prepared from PE, TMP, soy oil, and IPA with an acid number of 8.6 is reacted with glycidyl methacrylate (GMA). Using zirconium and cobalt driers, films through dried in 9 hours, in contrast to >11 to <20 hours for the unmodified resin [30].

15.7. URALKYDS AND OTHER AUTOXIDIZABLE URETHANES

Diisocyanates are used to make a variety of resins that share similar characteristics with alkyds, as discussed in this section. For a description of the isocyanates, see Section 12.3.

15.7.1. Uralkyds

About 39,000 metric tons of uralkyds were used in the United States in 1997 [31]. *Uralkyds* are also called *oil-modified urethanes*. The largest use for uralkyds is as the vehicle for urethane varnishes for use by contractors and the do-it-yourself market. The abrasion and hydrolytic resistance of such coatings are greatly superior to that obtained with conventional varnishes or alkyd resins. Many "varnishes" sold to consumers today are based on uralkyds; they are not really varnishes in the original sense of the word. They are used as transparent coatings for furniture, woodwork, gymnasium floors, and hardwood floors; applications in which good abrasion, mar, scuff, chemical, and saponification resistance are important. They are also widely used in maintenance paints.

To prepare uralkyds, one transesterifies a drying oil with a polyol such as glycerol or PE to make a "monoglyceride," which is then reacted with somewhat less diisocyanate than the equivalent amount of NCO based on the free OH content. To assure that no NCO groups remain unreacted, methyl alcohol (or other low MW alcohol) is commonly added at the end of the process. For lower cost, one can use a combination of phthalic anhydride and diisocyanate. Color retention is superior with aliphatic diisocyanates, but T_g is higher and cost is lower with aromatic diisocyanates. An extensive review paper is available [32].

A comparison of the properties of uralkyds, alkyds, and 2K urethane coating has been published [33]. Four uralkyds prepared from linseed oil and safflower oil, each with TDI or MDI, were compared with linseed and safflower alkyds. All of the alkyds and uralkyds had an oil length of 60%. They were compared with two 2K polyester–MDI resin systems. Primers and pigmented top coats were formulated with each resin. The cohesive strengths of the uralkyd paint films were greater than those of the alkyd films and approached those of the 2K coatings. Of the uralkyds, the highest cohesive strength was with films made using the linseed oil–TDI resin. Scratch resistance and tensile strength tests showed the same ranking of the films made from the eight resins. Salt spray resistance and humidity resistance of the uralkyd coatings were superior to those of the alkyd coatings but inferior to the 2K urethane coatings. Particularly notable, the chemical and solvent resistance of the uralkyd films were markedly better than the alkyd films, although somewhat inferior to the 2K films. Studies of the permeability rate of water into uralkyd and alkyd films indicated that alkyd films are more permeable than uralkyd films [34].

By far the most widely used diisocyanate is TDI. A uralkyd with improved color retention compared to that of a uralkyd made with TDI can be made by reacting the polyol made by transesterification of linseed oil with PE, then reacting with $H_{12}MDI$ [35].

Another advantage of uralkyds over alkyds is ease of manufacture. The time for the reaction of the isocyanate groups is substantially shorter and the reaction temperature is on the order of 70°C, compared to 220 to 245°C for the esterification of alkyds. This results not only in lower production costs and higher equipment utilization but also in less dimerization of the unsaturated chains, hence reduced viscosity at the same molar ratios.

Traditionally VOC of uralkyd varnishes has been over 500 $g\,L^{-1}$. As of 2005, EPA VOC regulations for varnishes require less than 450 $g\,L^{-1}$, California south coast as well as northeastern states regulations require less than 350 $g\,L^{-1}$, and the California regulations will be further reduced to 275 $g\,L^{-1}$ in 2006. It is reported that uralkyds with a VOC of 345 $g\,L^{-1}$ can be made by reducing the MW. Meeting the 275 $g\,L^{-1}$ regulation will require greater changes. With careful balancing of driers and accelerators, the dry time and performance of higher VOC uralkyds can be approached. One approach is to use the exempt solvent 4-chlorobenzotrifluoride (PCBTF) to replace part of the mineral spirits solvent (Section 18.9.1). The higher-solids varnishes have the advantage that two coats are sufficient instead of the usual three; however, great care must be taken to avoid too great a film thickness. Water-reducible urethane varnishes can be used (see the next paragraph). Autoxidizable acrylic–urethane hybrid dispersions permit preparation of high quality products at a higher cost (Section 15.7.2). For the contractor market, 2K waterborne urethanes have many advantages but are not suitable for the do-it yourself market (Section 12.7.3) [36].

As with other types of coatings, VOC regulations stimulated development of water-reducible uralkyds. An example is a maleated uralkyd prepared from a partial ester of linseed oil fatty acid with PE, which is reacted with MDI and then with maleic anhydride [37]. The resin is diluted in 2-butoxyethanol, neutralized with TEA, and diluted with water. The resin is much more resistant to hydrolysis than is a corresponding alkyd.

15.7.2. Autoxidizable Polyurethane Dispersions

Water-reducible polyurethane dispersions (PUDs) (Section 12.7) can be made autoxidizable by introducing appropriate fatty acids. For example, a PUD made by reacting a diisocyanate with a diol, a fatty acid monoglyceride, and dimethylolpropionic acid (DMPA) is neutralized with an amine and then dispersed in water. Water acts as a chain extender for terminal isocyanate groups [38]. Hydrolytic stability of the aqueous dispersions is excellent, and the films also have the expected abrasion resistance. Drying speed, color, and cost are dependent on the drying oil and diisocyanate used. For example, a PUD is made from a dehydrated castor oil, pentaerythritol, phthalic alkyd reacted with DMPA, dimethylisopropylamine, and isophorone diisocyanate (IPDI) [39]. A PUD for wood flooring coatings is prepared from an unsaturated polyol prepared by transesterification of castor oil and soy oil, DMPA, H_{12}MDI, neutralized with TEA, dispersed in water, and chain-extended with hydrazine hydrate and ethylenediamine [40]. The coatings are said to resist solvents, abrasion, and heel marking.

Acrylic–urethane hybrid dispersions have lower cost. For example, a drying oil fatty acid amide of diethanolamine is reacted with DMPA, cyclohexanedimethanol, a monomethyl ether of polyethylene glycol, and TDI in *N*-methylpyrrolidone (NMP), methyl methacrylate is added, the product is diluted with dipropylene glycol monomethyl ether, neutralized with dimethylaminoethanol (DMAE), and then diluted with water [41]. After dilution with water, the methacrylate monomer is polymerized; the resulting PUD gives films that cross-link by autoxidation.

15.8. EPOXY ESTERS

BPA epoxy resins can be converted to what are commonly called *epoxy esters* by reacting with fatty acids. Drying or semi-drying oil fatty acids are used so that the products cross-link by autoxidation. The epoxy groups undergo a ring-opening reaction with carboxylic acids to generate an ester and a hydroxyl group (Section 13.3.2). These hydroxyl groups, as well as the hydroxyl groups originally present on the epoxy resin, can esterify with fatty acids. They are generally made by starting with a low MW epoxy resin (i.e., the standard liquid resin, $n = 0.13$) and extending with BPA by the advancement process (Section 13.1.1) to the desired MW. Off-specification epoxy resin is often used to reduce cost. The fatty acids are added to the molten, hot resin, and the esterification reaction is continued until the acid number is low, usually less than 7 mg of KOH per gram of resin. In the esterification reaction with fatty acids, the average number of sites for reaction is the n

value, corresponding to the number of hydroxyl groups on the resin, plus twice the number of epoxy groups. The esterification is carried out at high temperatures (220 to 240°C). The rate of esterification slows as the concentration of hydroxyl groups diminishes, and side reactions occur, especially dimerization of the drying oil fatty acids (or their esters). It is not practical to esterify more than about 90% of the potential hydroxyl groups, including those from ring opening the epoxy groups.

Tall oil fatty acids are commonly used because of their low cost. Linseed fatty acids give faster cross-linking coatings due to higher average functionality. However, their viscosity is higher because of the greater extent of dimerization during esterification, and their cost is higher. For still faster cross-linking, part of the linseed fatty acids can be replaced with tung fatty acids, but the viscosity and cost are still higher. The color of epoxy esters from linseed and linseed–tung fatty acids is darker than the tall oil esters. Dehydrated castor oil fatty acids give faster curing epoxy esters for baked coatings. The rate of formation of a dry film from epoxy esters depends on two factors: the average number of diallylic groups $\bar{f}_n$ and the ratio of aromatic rings to long aliphatic chains. The $\bar{f}_n$ can be maximized by using higher MW BPA epoxy resin and by using enough fatty acid to react with a large fraction of the epoxy and hydroxyl groups. The ratio of aromatic rings to fatty acids can be maximized by using high MW epoxy resin and esterifying a smaller fraction of epoxy and hydroxyl groups.

Epoxy esters are used in coatings in which adhesion to metal is important. Although the reasons are not completely understood, it is common for epoxy coatings, including epoxy esters, to have good adhesion to metals and to retain adhesion after exposure of the coated metal to high humidity, a critical factor in corrosion protection. A distinct advantage of epoxy esters over alkyd resins is their greater resistance to hydrolysis and saponification. The backbone of alkyds is held together with esters from PA and the polyol, whereas in epoxy esters, the backbone is held together with C—C and ether bonds. Of course, the fatty acids are bonded to the backbone with ester groups in both cases, but the fraction of polymer bonds in a dry film subject to hydrolysis is substantially lower in the case of epoxy esters. On the other hand, exterior durability of epoxy ester coatings is poor, as is the case with all films made with BPA epoxy resins. As a result of these advantages and disadvantages, the major uses for epoxy resins are in primers for metal and in can coatings, such as for crowns (bottle caps), in which the important requirements are adhesion and hydrolytic stability. In baking primers, it is sometimes desirable to supplement the cross-linking through oxidation by including a small amount of MF resin in the formulation to cross-link with part of the free hydroxyl groups on the epoxy ester.

Epoxy ester resins with good exterior durability (better than alkyds) can be prepared by reacting epoxy-functional acrylic copolymers (made with glycidyl methacrylate) with fatty acids. The product is an acrylic resin with multiple fatty acid ester side chains. By appropriate selection of acrylate ester comonomers and MW, the T_g of the resin can be designed so that a tack-free film is obtained by solvent evaporation; then the coating cross-links by autoxidation. For an application such as repainting an automobile at ambient temperatures, the cross-linking can proceed relatively slowly and need not be catalyzed by metal salt driers. The rate of cross-linking is slower without driers, but exterior durability is better.

Epoxy esters can also be made water-reducible: for example by reacting maleic anhydride with epoxy esters prepared from dehydrated castor oil fatty acids. Subsequent addition of a tertiary amine such as 2-(dimethylamino)ethanol in water results in ring opening of the anhydride to give amine salts. Like other water-reducible resins

(Section 8.3), these resins are not soluble in water, but form a dispersion of resin aggregates swollen with water and solvent in an aqueous continuous phase. The hydrolytic stability of these epoxy esters is better than corresponding alkyds and is sufficient for use in anionic electrodeposition primers (Section 27.1), now largely replaced by cationic primers. Water-reducible epoxy esters are still used in spray applied baking primers and primer-surfacers. They are also used in dip coating primers, in which nonflammability is an advantage.

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16

Silicon Derivatives

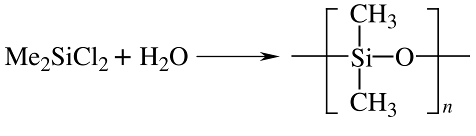
Three classes of silicon derivatives are used in coatings: silicones, reactive silanes, and orthosilicates. Orthosilicates are also covered for their use in organic/inorganic coatings.

16.1. SILICONES

Silicones, more properly called *polysiloxanes*, are polymers with backbones consisting of —Si(R)$_2$—O— repeating units. Polysiloxanes are prepared from chlorosilanes. The principal commercial monomers are the following methyl and phenyl substituted silanes.

Me_3SiCl	trimethylchlorosilane
Ph_2SiCl_2	diphenyldichlorosilane
$PhSi(Me)Cl_2$	phenylmethyldichlorosilane
Me_2SiCl_2	dimethyldichlorosilane
$PhSiCl_3$	phenyltrichlorosilane
$MeSiCl_3$	methyltrichlorosilane

Chlorosilanes react with water to form silanols, which in turn can condense to form siloxanes. For example, dimethyldichlorosilane reacts with water to form a polysiloxane, often represented as a linear polysiloxane.

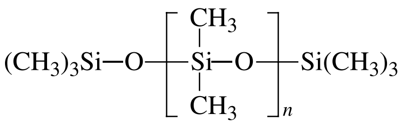


$$Me_2SiCl_2 + H_2O \longrightarrow \left[\begin{array}{c} CH_3 \\ | \\ -Si-O- \\ | \\ CH_3 \end{array} \right]_n$$

Organic Coatings: Science and Technology, Third Edition, by Zeno W. Wicks, Jr., Frank N. Jones, S. Peter Pappas, and Douglas A. Wicks

Structures of the polymers can be more complex than represented by this linear structure. Siloxanes are more apt than hydrocarbons to form large ring cyclic structures such as $(Me_2SiO)_4$. Such cyclic compounds are intermediates in the polymerization and are present to varying degrees in the finished product.

Oligomers are made using monochlorosilanes as chain-terminating groups; molecular weight (MW) is reduced in proportion to the monochlorosilane/dichlorosilane ratio. The oligomeric products are called *silicone fluids* or *silicone oils*. As discussed in Chapter 23, small amounts of silicone fluids are used as additives in coatings. Poly(dimethylsiloxane) fluids reduce surface tension because the ease of rotation around the Si—O—Si bonds leads to rapid orientation of methyl groups at the surface. The methyl groups give a surface with very low surface tension. Low MW silicone fluids can be used as VOC exempt solvents.



$$(CH_3)_3Si{-}O{-}\left[\begin{array}{c}CH_3\\ |\\ Si{-}O\\ |\\ CH_3\end{array}\right]_n{-}Si(CH_3)_3$$

A silicone fluid

Poly(dimethylsiloxanes) have limited compatibility with many coatings resins. Chemically modified silicone fluids with broader ranges of compatibility have been described [1]. Examples are polysiloxane–polyether block copolymers, polyether copolymers that also have some longer alkyl chains on the siloxane groups, and poly(dimethylsiloxanes) modified with esters and aryl-substituted alkyl groups. Siloxanes with a polyether terminal group or side chain have been reported to be excellent surface tension additives to prevent film defects in waterborne coatings. They are prepared by reacting allyl-terminated polyethers with poly(dimethylsiloxanes) having Si—H bonds [2].

16.1.1. Silicone Rubbers and Resins

Silicone rubbers are cross-linked polysiloxanes, and *silicone resins* are usually branched polysiloxanes. In both cases, trichlorosilanes are used to provide chain branching and ultimately, cross-linking. They can be copolymerized with dichlorosilanes to make silicone rubbers. Although silicone rubbers are expensive, they have unique and useful properties; they exhibit excellent resistance to oxidation accompanied by retention of flexibility at low temperatures. They have a low T_g as a result of the ease of rotation around the Si—O—Si bonds.

Chain branching is not the only possible outcome when trichlorosilanes are copolymerized. They can react with water to form three-dimensional cluster compounds (silsesquioxanes), exemplified by the cubic octamer $(C_6H_5)_8Si_8O_{12}$.

Polymerization of a mixture of mono-, di-, and trichlorosilanes, carried out by hydrolyzing a solution of the monomers in a water-immiscible solvent, results in a silicone resin with some unreacted hydroxyl groups. The silicone resin is separated from the acidic water phase, and residual acid is removed. A stable solution of a silicone resin is obtained if the last water is removed from the reaction mixture at relatively low temperatures in the absence of catalyst. The $\bar{M}_n$ of such resins is generally in the range 700 to 5000. Different copolymerization processes yield different proportions of linear, branched, cyclic, and three-dimensional cluster structures; the composition affects properties.

Silicone resins can be baked to form cross-linked films. The cross-linking process is reversible. A typical cure schedule is 1 hour at 225°C, but the time and temperature can be reduced with catalysts such as zinc octanoate. Since the cross-linking reaction is reversible, silicone films are sensitive to water, especially under basic conditions. Ammonia and amines are especially destructive to such films. Evidence has been presented that aminolysis occurs selectively at Si groups with three oxygens (i.e., at cross-linking sites), probably resulting from the greater electrophilicity of such Si groups with three electronegative oxygen atoms [3].

The MW and viscosity of silicone resins depend on the proportion of monochloro-, dichloro-, and trichlorosilane monomers and on the process. The ultimate cross-link density depends on the fraction of trichlorosilane in the recipe and on the fraction of this monomer that forms branched rather than cyclic or cluster structures during the process.

Most silicone resins are copolymers of methyl and phenyl substituted monomers; other alkyl monomers are sometimes included. Properties depend on the phenyl/methyl ratio, as summarized in Table 16.1. The rate of the cross-linking reaction is faster with high-methyl substituted silicone resins. Consequently, a larger amount of material is lost during heat curing of high-phenyl resins, since low MW components evaporate in the oven to a larger degree before polymerizing. The faster cure rate of the high-methyl substituted silicones and the longer package stability of the high-phenyl substituted silicones follow from the same factor. The greater UV resistance of high-methyl relative to high-phenyl substituted silicone resins gives greater gloss retention during exterior exposure. The exterior durability of well-formulated silicone coatings is better than that of acrylic–MF, polyester–MF, or urethane coatings, and approaches that of highly fluorinated polymers.

On the other hand, high-phenyl silicones are superior to high-methyl silicones for applications requiring high temperature resistance, and far superior to other organic coatings except certain fluoropolymers. The thermal stability of high-methyl silicones, although inferior to that of high-phenyl silicones, is much greater than that of silicones with longer alkyl groups. The half-lives at 250°C, based on weight loss studies, are reported to exceed 100,000 hours for phenylsilicone films compared with over 10,000 hours for methyl silicone films and only 2 hours for propyl silicone films [4]. The useful life of a methyl silicone film at 350°C is given as 1000 hours; for comparison a "polyester" film (presumably cross-linked with a MF resin) has a useful life of 1000 hours at 223°C.

When silicones are thermally decomposed, the ultimate product is silicon dioxide, which, though brittle, can serve as a temperature-resistant coating binder. For example, chimney paints are made from silicone resins pigmented with aluminum flake for use at over 500°C for years. At the high service temperature, the organic substituents burn off, leaving behind a film of the aluminum pigment in a matrix of silicone dioxide with perhaps some aluminum silicate—essentially glass. Although it is brittle, this film

TABLE 16.1. Properties of High-Methyl Versus High-Phenyl Silicone Resins

High-Methyl	High-Phenyl
Lower weight loss in curing	Greater weight loss in curing
Faster cure rate	Longer package stability
Higher UV stability	Higher heat stability
Lower temperature flexibility	Greater oxidation resistance

Source: Adapted from Ref. [4].

continues to provide protection if it is not damaged mechanically. (See Ref. [4] for discussion of coatings with varying heat resistance.)

As expected from the greater rigidity of aromatic rings, coatings from methyl silicone resins have low temperature flexibility superior to those from phenylsilicone and also superior to most other organic coatings. They also combine the properties of being repellant to liquid water but permeable to water vapor.

16.1.1.1. Modified Silicone Resins High-solids silicone resins have been made available that cure either directly using zinc octanoate catalysts or by cross-linking with trialkoxysilanes using a titanate catalyst [5]. Waterborne silicone resins have also been developed. One approach is to emulsify a silicone resin in water using an emulsifying agent [6]. Emulsions of methyl silicone resins, an amino-functional polysiloxane emulsion, and a styrene–acrylic latex are used to formulate exterior house paints. Such coatings have been used on a large scale in Europe for many years but are just being introduced into the United States. They have outstanding exterior durability [7].

Silicone resins can be modified with a variety of functional groups. Epoxy-functional resins are prepared by reacting methylphenyldimethoxysilane, phenyltrimethoxysilane, and dimethyldimethoxysilane with water with KOH as catalyst followed by reacting the resulting resin with 3-glycidyloxypropyltriethoxysilane. Thermosetting coatings can be formulated by cross-linking the epoxy silicone with a diaminodialkoxysilane [8]. Epoxy-functional silicone resins cross-linked with carboxylic acid–functional acrylic resins are used to formulate marine finishes with excellent durability [9].

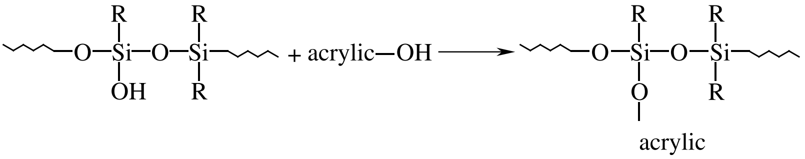
Carbamate-functional siloxanes are prepared from hydroxy-terminated siloxanes. Dimethylsiloxane oligomers with 4 to 5 units and two silicon hydride groups are reacted with the allyl group of trimethylolpropane monoallyl ether using chloroplatinic acid as the catalyst to give the hydroxy-functional siloxane. The hydroxy-functional oligomer is then reacted with 1-methoxy-2-propylcarbamate using butyl stannoic acid and triphenylphosphite as catalysts to give the carbamate-functional oligomer. The resin is combined with a carbamate-functional acrylic resin and an MF resin to formulate automobile clear coats with excellent scratch resistance [10].

16.1.2. Silicone-Modified Resins

The high cost of pure silicone coatings and the long, high temperature cures can be reduced by combining silicones with other coating resins. The earliest approach was simply to add a silicone resin to an alkyd resin in the reactor at the end of the alkyd cook. Although some covalent bonds between silicone resin and alkyd might form, probably most of the silicone resin simply dissolves in the alkyd. The exterior durability of silicone-modified alkyd coatings made this way is significantly better than unmodified alkyds. The improvement in durability is roughly proportional to the amount of added silicone resin; 30% silicone resin is a common degree of modification. Silicone resins designed for this purpose may contain higher alkyl as well as methyl and phenyl groups to improve compatibility. Alkyd coatings modified with predominantly phenylsilicone resins are reported to have greater thermoplasticity, faster air drying, and higher solubility than predominantly methyl silicone–modified alkyds. These results can be understood when we consider that the higher rigidity of the aromatic rings leads to a "solid" film at an earlier stage of cross-linking. Less cross-linking in the phenylsilicone-modified coatings makes them more thermoplastic and soluble.

Further improvements in exterior durability are obtained by coreacting a silicone intermediate during synthesis of the alkyd. Such intermediates react readily with free hydroxyl groups. Silicone-modified alkyds made this way are said to impart better durability than alkyds in which the silicone resin is cold blended. They are used mainly in outdoor air dry coatings where application is expensive (e.g., in a top coat for steel petroleum storage tanks) and a longer coating service life more than offsets the extra cost.

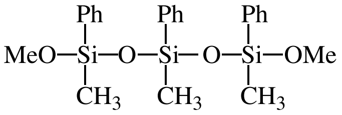
Silicone-modified polyester and acrylic resins are made by reacting silicone intermediates with the hydroxy-functional resins; in some cases, the silicone intermediates have silanol (Si—OH) groups. These can undergo co-condensation with hydroxyl groups on the resin to be modified as well as self-condensation with other Si—OH groups. The ratio of the two reactions is controlled by catalyst choice. The best catalysts for promoting the desirable co-condensation between the resin and the silicone intermediate are titanates such as tetraisopropyl- or tetraisobutyltitanate. In model compound studies, tetraisopropyltitanate was shown to favor co-condensation over self-condensation by 3.4 : 1 as compared to a 0.23 : 1 ratio with no catalyst. Co-condensation between a hydroxy-functional silicone intermediate and acrylic polyol is shown below.



$$\sim\!\!\sim O-\underset{OH}{\overset{R}{Si}}-O-\underset{R}{\overset{R}{Si}}\sim\!\!\sim + \text{acrylic}-OH \longrightarrow \sim\!\!\sim O-\underset{\underset{\text{acrylic}}{O}}{\overset{R}{Si}}-O-\underset{R}{\overset{R}{Si}}\sim\!\!\sim$$

Self-condensation between silicone intermediates can also occur resulting in some Si—O—Si cross-links. Excessive self- or co-condensation of a polyfunctional silicone intermediate and a polyfunctional resin can result in gelation.

It is easier to control the reaction when the reactive functional groups on the silicone intermediates are silylmethoxy (Si—OMe) rather than silanol (Si—OH) groups. A methoxylated silicone intermediate has been described which has a weight average MW of 470 and an equivalent weight of 155 [4]. An idealized structure of the intermediate is



$$MeO-\underset{CH_3}{\overset{Ph}{Si}}-O-\underset{CH_3}{\overset{Ph}{Si}}-O-\underset{CH_3}{\overset{Ph}{Si}}-OMe$$

A solution of the polyester or acrylic is heated with the desired amount of silicone intermediate and the titanate catalyst at 140°C until a predetermined viscosity is reached. The reaction is relatively slow at 140°C; higher temperatures reduce reaction time and hence cost but increase the risk of overshooting the desired viscosity as well as the risk of gelation. Typical silicone-modified polyesters and acrylics have 30 to 50 wt% silicone. Modification with less than about 25% silicone provides little improvement in exterior durability. Exterior durability is enhanced with increasing silicone content above 30%, but cost also increases.

The same reactions occur during cross-linking after the coating is applied. Usually, zinc octanoate is used as the catalyst for cross-linking the coating since titanate esters are hydrolyzed by the water brought into the coating by pigments. The principal applications are in baking coatings, especially in coil coatings for metal siding (Section 30.4), where a typical cure schedule is 90 seconds at peak metal temperatures of 300°C. Such coatings tend to soften when exposed to high humidity for prolonged periods. The softening is called *reversion*. It is speculated that it is caused by reversible hydrolysis of the cross-links, which, as discussed above, have three oxygen atoms bound to a single silicon atom. The film hardens again if the ambient humidity decreases, but the film is vulnerable to physical damage if scraped while it is soft. To minimize this problem, a small amount of MF resin can be added as a secondary cross-linker.

Waterborne silicone-modified resins can be prepared from water-reducible acrylic and polyester resins. Also, acrylic latexes prepared with hydroxyethyl (meth)acrylate as a comonomer can be modified with silicone intermediates [6]. Silicone-modified epoxy resins have also been made [11]. See Ref. [4] for examples of formulations and preparation of several examples of silicone-modified resins.

16.2. REACTIVE SILANES

Reactive silane is the term used to identify compounds having a trialkoxysilyl group and an alkyl group bearing a reactive substituent. They have been used in coatings in several different ways (Refs. [11] and [12] are review papers). Commercially available reactive silanes include 3-aminopropyltriethoxysilane, *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane, 3-glycidyloxypropyltrimethoxysilane, and 3-methacryloxypropyltrimethoxysilane, among others.

Trialkoxysilyl groups can react directly, or indirectly in the presence of water, with hydroxyl groups; the other functional group can participate in the cross-linking reaction with the resins in a coating. For example, the trialkoxysilyl group on 3-aminopropyltriethoxysilane can react with hydroxyl groups on the surface of glass, while the amine group can react with epoxy groups in an epoxy resin. The interactions with surfaces are complex [11]. The relative rates of hydrolysis of the alkoxysilyl groups to silanol groups, self-condensation reactions, and reactions with substrate hydroxyl groups vary with pH, water concentration, alcohol concentration, reactivity of the substrate hydroxyl groups, and rates of reverse reactions. In the case of amino-functional silanes, the situation can be further complicated by the competing possibility of adsorption of amine groups on the substrate. An idealized picture of the interaction of 3-aminopropyltrimethoxysilane with the surface of glass and an epoxy resin is shown in Scheme 6.2 in Section 6.4.3. Before the advent of reactive silanes it was difficult to achieve adhesion to glass that would resist displacement with water. Use of reactive silanes has made possible coatings and sealants with excellent adhesion to glass in the presence of water. Although water can hydrolyze some of the linkages, the reaction is reversible. With multiple attachments, adhesion is not lost. (See Section 6.4.3 for further discussion.)

Reactive silanes also form stable condensation products with other oxides, such as those of aluminum, zirconium, tin, titanium, and nickel; less stable bonds are formed with oxides of carbon, iron, and boron [12]. Reactive silane additives are used not only as adhesion promoters but also to treat the surface of oxide pigments to improve dispersion properties.

Bis(trisilylalkoxy)alkanes are being investigated to treat the surface of steel to increase adhesion [13]. Clean steel is rinsed with water and then the wet steel is dipped in an aqueous solution of bis(trimethoxysilyl)ethane (BTSE) followed by dipping in an aqueous solution of a reactive silane. The BTSE reacts with water and hydroxyl groups on the steel and silanols from other molecules of BTSE to give a water-resistant anchor to the steel. The reactive silane reacts with other silanol groups from the BTSE, and the reactive group can react with a coating binder. There are many variables in the treatment, excellent results have been obtained in laboratory work, and commercial use is anticipated. A mixture of bis(trimethoxysilylpropyl)amine and vinyltriacetoxysilane has been reported to provide corrosion protection equal to chromate primers on aluminum, galvanized steel, stainless steel, steel, and cobalt–chromium alloy [14]. (See Sections 6.4.3 and 7.3.2 for further discussion.)

Resins with multiple trialkoxysilyl groups can be used as binders for moisture-curable coatings. For example, an isocyanate-terminated resin can be reacted with 3-aminopropyltrialkoxysilane to give a resin with terminal trialkoxysilyl groups. Coatings made using such resins cross-link to a polymer network after application and exposure to humid air. Multifunctional isocyanates may be used to prepare resins with increased cross-link density. An advantage of the triethoxysilyl resin over the isocyanate resin is that part of the solvent can be ethyl alcohol. The ethyl alcohol permits a reasonable pot life in the presence of water such as comes into a coating from pigment surfaces. If free isocyanate groups are present, the coating is not stable in the presence of either ethyl alcohol or water. The trialkoxysilyl approach also avoids formation of CO_2, which can lead to film imperfections such as pinholing in moisture-curable urethanes. After the alcohol evaporates, the reaction with water proceeds rapidly at ambient temperature. For example, isocyanate-terminated urethanes prepared by reacting polyols and MDI are end-capped with 3-aminotrimethoxysilane to prepare a resin used in moisture-curable coatings [15].

Trialkoxysilyl-functional acrylic resins can be made by copolymerizing a trialkoxysilylalkyl methacrylate with other acrylic monomers [16–18]. Coatings based on such resins cure on exposure to atmospheric moisture; the reaction is catalyzed with organotin compounds or organic acids. The resulting coatings are reported to have excellent exterior durability, resistance to environmental etching and marring, and adhesion to aluminum. They are used in automobile OEM and refinish clear coats. In baking automotive clear coats for plastics, trimethoxypropylsilyl-functional acrylic resins; a methoxy group hydrolyzes at room temperature and then reacts with another silanol group during baking to cross-link the coating. The scratch and mar resistance before and after weathering are superior to MF cross-linked coatings [19].

Automotive clear coats are being made by combining trialkoxysilylalkyl-functional and hydroxy-functional acrylic resins with MF resins or blocked isocyanates [18]. No detailed studies of the cross-linking reactions have been published, but one can speculate that they include hydrolysis and condensation of the trialkoxysilyl groups to form siloxane cross-links, reaction of hydroxyl groups with MF resins or blocked isocyanates, and transetherification of the hydroxyl groups with the trialkoxysilyl groups. The resulting coatings are reported to have excellent exterior durability and very good resistance to environmental etching and marring. Another advantage is that formaldehyde emissions are reduced because lower levels of MF resin are used.

Trialkoxysilylated acrylic and vinyl acetate latexes can be prepared using 3-methacryloxypropyltriisobutoxysilane as a comonomer in emulsion polymerization [20]. The isobutoxysilyl derivatives are used since they are more resistant to hydrolysis at polymerization temperatures. The latexes are storage stable; they do not cross-link until water evaporates from a film. Possibly the alkoxysilyl groups hydrolyze during storage, but the silanols formed do not condense until after a film is formed because of the large excess of water present. Coatings made from them are reported to have superior adhesion as well as high chemical, solvent, and mar resistance. Carboxylic acid–functional acrylic latexes can be cross-linked using β-(3,4-epoxycyclohexyl)ethyltriethoxysilane [21].

16.3. ORTHOSILICATES

Tetraethylorthosilicate (TEOS), $Si(OEt)_4$, is used in making binders for zinc-rich primers, which are widely used primers for corrosion protection of steel (Sections 7.4.3 and 33.1.2). When exposed to water vapor in the atmosphere, $Si(OEt)_4$ hydrolyzes, with acid or base catalysis, to give a complex polysilicic acid network that forms the coating binder.

$$Si(OC_2H_5)_4 + H_2O \longrightarrow (C_2H_5O)_3Si{-}O{-}Si(OC_2H_5)_3 + CH_3CH_2OH$$

To make the primers, an ethyl alcohol solution of $Si(OEt)_4$ is partially polymerized by the addition of a small amount of water (just enough to increase the MW sufficiently to give the desired viscosity), and the zinc powder pigment is dispersed in the resulting oligomer solution. Note that the reaction is reversible; the ethyl alcohol solvent retards polymerization by small amounts of water in the coating formulation during storage. When the coating is applied and the alcohol evaporates, water is absorbed from the atmosphere, and the cross-linking reaction continues to completion at ambient temperatures. Although the cross-linked binder is predominantly polysilicic acid, zinc salts are incorporated in the matrix. They form by reaction with the zinc hydroxide and zinc carbonate always present on the surface of zinc metal pigments. Iron salts from the steel surface may also be incorporated in the matrix. (The chemistry and properties of zinc-rich primers based on $Si(OEt)_4$ are reviewed in Ref. [22].) For waterborne zinc-rich primers, aqueous solutions of potassium, sodium, and/or lithium silicate are being used.

16.3.1. Sol-Gel Coatings

Tetraethyl orthosilicate (TEOS) is used with various other components to prepare sol-gel hybrid organic–inorganic vehicles for coatings. Such systems are commonly called *sol-gel coatings*; another name is *ormosil*. For example, a sol-gel composed of the condensate of ethylsilane and tetramethyltetravinyl-cyclotetrasiloxane with water and a base gives a tetrasilanol, which when combined with TEOS and an acid catalyst gives a clear coat to be applied over a base coat–clear coat automotive coating. The resulting finish had a better resistance to automatic car washing and sulfuric acid spot tests than that of a control without the sol-gel coating [23]. Another application is treatment of metals for corrosion protection replacing chromate pigmented primers. For example, TEOS is added to water acidified with nitric acid; after hydrolysis, glycidoxypropyltrimethoxysilane is added and the resulting ormosil was applied to aluminum. Various tests indicate that corrosion protection can be expected to exceed other approaches [24].

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17

Other Resins and Cross-Linkers

The types of resins and cross-linkers used in the largest volumes in coatings were described in Chapters 8 to 16. In this chapter, other commercially important materials and selected promising developments are discussed.

17.1. HALOGENATED POLYMERS

Halogenated polymers have desirable properties for certain applications, including low water permeability. Some are used in top coats for corrosion protection. Others serve as binders for adhesion promoting primers for plastics.

17.1.1. Solution Grade Thermoplastic Vinyl Chloride Copolymers

Solution grade vinyl chloride resins are copolymers of vinyl chloride and vinyl acetate, frequently with a small amount of a third monomer to impart special properties. The vinyl acetate lowers T_g and broadens the range of applicable solvents. For example, a terpolymer of vinyl chloride, vinyl acetate, and maleic acid with a weight ratio of 86 : 13 : 1 (mole ratio 81 : 17 : 1) and an $\bar{M}_w$ on the order of 75,000 has been used in interior coatings for beverage cans. The maleic acid promotes adhesion; other solution vinyl resins are made with hydroxy functionality. Use of solution vinyl resins has declined because of the low solids required for application, about 10 to 12 nonvolatile volume solids (NVV).

Vinyl chloride copolymers require stabilization to prevent thermal and photochemical degradation. As discussed in Section 5.3, the polymers undergo dehydrochlorination in an autocatalytic chain reaction. A variety of stabilizing agents are used, including organotin

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Organic Coatings: Science and Technology, Third Edition, by Zeno W. Wicks, Jr., Frank N. Jones, S. Peter Pappas, and Douglas A. Wicks

esters such as dibutyltin dilaurate; barium, cadmium, and strontium soaps; maleates; and oxirane compounds.

17.1.2. Vinyl Chloride Dispersion Copolymers

Dispersion grade vinyl chloride copolymers having high molecular weights (MW) can be used in high-solids coatings. They are prepared by suspension polymerization as particles with an average diameter of a few micrometers. In this process, a solution of an initiator in the monomer mixture is added with vigorous stirring to a hot dilute solution of poly(vinyl alcohol) (PVA) in water. The monomers are dispersed into small droplets, inside of which the polymerization is initiated and completed, resulting in the formation of particles. A monomer-soluble initiator is used in suspension polymerization in contrast to the water-soluble initiators used in emulsion polymerization. The PVA stabilizes the suspension by minimizing coalescence of the particles when the temperature of the reaction is above the T_g. Since the PVA has many easily abstractable hydrogens, graft side chains grow on the PVA. After polymerization is complete, the polymer particles are separated by filtration, washed, and dried. The MW of polymers made by suspension polymerization depends primarily on initiator structure and on the combination of reaction temperature and initiator concentration. Commonly, $\bar{M}_w$ is on the order of 100,000.

In plastics, dispersion grade vinyl chloride copolymers are used in plastisols. Plastisols are polymer particles dispersed in a plasticizer. Since the T_g of the polymer is well above room temperature, and also because the polymer is partially crystalline, the polymer does not dissolve in the plasticizer at room temperature at an appreciable rate. When the plastisol is heated above the polymer T_g and above the melting point of the crystalline regions in the polymer, the polymer dissolves in the plasticizer and the particles coalesce to a molten state. When cooled, the product is a plastic consisting of a homogeneous solution of polymer and plasticizer. The viscosity of plastisols is generally too high for application as coatings. The viscosity can be lowered by addition of solvent. Solvents must be chosen that dissolve the plasticizer without significantly swelling the polymer particles. Application viscosities can generally be achieved with 20% solvent or less. These systems are properly called *organosols*, but they are also frequently called *plastisols* even though there is volatile solvent present.

17.1.3. Chlorinated Rubber, Chlorinated Ethylene Vinyl Acetate Copolymers, and Chlorinated Polyolefins

Chlorinated rubber is used in top coats for heavy duty maintenance paints because of the barrier properties resulting from its low water permeability. It is also used in tie coats on polyolefin plastics. Chlorinated rubber is compatible with some alkyd resins and is used to impart fast drying qualities to alkyd-based traffic paints. Like PVC, chlorinated rubber dehydrochlorinates and requires stabilizers similar to those used with PVC. Some metal salts, especially iron, tend to promote degradation of chlorinated rubber so it degrades when applied over rusty steel [1].

Chlorinated rubber is prepared from natural rubber that has been milled to reduce its MW. A solution of milled rubber in CCl_4 is reacted with chlorine or some other chlorinating reactant. The reactions are complex: Addition to the double bonds, substitution, and cyclization reactions all occur. To eliminate most of the double bonds from the rubber, the final product contains 65 to 68 wt% chlorine. Various MW grades are manufactured.

Polymer strength increases with MW, but the viscosity of solutions also increases. The formulator makes an appropriate compromise between coating solids and film properties for a particular application. Environmental regulations in the United States have increased the cost of producing chlorinated rubber to prohibitive levels; production has been discontinued, and only imported material is available.

Chlorinated ethylene/vinyl acetate copolymers have been developed which can be used to replace chlorinated rubber in at least some applications [2]. Since the initial resin does not contain double bonds, the chlorine content need not be as high as in chlorinated rubber; grades with 52, 55, and 58% chlorine are available. The higher the chlorine content, the better the barrier properties but the lower the flexibility and impact resistance. Performance is said to be comparable to chlorinated rubber, with the advantage of better storage stability.

Chlorinated polyolefins (CPOs) are an important class of adhesion promoters in primers for plastics such as "thermoplastic polyolefin" (TPO) (Section 31.2.2). TPO is used in a large volume by the auto industry: for example, for bumpers. The predominant CPO is a chlorinated polypropylene that has been modified with maleic anhydride.

17.1.4. Fluorinated Polymers

Polytetrafluoroethylene, PTFE, $\text{+}CF_2CF_2\text{+}_n$, has the greatest exterior durability and heat resistance of any polymer used in coatings. However, PTFE is insoluble in solvents and its fusion temperature is so high that its coating uses are limited to applications in which the substrate can withstand high temperatures [3]. For example, aqueous dispersions of PTFE are used for coating the interior of chemical processing equipment and cookware [4]. After application the polymer particles are sintered at temperatures as high as 425°C. Like all highly fluorinated compounds, PTFE has such a low surface free energy that it is not wet by either water or oils; hence, it provides a "non-stick" cooking surface. Adhesion of PTFE is also problematic; in general, the metal surface is roughened so that "dovetail joints" can be formed when the coating and substrate are baked (Section 6.1).

Since its fusion temperature is somewhat lower, poly(vinylidene fluoride), PVDF, $\text{+}CH_2CF_2\text{+}_n$, can be used in additional applications. PVDF is used in coil coatings as a plastisol-like dispersion in a solution of acrylic resin [3,5]. The fusion temperature of the films is reported to be 245°C. The exterior durability is outstanding, but the cost is high and only low gloss coatings are possible. Copolymers of vinylidene fluoride (VDF) are also finding use in powder coatings.

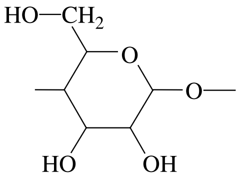
Vinylidene fluoride copolymer latexes are said to permit formulation of paints that form films at ambient temperatures. The latex is made from a seed latex that is a copolymer of vinylidene fluoride and another perfluorinated monomer, resulting in a less crystalline copolymer. With this seed, polymerization is continued with acrylic monomers, resulting in latex particles with uniform distribution of acrylate and fluorinated polymers that are film formers at ambient temperature. Film properties are reported to be excellent with exterior durability with the same rating as solventborne PDVF [6].

Fluorinated copolymers with functional groups such as hydroxyl groups can be crosslinked after application. Copolymers of VDF with a hydroxy-functional monomer crosslinked with a polyisocyanate give coatings with superior wet adhesion and corrosion as compared with PVDF homopolymer [7]. Perfluoroalkyl acrylate esters have been copolymerized with hydroxyethyl methacrylate (HEMA) to form solvent-soluble resins; however, the monomers are expensive. Halofluoroethylene $CF_2{=}CFX$/vinyl ether copolymers have been used in steel building panels and to a limited extent in clear coats for automobiles [3]. Vinyl ethers and $CF_2{=}CFX$ form alternating polymers. Functional groups can be introduced by copolymerizing hydroxy- and/or carboxy-substituted vinyl ether comonomers. The T_g is controlled by the ratio of fluorinated monomer to vinyl ether monomers and by the chain length of the alkyl group on the vinyl ether. Copolymers with hydroxyl groups can be cross-linked with MF resins or polyisocyanates. Gloss retention on exterior exposure is reported to be superior to that of acrylic coatings.

Acrylic monomers that have fluorinated side chains (e.g., 2,2,2-trifluoroethyl methacrylate and perfluoroalkyl acrylate) are available. Polymers containing such monomers tend to have very low surface energies and have been studied for applications such as antifouling and antigraffiti coatings. Concern is being expressed about environmental contamination by perfluoroalkylcarboxylic acids that apparently are derived by photoxidation of perfluoroalkanols and are accumulating in fish and animals, especially in the arctic [8].

17.2. CELLULOSE DERIVATIVES

Cellulose is a naturally occurring polymer of repeating anhydroglucose units; as the main building block of plant structures, it is insoluble in water and organic solvents. Cellulose derivatives that are soluble in water and others that are soluble in organic solvents can be made by reactions of the hydroxyl groups.

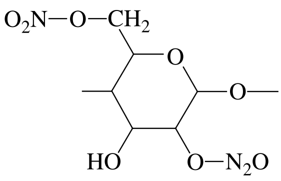


Anhydroglucose unit

Many solvent soluble cellulose derivatives have been prepared. Those of most importance in coatings are nitrocellulose (NC) and cellulose acetobutyrate (CAB); ethyl cellulose, cellulose acetate, and cellulose propionate have been used to some extent. Water-soluble cellulose derivatives are used to modify the flow properties of latex paints and are discussed in Chapter 32.

17.2.1. Nitrocellulose

Nitrocellulose (NC) is another example of poor nomenclature since it is not a nitro compound. It is a nitrate ester and should be called *cellulose nitrate*. Three types of NC are available with differing extents of esterification. Their compositions are given in Table 17.1. An isomeric dinitroanhydroglucose unit of nitrocellulose is



Dinitroanhydrocellulose

TABLE 17.1. Composition of Nitrocellulose Types

Type	Nitrogen	$-ONO_2$ Groups (%) per Anhydroglucose Unit
SS (spirit soluble)	10.7–11.2	1.9–2.0
RS (regular solubility)	11.8–12.3	2.15–2.25
Explosive	12.3–13.5	2.25–2.5

The SS type is alcohol soluble and is used in flexographic printing inks but has few uses in coatings. The RS type is soluble in esters and ketones and is generally used in coatings. The explosive type is included in Table 17.1 to emphasize the hazards of nitrocellulose. The RS type used in coatings is not explosive but is highly flammable. To reduce the handling hazard, nitrocellulose is shipped wet with a nonsolvent. In most cases for the RS type, alcohols are used and the NC is shipped at 70 NVW, with the balance being ethyl or isopropyl alcohol. Although RS nitrocellulose is not soluble in alcohol, it is soluble in mixtures of ketones and esters with alcohols and hydrocarbons (Section 18.2).

Nitrocellulose is made by reacting cellulose with nitric acid. Small amounts of water are present, and some hydrolysis of the cellulose occurs, reducing the MW. A range of MW grades is available. The higher the MW, the greater the polymer strength but the lower the solids of coatings that can be made. Viscosity of nitrocellulose solutions is tested with a falling ball viscometer, in which the time for a ball to fall a specified distance through a nitrocellulose solution of standard concentration is measured. The various MW grades are designated as $\frac{1}{4}$, $\frac{1}{2}$, 1 second, and so on. The times are proportional to the time in the falling ball viscosity test. The larger the number of seconds, the higher the MW.

Nitrocellulose was used in lacquers for automobile top coats before acrylic lacquers, which have better exterior durability, were developed. They continued to be used for some years in refinish lacquers for repairing automobiles because they polished more easily and gave a deeper gloss appearance than room temperature dried acrylic lacquers. Nitrocellulose lacquer primers continue to be used to some degree in refinishing automobiles. The principal remaining use of NC lacquers is in wood finishing (Section 31.1). These lacquers have relatively low solids but continue to be used to a significant, if decreasing, extent because they enhance the appearance of wood grain to a greater extent than any other coating. Other desirable characteristics for NC lacquers for wood finishing are rapid drying, which permits handling and shipment soon after finishing, and easy damage repair, since the films are thermoplastic. Increasingly stringent VOC emission regulations can be expected to force further reductions in use of NC.

Use of nitrocellulose lacquers has declined substantially in the United States and Europe because of their high VOC, but use in other parts of the world is still substantial. For example, it is reported that worldwide use in 2001 in furniture finishes was 533,000 metric tons [9]. Similarly, substantial amounts of automobile refinish nitrocellulose lacquer continue to be used.

17.2.2. Cellulose Acetobutyrate

A variety of organic esters of cellulose are used in fibers, plastics, and to a degree, in coatings. The only one still used to a significant extent in coatings is a mixed acetate, butyrate ester (CAB). CAB lacquers are used to some extent; they exhibit lighter color and better color retention with reduced handling risk relative to NC lacquers. The principal use has been as a component in acrylic automotive coatings. CABs help control flow, particularly to facilitate orientation of aluminum flakes parallel to the surface of the film during application and film formation. Orientation of the flakes in the final film enhances the appearance of metallic finishes. (See Ref. [10] and Chapter 29.)

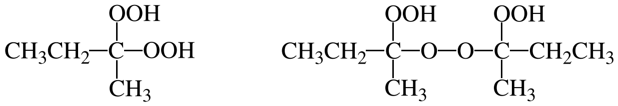
Several types of CAB are available with different ratios of acetate/butyrate/unesterified hydroxyl groups and with differing MWs. The ratio affects the solubility and compatibility of the polymer. The larger the ratio of butyrate ester, the larger the amount of aromatic hydrocarbon that can be tolerated in a solvent mixture. Also, as the butyrate content increases, the T_g tends to be lower. Compatibility with acrylic resins is dependent on both the CAB and the acrylic polymer. An example of a CAB grade used in acrylic lacquers has an average of 2.2 acetate group, 0.6 butyrate group, and 0.2 unreacted hydroxyl group per anhydroglucose unit. This corresponds to about 30% acetyl content, 17% butyryl content, and 1.5% hydroxyl content, based on the total weight of polymer.

17.3. UNSATURATED POLYESTER RESINS

Unsaturated polyester resins are maleic acid–containing polyesters dissolved in styrene. They contain unsaturated maleate [*Z*-(*cis*) configuration] and fumarate [*E*-(*trans*) configuration] groups in the backbone. These resins are used on a large scale in glass-reinforced plastics, commonly called *fiberglass plastics*. They are used on a smaller scale in some coating applications.

A variety of diacids and diols can be used to make unsaturated polyesters; the most common are phthalic anhydride (PA), maleic anhydride, and propylene glycol (or a mixture of propylene glycol and propylene oxide). These are the lowest cost raw materials; furthermore, the initial reaction can be carried out at moderate temperatures, and a minimum amount of water is formed. During esterification, some of the maleate ester groups isomerize to fumarate ester groups. The fraction isomerized depends on processing time and temperature and can also vary depending on the other components of the polyester. Fumarate groups are more reactive during cross-linking than maleate groups. Reaction conditions during esterification must be carefully controlled to ensure that the extent of isomerization is reproducible from batch to batch. Use of fumaric acid instead of maleic anhydride results in a higher fumarate diester content; such polyesters generally give harder plastics than those made with maleic anhydride. More flexible plastics can be obtained by substituting aliphatic diacid (e.g., adipic acid) for part of the PA to reduce T_g. Although other glycols can be used, economics favor use of propylene glycol (or propylene oxide). The properties of the cured materials are also affected by the ratio of polyester to styrene; typically, a 70 : 30 ratio is used.

The resin/styrene solution is cross-linked using free-radical initiators. The product is a complex mixture derived from copolymerization of styrene with the maleate or fumarate double bonds, graft copolymerization, and homopolymerization of styrene. Cross-link density is affected by the MA/PA ratio in the resin, commonly 15 to 40 mol% of maleic anhydride. Peroxides such as benzoyl peroxide are used at temperatures of 70 to 100°C. Many applications require cross-linking at ambient temperatures. In these cases, an initiator such as methyl ethyl ketone (MEK) peroxide, and promoters such as a mixture of dimethylaniline and cobalt naphthenate, are added to the resin/styrene solution just before use. The combination reacts rapidly at room temperature to generate free radicals, which initiate cross-linking. MEK peroxide is a complex mixture in which the major components contain both peroxide and hydroperoxide groups [11], as shown. The cobalt salt acts as a redox catalyst for the decomposition of the peroxide and hydroperoxide groups into free radicals; dimethylaniline further promotes that reaction.



$$\mathrm{CH_3CH_2{-}\overset{\displaystyle OOH}{\underset{\displaystyle CH_3}{C}}{-}OOH} \qquad \mathrm{CH_3CH_2{-}\overset{\displaystyle OOH}{\underset{\displaystyle CH_3}{C}}{-}O{-}O{-}\overset{\displaystyle OOH}{\underset{\displaystyle CH_3}{C}}{-}CH_2CH_3}$$

Major components of MEK hydroperoxide

Gel coats are pigmented unsaturated polyester/styrene coatings (with initiator and promoter); they are sprayed on the inside of a mold surface (Section 31.2.1). The exposed (back) surface of the gel coat is then sprayed with glass fiber–loaded unsaturated polyester/styrene compound and then covered with plastic film and cross-linked. After the part is taken from the mold, the surface is the gel coat that cured in the absence of oxygen. Many glass-reinforced plastic objects, ranging from prefabricated shower stalls to boat hulls, are made this way. In the case of boat hulls, hydrolytic stability is particularly important, so the surface retains gloss after outdoor exposure and immersion in water. Unsaturated polyesters made using neopentyl glycol, MA, and isophthalic acid provide better gloss retention than those made from propylene glycol and PA, but the cost is higher.

The free radical polymerization is oxygen inhibited. This is not a problem for many plastics applications since the reaction is commonly carried out in a mold, so the resin surface is not exposed to air. In most coating applications, the top surface is exposed to the air and will remain sticky after the polymerization is complete below the surface. A further problem is the volatility of styrene. These problems can be minimized by incorporating some insoluble semicrystalline paraffin wax in the formulation. After the coating is applied, the low surface tension wax particles come to the surface preferentially. The wax layer reduces the rate of styrene loss and also reduces oxygen concentration in direct contact with the polymerizing coating, thereby minimizing the difficulty of surface cure. The wax layer, however, results in a relatively uneven low gloss surface, suitable for some applications but not for others.

Unsaturated polyesters can be used in UV cure coatings (Section 29.2.4). A photoinitiator is used that generates free radicals on exposure to UV radiation. High intensity radiation sources are used which generate very large numbers of free radicals sufficiently rapidly at the surface so the oxygen in the air at the surface is depleted (by reaction with radicals), and polymerization can proceed. Acrylate systems are more widely used than styrene/unsaturated polyesters.

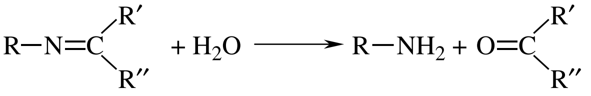
Oxygen inhibition can be minimized using coreactants having allyl groups with styrene/unsaturated polyesters [12]. A free radical abstracts a hydrogen atom from the methylene group activated by both the adjacent double bond and the ether oxygen. The resulting free radicals from this reaction then react with oxygen to form peroxy free radicals, which in turn abstract hydrogen from the activated methylene groups to form hydroperoxides. The reactions consume some of the oxygen at the surface and generate new hydroperoxide in a chain reaction; as a result, oxygen inhibition is reduced.

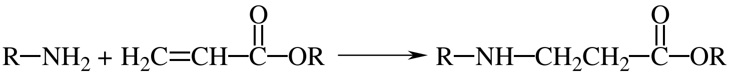
Use of allyl ether reactions has been extended to waterborne unsaturated polyester resins. A low MW ester is prepared by reacting 2 mol of maleic anhydride with 1 mol of a mixture of low MW diols and polyalkylene glycols. The resulting partial ester is further esterified with 2 mol of trimethylolpropane diallyl ether [13]. The polyalkylene glycol ester segments are efficient emulsifying agents so the polyester can be emulsified in water for application. Films can be cured either with hydroperoxide/cobalt initiators or by photoinitiators and UV radiation.

17.4. (METH)ACRYLATED OLIGOMERS

Thermosetting resins can be made with (meth)acrylate double bonds as cross-linkable groups. Such resins are used in radiation cured coatings (Section 29.2.4). They can also be used in ambient cure and at somewhat elevated temperatures (force-dry) with free radical initiators. Both acrylate and methacrylate polymerizations are air inhibited, particularly methacrylate systems, which generally require higher cure temperatures to minimize the effect of oxygen inhibition.

Acrylated oligomers can also be cross-linked with polyfunctional primary amines by a Michael addition reaction, as illustrated for monofunctional reactants. This reaction is fast, so practical systems are based on blocked amines, commonly ketimines [14]. When a coating film is exposed to atmospheric moisture, the ketimine reacts with water to release the free primary amine.



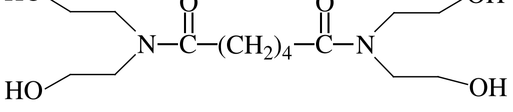


$$R{-}NH_2 + H_2C{=}CH{-}\overset{O}{\overset{\|}{C}}{-}OR \longrightarrow R{-}NH{-}CH_2CH_2{-}\overset{O}{\overset{\|}{C}}{-}OR$$

Acrylated oligomers can also be cross-linked by a Michael reaction with acetoacetylated resins and their enamine derivatives, as discussed in Section 17.6.

17.5. 2-HYDROXYALKYLAMIDE CROSS-LINKERS

Esterification of most alcohols with carboxylic acids is too slow for practical use as a cross-linking reaction. However, 2-hydroxyalkylamides undergo esterification reactions more rapidly than simple alcohols. Polyfunctional 2-hydroxyalkylamides (e.g., the tetrafunctional hydroxyalkylamide derived from aminolysis of dimethyl adipate with diisopropanolamine) can serve as cross-linkers for carboxylic acid-functional acrylic or polyester resins [15].

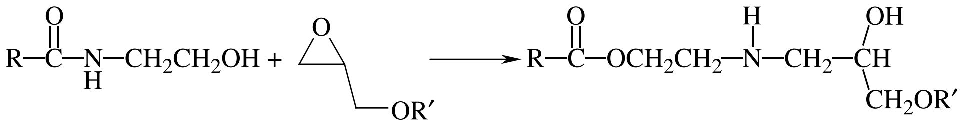


The properties of coatings obtained by cross-linking carboxylic acid–functional acrylic resins with hydroxyalkylamides compare favorably with those obtained using MF resins as cross-linkers with the same resins. An advantage relative to MF cross-linkers is the absence of formaldehyde, which is emitted in low concentrations when MF based coatings are baked. A disadvantage is that high baking temperatures are required; the lowest reported satisfactory bake is 150°C for 30 minutes.

Hydroxyalkylamides are soluble in both water and common coating solvents and hence are useful as cross-linkers in either waterborne or solventborne coatings. Tetra-*N*,*N*,*N*′,*N*′-(2-hydroxyethyl)adipamide is a solid well suited for use in powder coatings [16] (Section 28.1.3). However, some discoloration can occur on baking [17], presumably due to formation of some free amine groups by thermal rearrangement of the hydroxylalkylamides.

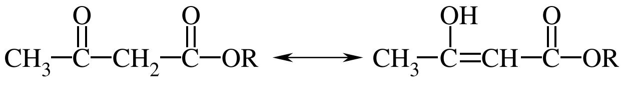
The cross-linking reaction exhibits unique features, compared to general esterification reactions. It is not catalyzed by acid; also, 2-hydroxyalkylamides with secondary hydroxyls esterify more rapidly than a corresponding primary alcohol derivative. Aromatic carboxylic acids esterify faster than aliphatic carboxylic acids, the reverse of other alcohols. In addition to the faster reaction of 2-hydroxyalkylamides with aromatic acids, the saponification resistance of the products is greater than of the corresponding esters from aliphatic acids. Mechanistic studies of the hydroxyalkylamide/carboxylic acid esterification reaction, as well as related reactions, have been reported. An explanation of the results, involving participation of the amide group and intermediate formation of oxazolinium groups, has been advanced that is consistent with the experimental observations [18]. Direct evidence for formation of oxazolinium intermediates has been obtained [17].

It has also been shown that 2-hydroxyalkylamides react with epoxies. At elevated temperatures, the amide rearranges to the aminoester, and the resulting amine group then reacts with the epoxy [19].



17.6. ACETOACETATE CROSS-LINKING SYSTEMS

The chemistry of β-keto esters such as acetoacetic esters has been widely studied. Acetoacetic esters are weak acids and exist to a significant degree in the tautomeric enol form.

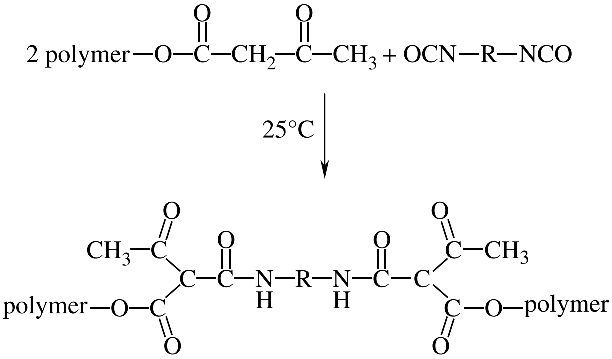


$$\mathrm{CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OR} \longleftrightarrow \mathrm{CH_3-\overset{OH}{\overset{|}{C}}=CH-\overset{O}{\overset{\|}{C}}-OR}$$

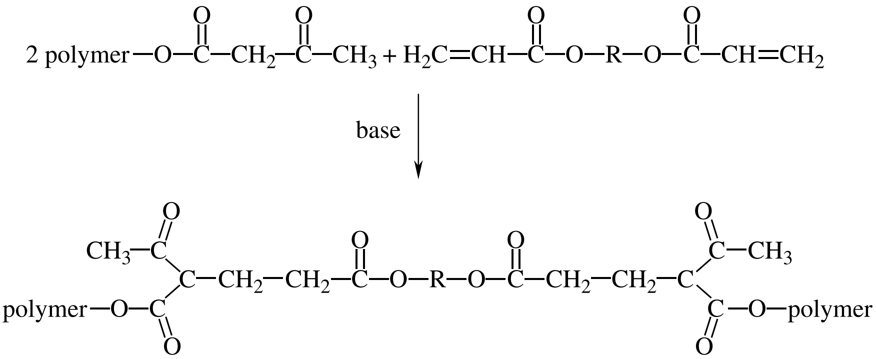
They undergo a wide range of reactions, some of which can be adapted for coatings purposes. Several methods are available to prepare resins bearing acetoacetate groups. Acetoacetoxy-functional acrylic solution resins can be made by copolymerizing acetoacetoxyethyl methacrylate (AAEM) with other acrylate monomers [20,21]. One can also use AAEM to make acrylic latexes [22]. However, the long-term stability of acetoacetic ester polymers in aqueous media has been questioned. Hydroxy-functional resins can be reacted with diketene or transesterified with methyl acetoacetate to form acetoacetylated resins. Replacement of the hydroxyl group with the less polar acetoacetate group leads to a reduction in viscosity, permitting higher solids at the same application viscosity.

A variety of coreactants with acetoacetylated resins have been investigated. Melamine–formaldehyde resins react with acetoacetate groups in the presence of an acid catalyst, although somewhat less rapidly than with hydroxyl groups [20]. Film properties of the resulting coatings using acetoacetylated resins are reported to be comparable with those made from hydroxy-functional resins. There are indications of improved wet adhesion, perhaps resulting from chelating interactions with metal surfaces.

Isocyanates also react with acetoacetate groups; the cure rate is slower than with hydroxyl groups, but the pot life is longer. Film properties are reported to be similar to those of conventional polyurethanes [20]. In other examples of 2K coatings, based on MDI, the solids at equal viscosity were about 10% higher with the acetoacetylated resin than with the original hydroxy resin, while retaining excellent film properties [23].

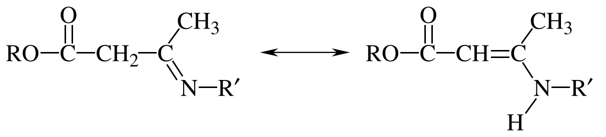


Polyacrylates (e.g., trimethylolpropane triacrylate) undergo Michael reactions with acetoacetate groups at ambient temperatures in the presence of strongly basic catalysts such as tetramethylguanidine (TMG) [22]. Formic acid has been reported to be an effective volatile blocking agent to extend pot life when 1,8-diazabicyclo[5.4.0]undec-7-ene is used as a catalyst [21].



Amines react rapidly with acetoacetic esters; hence, polyamines can be used as cross-linkers for acetoacetate-functional latexes [22]. Amines have also been reported to be excellent cross-linkers for acetoacetate-functional water-reducible acrylic resins. Reactions are too rapid under many conditions to have sufficient pot life even as 2K coatings. However, it has been found that if the resin is neutralized with ammonium hydroxide and the solids of the vehicle are restricted to 15 to 20%, stability is improved. For example, a copolymer of AAEM, MAA, BA, and MMA, neutralized with an equal equivalent of NH_4OH at 18% solids, blended with 1,6-hexamethylenediamine, is storage stable for a year. It was proposed that part of the acetoacetoxy groups react with the NH_4OH to form the amino-enamine, thus minimizing cross-linking by the hexamethylenediamine. After application, the ammonia evaporates and the resin is cross-linked by the hexamethylenediamine [24].

In solution coatings, the reaction is so fast at ambient temperatures that pot life is limited. This problem can be minimized by blocking the amine groups with ketones. The resulting ketimine hydrolyzes in the presence of water, permitting the cross-linking reaction to proceed [25]. The cross-links are tautomeric ketimine–eneamine groups that are thought to interact strongly with metal surfaces [26]. A ketimine–acetoacetate cross-linking primer is reported to give excellent adhesion and corrosion resistance when applied to an aircraft grade aluminum alloy with a chromate-free pretreatment.



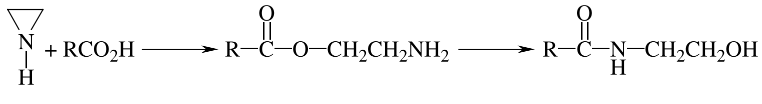
Ketimine Enamine

Ketimine/eneamine tautomers can also serve as Michael reactant cross-linkers with polyacrylates [27]. Acetoacetate pendant resins also can be cross-linked by reaction with aldimines at room temperature [28].

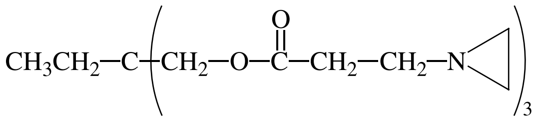
17.7. POLYAZIRIDINE CROSS-LINKERS

Aziridine, the nitrogen three-membered ring counterpart of oxirane, and its derivatives have been studied for many years; in some cases polyaziridines have been used as cross-linkers. The common name of aziridine is ethyleneimine. Ethyleneimine is highly toxic and may be carcinogenic. Propyleneimine is somewhat less toxic. Polyaziridines are skin irritants, and some individuals may become sensitized. The mutagenicity of polyaziridines is controversial; however, dilution by coating vehicles reduces possible toxic effects [29]. Ethyleneimine is even more reactive with acids than is ethylene oxide. In the presence of relatively strong acids it polymerizes very rapidly to yield poly(ethyleneimine), $\left(CH_2CH_2NH \right)_n$.

Among the many reactions of aziridines, the one of greatest interest in coatings applications is the reaction of a polyaziridine with a polyfunctional carboxylic acid to form 2-aminoester cross-links. Some 2-aminoesters can spontaneously rearrange to the corresponding 2-hydroxyamides, but this reaction does not break the cross-link.



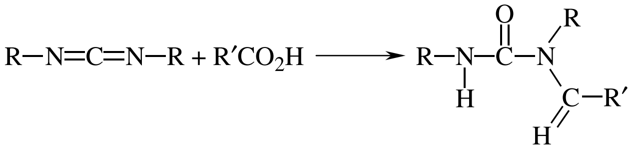
A variety of polyfunctional aziridines have been investigated. An example is the trifunctional Michael addition product of 3 mol of aziridine to 1 mol of trimethylolpropane triacrylate. A review paper covers tris-3-(1-aziridino)propionates and their uses. Trimethylolpropane tris[3-(2-methylaziridino)propionate], trimethylolpropane tris(3-aziridinopropionate), and pentaerythritol tris(3-aziridinopropionate) are evaluated [30].



Carboxy groups, amines, alcohols, and mercaptans react by opening the ring, giving a secondary amine as a cross-link. The reactions are acid catalyzed. The main use of such polyaziridines is to cross-link with carboxylic acid groups on latexes and waterborne polyurethanes. They are particularly useful for cross-linking COOH-functional latexes in coatings for factory-coated wood cabinetry and flooring, where a modest degree of cross-linking improves film properties over those attainable with un-cross-linked latexes. Reaction with the carboxylic acid is much faster than the reaction of water with aziridine groups, but the reaction rate with water is such that the pot lives are 48 to 72 hours [29]. With water the aziridine hydrolyzes to an amino alcohol, but it is said that there is no indication that the hydrolyzed aziridine affects film properties adversely. Additional cross-linker can be added to restore reactivity. Solvent swelling tests on cured films show that cross-linking is more complete with the aziridine than comparison tests with carbodiimide or MF resin cross-linked PUD. (See Section 12.7.1 for further discussion.) In view of the potential toxic hazards, manufacturers' recommendations for safe handling should be followed carefully.

17.8. POLYCARBODIIMIDE CROSS-LINKERS

Carbodiimides react with carboxylic acids and react slowly enough with water so they can be used in waterborne coatings, including latexes. The product of the reaction with a carboxylic acid is an *N*-acylurea:



Multifunctional carbodiimides are available to cross-link carboxylic acid–functional resins, including latexes, polyurethane dispersions, and blends of the two [31]. Cross-linking occurs within several days at ambient temperature and much faster with heat [32]. In one study, with latexes, curing conditions ranged from 60 to 127°C for 5 to 30 minutes, and the higher temperatures gave better films [31]. Apparently, film properties depend on physical film formation as well as on the extent of chemical cross-linking.

A water-emulsifiable polycarbodiimide that is terminated with a mixture of the methyl ether of diethylene glycol and a methyl ether of a polyethylene glycol is used as a cross-linker for COOH-functional latexes. The design of the latex markedly affected properties. The best properties were obtained with a BA/MMA/MAA latex that was prepared with the core containing 2% MAA and the shell 1% MAA [33].

17.9. POLYCARBONATES

Polytrimethylene carbonate polyols have been recommended as reactive diluents for acrylic polyols in coatings cross-linked with HDI isocyanurate. Best results were obtained with relatively low MW triols made by reacting trimethylene carbonate with TMP. VOC was reduced while increasing film flexibility and maintaining hardness, weather resistance, and mechanical properties [34].

Semi-crystalline polycarbonate resins are prepared by cationic ring-opening polymerization of dimethyl dimethylene carbonate with polyols using fumaric acid as a catalyst. Various polyols can be used. There was particular interest in low MW resins prepared using neopentyl glycol. As discussed in Section 28.1.6, methacrylate esters are of interest in UV cure powder coatings [35].

The possibility of using polycyclic carbonates as resins that can be cross-linked by polyamines to polyhydroxyurethanes is being explored. A paper reviewing the preparation and reactions of polycarbonate resins has been published [36]. The cyclic carbonate polymers can be synthesized by transesterification of glycerol carbonate with MMA, copolymerizing the resulting carbonate methacrylate, and reaction of glycidyl methacrylate with CO_2, and copolymerizing. The polyfunctional carbonates can then be cross-linked with polyamines.

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18

Solvents

Most coatings contain volatile material that evaporates during application and film formation. The volatile components reduce viscosity for application and control viscosity changes during application and film formation. In some cases, the volatile material must be a solvent for the resins in a formulation; in other cases, nonsolvent volatile components are desired. Usually, any volatile organic material is called a solvent whether or not it dissolves the resin. Too often, formulators do not consider the effects that solvent choice can have on coating performance. Selection of volatile components affects popping, sagging, and leveling and can affect adhesion, corrosion protection, and exterior durability.

As discussed in Sections 18.7, 18.8, and 18.9 almost all solvents are classified by the U.S. Environmental Protection Agency (EPA) as photochemically reactive *volatile organic compounds* (VOCs), and their use has been regulated to reduce air pollution since the 1970s. In 1990, the U.S. Congress listed certain common solvents as *hazardous air pollutants* (HAPs), further limiting their use.

18.1. SOLVENT COMPOSITION

Various organic compounds and mixtures are used as solvents. They can be classified in three broad categories: weak hydrogen-bonding, hydrogen-bond acceptor, and hydrogen-bond donor–acceptor solvents.

Weak hydrogen-bonding solvents are aliphatic and aromatic hydrocarbons. Commercial aliphatic solvents are mixtures of straight chain, branched chain, and alicyclic hydrocarbons. They vary in volatility and solvency. Varnish makers and painters (VM&P) naphthas are aliphatic solvents with high volatility. Mineral spirits are slower-evaporating aliphatic hydrocarbons; special grades with low aromatic content, and hence less odor,

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Organic Coatings: Science and Technology, Third Edition, by Zeno W. Wicks, Jr., Frank N. Jones,
S. Peter Pappas, and Douglas A. Wicks

are available. An advantage of aliphatics is low cost, especially on a volume basis since their densities as well as their price per unit weight are low. Aromatic hydrocarbon solvents are more expensive than aliphatic ones but dissolve a broader range of resins. Toluene, xylene, and high flash aromatic naphthas have been in widely use. Commercial xylene is a mixture of isomeric xylenes and ethyl benzene. Higher-boiling mixtures of aromatic hydrocarbons (high flash aromatic naphthas) are predominantly mixed alkyl and dialkyl benzenes with three to five carbons in the substituent groups. Use of benzene is prohibited because of toxicity. Toluene and xylene have been used on a large scale; however, they are listed as HAPs (Section 18.8).

Chlorinated solvents, in general, are no longer used in coatings, primarily because most of them lead to ozone depletion in the stratosphere. However, *p*-chlorobenzotrifluoride (PCBTF) is inert and is exempt as a VOC and HAP. The solvency is similar to that of xylene. Ostrowski discusses formulation with PCBTF [1].

Esters and ketones are *hydrogen-bond acceptor solvents*. Ketones are generally less expensive than esters with corresponding vapor pressures. The cost differential is particularly marked on a volume basis since ketones have lower densities. Use of methyl ethyl ketone (MEK) and methyl isobutyl ketone (MIBK) is being reduced because they are on the HAP list; use of acetone is increasing because it is exempt as either a VOC or a HAP. Use of esters is increasing. Slow evaporating esters such as 1-methoxy-2-propyl acetate and 2-butoxyethyl acetate are often preferred over slow evaporating ketones such as isophorone and methyl *n*-amyl ketone because of odor. Methyl acetate and *t*-butyl acetate are exempt as either VOC or HAP. Esters of 2-ethoxyethanol were widely used at one time but are on the HAP list, but no control is required if emissions are less than 10 tons per year. (See Section 18.8 for a list of HAPs.)

Esters should not be used as solvents for resins bearing primary or secondary amine groups because aminolysis converts esters to amides. An exception to this statement is *t*-butyl acetate. It has been shown that epoxy–amine coatings lose amine almost as slowly in *t*-butyl acetate as in xylene [2].

Nitroparaffins such as 2-nitropropane are highly polar hydrogen-bond accepting solvents. Their high polarity results in increased electrical conductivity, which is useful for adjusting solvent combinations in electrostatic spraying (Section 23.2.3).

Alcohols are strong *hydrogen-bond donor–acceptor solvents*. The most widely used volatile alcohols are methyl, ethyl, isopropyl, *n*-butyl, *sec*-butyl, and isobutyl alcohols. Most latex paints contain a slow evaporating water-soluble solvent such as propylene glycol that does not dissolve in the polymer particles; it serves as antifreeze (Section 32.1). In water-reducible acrylic and polyester resin coatings, low volatility ether alcohols such as 1-propoxypropan-2-ol and 2-butoxyethanol are used.

The value of solvents in the U.S. manufacture of paints and coatings in 1997 and 2002 are shown in Table 18.1. The comparisons may be affected to some extent by relative

TABLE 18.1. Value of Solvents Used in Paint and Coatings (Millions of Dollars)

Solvent Class	1997	2002
Hydrocarbons	223.5	206.4
Alcohols	77.7	62.5
Esters	103.4	136.0
Ketones	106.7	101.9
Glycol and derivatives	108.0	141.8

Source: Ref. [3].

differences in prices. Overall use has declined. The use of hydrocarbons and ketones was particularly affected by the HAP limitation. The increase in glycol derivatives results from their use in the growing field of waterborne coatings.

18.2. SOLUBILITY

In the early days of the paint industry, there was little problem selecting solvents—almost all resins dissolved in hydrocarbons. An exception was shellac, which dissolved in ethyl alcohol. Early in the twentieth century, nitrocellulose lacquers were introduced, and solvent selection became a greater challenge. RS nitrocellulose (Section 17.2.1) is soluble in esters and ketones but not in hydrocarbons or alcohols. However, RS nitrocellulose does dissolve in a mixture of ketones or esters and hydrocarbons, which reduces solvent cost. If ethyl alcohol is included in the solvent mixture, a higher ratio of hydrocarbons can be used, further reducing cost. In those days, esters and ketones were classified as *true solvents*, hydrocarbons as *diluents*, and alcohols as *latent solvents*.

To control the drying rate of nitrocellulose lacquers under various conditions, mixtures of solvents are required. At a minimum, the solvent blends contain two esters or ketones, two hydrocarbons, and an alcohol. Solvent mixtures must be selected to maintain solubility throughout solvent evaporation from films. If the slowest evaporating solvent were a hydrocarbon, nitrocellulose would precipitate before all the solvent was gone to give an uneven film with poor appearance and physical properties. As many as 10 solvents are blended to control drying and solubility through the drying cycle at the lowest volume cost.

18.2.1. Solubility Parameters

After 1930, more and more types of resins were adopted for coatings, and empirical selection of solvents and solvent mixtures became more difficult. The general rule of "like dissolves like" was broadened by the experience with nitrocellulose that mixtures of weak hydrogen-bonding hydrocarbons with strong hydrogen-bonding alcohols give solvency similar to medium hydrogen-bonding esters and ketones. In the 1950s, Burrell initiated studies to develop a more scientific basis for selecting solvents and formulating solvent mixtures [4]. He turned to the work of Hildebrand, who analyzed miscibility of small molecule organic compounds in terms of thermodynamics [5]. Hildebrand showed that the tendency of a pair of chemicals to mix spontaneously can be described in terms of Gibbs free energy equation:

$$\Delta G_{\mathrm{m}} = \Delta H_{\mathrm{m}} - T\,\Delta S_{\mathrm{m}}$$

Miscibility is thermodynamically favored when the change in free energy of mixing, ΔG_{m}, is negative. Hildebrand pointed out that the change in entropy ΔS_{m} is usually positive, since a solution is usually less ordered after mixing than before. (There are exceptions when strong interactions increase the entropic order of mixtures relative to the separate materials, resulting in a negative entropy change. But in most cases, ΔS_{m} is positive and the entropy change favors mixing.) Hildebrand focused on ΔH_{m}, the enthalpy of mixing, since it usually determines the sign of ΔG_{m}. Change in ΔH_{m} is in turn related to change in the energy of mixing ΔE_m; R is the gas constant and T is temperature (kelvin):

$$\Delta E_m = \Delta H_m - RT$$

Liquids have intermolecular attractive forces strong enough to hold the molecules together; otherwise, they would be gases. The forces can be measured by determining the energy needed to vaporize a liquid at that temperature. Results are expressed in terms of the molar energy of vaporization divided by the molar volume V. Hildebrand reasoned that the energy required to separate molecules during mixing is related to cohesive energy density $\Delta E_v/V$. He expressed the change in ΔE_m of ideal solvents by the following equation, where V_m is the average molar volume and ϕ_1 and ϕ_2 are the volume fractions of two components:

$$\Delta E_m = V_m \phi_1 \phi_2 \left[\left(\frac{\Delta E_v}{V} \right)_1^{-1/2} - \left(\frac{\Delta E_v}{V} \right)_2^{-1/2} \right]^2$$

The square root of cohesive energy density of a solvent was defined as the *solubility parameter* δ. A pair of solvents are miscible if the differences in solubility parameters approach zero. Then the ΔE_m of the pair approaches zero, the ΔH_m is small, and the free energy of mixing is controlled by ΔS_m. When ΔS_m is positive, the solvents are miscible. ΔE_v and V_m vary with temperature; therefore, δ varies with temperature. Most tables of solubility parameters give the values at 25°C, although commonly, no temperature is specified.

There is risk of confusion about units. The older units of solubility parameter were $(\text{cal cm}^{-3})^{1/2}$, sometimes designated as hildebrands. In the SI system, the proper units are $(\text{MPa})^{1/2}$; $1(\text{cal cm}^{-3})^{1/2} = 0.488(\text{MPa})^{1/2}$. The SI units have not been widely adopted and $(\text{cal cm}^{-3})^{1/2}$ units are still used, although frequently not stated.

When data are not available for energy of vaporization, solubility parameters can be estimated by using empirical equations relating boiling points, vapor pressure data, or surface tension data [6]. They can also be estimated by summation of Small's molar attraction constants, G, using the following equation, where ρ is density and M is molecular weight (MW):

$$\delta = \frac{\rho}{M} \sum G = \frac{1}{V} \sum G$$

Selected Small's constants are listed in SI units in Table 18.2. As with solubility parameters, the units for Small's constants are commonly not specified and are frequently the old units. Hoy [7] used Small's constants to calculate solubility parameters of 640 compounds.

Both Small's constants and solubility parameters of hydrogen-bond donor–acceptor molecules vary with the environment. The value for the alcohol hydroxyl group included in Table 18.2 depends on other groups in the solvent, with which the hydroxyl group might hydrogen bond, and on the polarity of other components in mixed solutions. Water is the most extreme case. Although specific values of a solubility parameter of water are

TABLE 18.2. Small's Molar Attraction Constants, $(MPa)^{1/2}$ $(cm^3\ mol^{-1})$ at 25°C

Hydrocarbon Group	*G*	Other Groups	*G*
$-CH_3$	284	O (ethers)	236
$-CH_2$	270	O (oxiranes)	361
$-CH-$	176	Cl	420
$=CH-$	249	CO (ketones)	539
$=CH_2$	259	COO (esters)	668
Phenyl	1400	OH	463
Phenylene	1370		

sometimes encountered, the values vary widely, since they are very dependent on the medium. Their usefulness is limited to comparing systems with similar compositions.

Burrell tried to apply solubility parameters to prediction of the solubility of resins [4]. The volatility of resins is so low that ΔE_v at 25°C cannot be directly measured. Burrell got around this by determining the solubility of a resin in a series of solvents with known solubility parameters. The solubility parameter range of a resin was taken as the range of solubility parameters of the solvents that would dissolve the resin. He found that in many cases, resins were not soluble in all the solvents with solubility parameters that fell within the solubility parameter range determined for the resin. Most of the cases, in which there were discrepancies, involved solvents and resins having markedly different potential for hydrogen-bonding. He divided solvents into poor, medium, and strong hydrogen-bonding, then determined the solubility of the resins in a series of each class of solvents. The resulting ranges of solubility parameters for a resin in the three groups of solvents permitted fairly good predictions of solubility. Burrell found that one can predict with some confidence whether a solvent mixture would dissolve a resin. One can calculate the weighted average solubility parameter of a mixture known to dissolve a resin using the following relationship, where the χ values are the mole fraction of solvents in the mixture:

$$\delta_{\text{mix}} = \frac{\chi_1 v_1 \delta_1 + \chi_2 v_2 \delta_2 + \chi_3 v_3 \delta_3 + \cdots}{\chi_1 v_1 + \chi_2 v_2 + \chi_3 v_3 + \cdots}$$

Since molar volumes for most solvents are fairly similar, a simplifying approximation is to use volume fractions to calculate the average solubility parameter:

$$\delta_{\text{mix}} = \phi_1 \delta_1 + \phi_2 \delta_2 + \phi_3 \delta_3 + \cdots$$

One does a similar calculation to determine the average degree of hydrogen bonding. Using this procedure, it was almost always possible to predict whether an alternative solvent mixture would also dissolve the resin. Next, Burrell applied the idea to prediction of solvents or solvent mixtures for new resins using Small's molar constants to estimate the solubility parameter of the new resin. Gram equivalent weight of the average repeating unit of the resin was used for the MW in Small's equation. Results were fair; in a majority, but not in all cases, the resins were soluble in solvents and solvent mixtures, with solubility parameters similar to those calculated for the resin, provided that the need for similar levels of hydrogen-bonding was taken into consideration.

A variety of refinements and extensions of Burrell's techniques have been proposed. Lieberman mapped solubility of polymers in a grid in which the axes are solubility parameter and hydrogen-bonding index [8]. The plot predicts that any solvent or solvent blend with solubility parameter and hydrogen-bonding index values that fall within the boundaries of the plot will dissolve the resin. Such plots can be useful, but their preparation requires substantial experimental effort [9].

18.2.2. Three-Dimensional Solubility Parameters

Other investigators considered this two-dimensional approach to be too simplistic and proposed three-dimensional systems. The system of Hansen [10] came to be most widely accepted. Hansen reasoned that since there are three types of interactive forces between molecules, there should be three types of solubility parameters: dispersion, δ_d; polar, δ_p; and hydrogen bond, δ_h. The total solubility parameter was arbitrarily set equal to the square root of the sum of the squares of the partial solubility parameters:

$$\delta = (\delta_d^2 + \delta_p^2 + \delta_h^2)^{1/2}$$

For mixed solvents, one can calculate a weighted average of the three partial solubility parameters:

$$\begin{aligned}\delta_{d(\text{blend})} &= (\varphi\delta_d)_1 + (\varphi\delta_d)_2 + \cdots + (\varphi\delta_d)_n \\ \delta_{p(\text{blend})} &= (\varphi\delta_p)_1 + (\varphi\delta_p)_2 + \cdots + (\varphi\delta_p)_n \\ \delta_{h(\text{blend})} &= (\varphi\delta_h)_1 + (\varphi\delta_h)_2 + \cdots + (\varphi\delta_h)_n\end{aligned}$$

Three-dimensional solubility parameters can be determined or calculated by a variety of methods. Although values are commonly given as three figures, it should not be inferred that the third figure is significant. Table 18.3 gives solubility parameters for some representative solvents selected from tables in Ref. [10] and the *Polymer Handbook* [11].

TABLE 18.3. Three-Dimensional Solubility Parameters, (MPa)$^{1/2}$

Solvent	Total	δ_d	δ_p	δ_h
n-Hexane	14.9	14.9	0	0
Toluene	18.2	18.0	1.4	2.0
o-Xylene	18.0	17.0	1.4	3.1
Acetone	19.9	15.5	10.4	7.0
Methyl ethyl ketone	19.0	16.0	9.0	5.1
Methyl isobutyl ketone	17.0	15.3	6.1	4.1
Isophorone	19.8	16.6	8.2	7.4
Ethyl acetate	18.2	15.8	5.3	7.2
Isobutyl acetate	16.8	15.1	3.7	6.3
n-Butyl acetate	17.4	15.8	3.7	6.3
Methyl alcohol	29.7	15.1	12.3	22.3
Ethyl alcohol	26.6	15.8	8.8	19.4
Isopropyl alcohol	23.5	16.4	6.1	16.4
n-Butyl alcohol	23.1	16.0	5.7	15.8
2-Butoxyethanol	20.9	16.0	5.1	12.3

Hansen determined three-dimensional solubility parameters for a group of resins by experimentally testing solubilities of 34 polymers in 90 solvents [10]. As an alternative to this laborious procedure, Hoy calculated three-dimensional solubility parameters of resins by a method analogous to use of Small's constants [12]. The values determined or calculated by various methods are frequently not the same; tables of (presumably) self-consistent values have been published and are available in computer databases. Three-dimensional solubility parameters are based on thermodynamic laws, but several assumptions and arbitrary choices are involved in their derivation and use. Assertions that they are "theoretically sound" can be misleading [6]. They are best regarded as an empirical method that has proven useful for finding alternative solvent mixtures with similar solvency characteristics.

Attempts have been made to apply solubility parameters to other problems, but the theoretical foundations are shaky and results have been erratic. For example, use of solubility parameters to predict solubility of one polymer in another (*compatibility*) frequently gives erroneous predictions. It has been increasingly recognized that three-dimensional solubility parameters are an oversimplification of the complex factors involved in solubility. The difficulties result from at least two interrelated factors. First, they neglect entropy changes, and second, the hydrogen-bond solubility parameter combines the effects of donors and acceptors. Entropy changes are particularly likely to be significant in hydrogen-bonding systems. Hansen has recognized the problem and in some cases suggests giving increased weight to the hydrogen-bond parameter [10].

The difficulties increase as polymer MW increases. As molecules get larger, interaction between solvent and polymer molecules must become greater to overcome intermolecular polymer–polymer interactions. Intramolecular interactions may also play a role. Estimates of solubility parameters of polymers by use of group attraction constants do not take MW into consideration.

People first working with polymers may be surprised by some of the solubility effects. They are accustomed to upper limits of solubility; for example, 36.1 g of NaCl dissolves in 100 g of water at 25°C. In general, there is no upper limit to the solubility of a polymer. If a small amount is entirely soluble, it is quite safe to conclude that any larger amount will be soluble in that solvent. However, it is common for there to be a lower limit of solubility. A high concentration of polymer may be soluble in some solvent(s), but on dilution, part of the polymer may precipitate. This phenomenon can be used to fractionate polymers by dilution. The fractions precipitating first are generally the highest-MW components. As dilution is continued further, progressively lower MW fractions are precipitated. In some cases, the fractionation is based on the polarity of parts of the resin. Many alkyds are soluble at high concentrations in aliphatic solvents, but precipitate partially on dilution. The first fractions precipitating are high molecular weight (MW) molecules with a larger than average number of hydroxyl and/or carboxylic acid groups. One can think of the situation in reverse: Some solvent is soluble in the polymer (resin), and all of the polymer is soluble in the combination of polymer and solvent. As more solvent is added, the solvency of the system changes, and parts of the polymer are not soluble in the more dilute polymer solution. The precipitate is highly swollen with solvent.

Hoy showed that glycol ethers can change apparent polarity to assume the polar nature of their surrounding environment [7]. In polar solvents, they behave as polar solutes. However, in nonpolar solvents, they undergo intramolecular bonding or intermolecular hydrogen bonding, to form dimers. In view of this consideration, it is not surprising that solubility predictions often fail, since the resins are often polydisperse, polyfunctional materials with multiple hydrogen-bond donor and acceptor sites.

18.2.3. Other Solubility Theories

Numerous refinements of solubility parameters have been proposed. Some have involved adding a fourth parameter, for example by dividing δ_h into hydrogen-bond donor and acceptor terms. Huyskens and Haulait-Pirson proposed equations that reflect changes in entropy and attempt to account for the differences resulting from both hydrogen-bond acceptor and donor groups [13]. They provide somewhat better predictions, but only the relatively simple cases of poly(vinyl acetate), poly(methyl methacrylate), and poly(ethyl methacrylate) were studied. They explain the shortcomings of the three-dimensional system but fall short of giving a broadly applicable alternative.

A major series of studies involving cooperative work in several laboratories led to the development of what a technical news story called a “universal solubility equation” [14]. The researchers themselves “believe this to be somewhat of an overstatement” [15]. The complexity of polymer solubility can be seen from the fact that this universal equation has 13 factors in a five-term equation and still does not take into consideration several important situations. Among the limitations critical to coatings is that thus far, the equation has been applied primarily to monofunctional solutes.

18.2.4. Practical Considerations

Meanwhile, what can formulators do? Solvent changes are frequent, motivated by new toxic hazard information, changes in relative cost, new regulations, temporary shortages, and so on. This is the type of problem for which solubility parameters are most useful, recognizing that the results may be imperfect. One can use solvent computer programs with data banks that include solubility parameters, evaporation rates, cost, density, and so on. This permits calculation of alternative solvent mixtures with solubility characteristics that do not change substantially during evaporation, while minimizing cost per unit volume. Solvent suppliers have developed sophisticated computer programs that can be used to calculate alternative solvent blends on a customer service basis. The result of such a calculation is given in Table 18.4, in which solubility parameter units are converted to $(\text{MPa})^{1/2}$ and rounded off [16]. Solvent blend 1 contained 2-ethoxyethyl acetate. which because of health concerns had to be removed from the formulation. Blends 2 and 3 were calculated to have close to equal average solubility parameters and evaporation rates. Blend 2 was unsatisfactory because the slowest evaporating solvent, xylene, was not a solvent for the resin. Blend 3 was a better starting point since the slowest evaporating solvent, 1-methoxy-2-propyl acetate, was a true solvent for the resin. Relative evaporation rates are also given in Table 18.4. Relative evaporation rates of mixed solvents must be viewed with caution (Section 18.3.3).

A second type of problem faced by formulators is to predict solvents and solvent combinations for a new resin. Solubility parameters may be useful, but in most cases, qualitative application of the idea that like dissolves like is just as effective for finding a starting point and takes less time. The problem of selecting solvents for new resins has become easier because, to increase solids, lower MW resins are being used. A wider range of solvents dissolves a resin as the resin’s MW gets lower.

TABLE 18.4. Solvent Blends, Weight Percents

Component	1	2	3
MEK	9.9	6.1	14.7
MIBK	29.7	32.8	19.7
Xylene	21.9	25.2	24.3
Toluene	20.1	18.4	18.2
n-Butyl alcohol	13.5	17.5	17.3
2-Ethoxyethyl acetate	4.9	—	—
1-Methoxy-2-propyl acetate	—	—	5.7
	Properties		
Solubility parameter, δ^a	19	19	19
δ_d	18	18	18
δ_p	5.7	5.7	5.3
δ_h	5.7	5.1	5.3
Relative evaporation rate	1.16	1.17	1.14
Cost^b	0.70	0.68	0.68

[a] $(\mathrm{MPa})^{1/2}$.

[b] At the time of study, in dollars per kilogram.

18.3. SOLVENT EVAPORATION RATES

During application and film formation, the volatile material evaporates out of the coating. The rate at which evaporation occurs affects not only the time required to convert a coating to a dry film, but also the appearance and physical properties of the final film. Like so many topics in the coatings field, evaporation rate appears simple but turns out to be complex.

18.3.1. Evaporation of Single Solvents

The rate of evaporation of a solvent is affected by four variables: temperature, vapor pressure, surface/volume ratio, and rate of air flow over the surface. The rate of evaporation of water is also affected by relative humidity.

The important temperature is the temperature at and near the surface. Although this temperature may initially be that of the surrounding air, it decreases as solvent evaporates. Whereas the surface is cooled by evaporation, it is warmed by thermal diffusion from within the sample and its surroundings. Depending on the circumstances, thermal diffusion may occur rapidly, so that surface temperature does not fall much during evaporation, or slowly, resulting in a sharp drop in surface temperature. The cooling effect is largest for those solvents and situations in which the solvent evaporates most rapidly. Also, the higher the heat of vaporization of the solvent, the greater the temperature drop if all other variables are equal.

Vapor pressure of the solvent at the temperature(s) at which evaporation occurs is the important vapor pressure. A common error is to assume that boiling points [the temperatures at which solvents have a vapor pressure of 101.3×10^2 kPa (1 mmHg = 0.1333 kPa; 1 atm = 101.3 kPa) are directly related to vapor pressures at other temperatures. However, boiling points are poor indicators. For example, benzene has a boiling point of 80°C and ethyl alcohol has a boiling point of 78°C, but at 25°C, their respective vapor pressures are 1.3 and 0.79 kPa. Consequently, benzene evaporates more rapidly than ethyl alcohol at

25°C under the same conditions. Similarly, at 25°C *n*-butyl acetate (bp 126°C) evaporates more rapidly than *n*-butyl alcohol (bp 118°C).

The ratio of surface area to volume is important because solvent evaporation occurs at the solvent–air interface. If 10 g of solvent is spread out over an area of 100 cm^2, it evaporates more rapidly than if the surface area is 1 cm^2. Accordingly, the concentration of the resin solution and the viscosity increase more slowly during solvent evaporation from thicker films having the same surface area. Solvent evaporates more slowly from a coating in an open can than after application as a film. When a coating is applied by a spray gun, it is atomized to small particles as it comes out of the orifice of the gun. The ratio of surface area to volume is very high, as is the rate of solvent loss. Thus, a major fraction of solvent evaporates after the spray droplets leave the orifice of the spray gun and before they arrive at the surface to which the coating is being applied.

The rate of air flow over the surface is important because the rate of evaporation depends on the partial pressure of the solvent vapor in the air at the air–solvent interface. If vaporized solvent molecules are not carried away from the surface quickly, the partial pressure of solvent builds up and evaporation is suppressed. Air flow rates vary substantially depending on the application method, and therefore the solvents used in a coating must be selected for the particular application conditions. For example, spraying a coating with an air spray gun results in significantly more loss of solvent than when the coating is sprayed from an airless gun because of the greater air flow over the surface of the droplets by the former method (Sections 23.2.1 and 23.2.2). The rate of solvent loss from a freshly coated surface depends on the rate of air flow through the spray booth. If the same coating is applied to the outside and the inside of a pipe, solvent evaporates more rapidly from the outside unless the inside is ventilated. Air flow effects cause nonuniform evaporation from coated objects; solvent evaporates more rapidly near the edges of a coated panel than from its center.

Relative humidity has little effect on the evaporation rates of most solvents; however, it has a major effect on the evaporation rate of water. The higher the relative humidity, the more slowly water evaporates when all other conditions are equal. As relative humidity approaches 100%, the rate of evaporation of pure water approaches zero. The evaporation rate of water from solutions can be negative at high humidity. Relative humidity decreases as air is warmed; sometimes it is feasible to compensate partially for the effects of humidity on drying by modestly increasing the air temperature, since warming the air both increases the vapor pressure of the water and decreases the relative humidity.

18.3.2. Relative Evaporation Rates

As mentioned in Section 18.2, the introduction of nitrocellulose lacquers led to the need to formulate complex solvent combinations. An important criterion involved in solvent selection is evaporation rate. From the standpoint of solvent selection, vapor pressure is an important variable that affects evaporation rate. However, it is difficult to look at vapor pressure data and judge how much more rapidly one solvent will evaporate than another. Procedures for measuring absolute evaporation rates were developed; and because of the difficulties of controlling air and heat flows in different types of measuring devices, *relative evaporation rates* were determined. Rates of solvent evaporation were related to the evaporation rate of *n*-butyl acetate, which at the time was a standard nitrocellulose solvent. Relative evaporation rate E is defined by Eq. 18.1, where t_{90} is the time for 90 wt% of a sample to evaporate in a given type of apparatus under controlled conditions:

$$E = \frac{t_{90}(n\text{-butyl acetate})}{t_{90}(\text{test sovlent})} \tag{18.1}$$

Using Eq. 18.1, the relative evaporation rate of *n*-butyl acetate is 1 by definition. Some authors express E as a percentage figure, corresponding to 100 for *n*-butyl acetate. In either case, the higher the E value, the faster the evaporation rate of the test solvent. One should be sure which reference point is being used; there is at least one paper in the literature in which an author used data from two different tables without realizing that he was mixing data that differed by a factor of 100; his conclusions were absurd.

Determination of relative evaporation rates requires measurement under carefully controlled standardized conditions. The Shell Thin Film Evaporometer is an example of an apparatus. A top loading balance is placed in an enclosure designed to minimize variation in air flow over the surface of the balance pan. A flow of 25°C air with a relative humidity of less than 5% at a rate of 21 L min^{-1} is maintained. A sample of 0.70 mL solvent is dispensed onto a piece of filter paper on the balance pan, and the time required to lose 90% of the sample weight is determined. Rates determined this way are volume-based relative evaporation rates. Although volume-based evaporation rates are the most common in the literature, some experimental procedures use a fixed weight rather than a fixed volume of solvent. Care must be taken not to mix data obtained by different methods. One should also avoid comparing relative evaporation rates determined using different instruments because different evaporation conditions can change not only the absolute evaporation rates, but also the relative evaporation rates.

A study by Rocklin illustrates the effects of changes in conditions on relative evaporation rates [17]. He compared the relative evaporation rates of 66 solvents measured by the standard procedure (evaporation from filter paper) with rates measured by evaporation directly from the flat aluminum pan of the balance. Table 18.5 gives his data for several solvents. Note that both sets of data are relative to *n*-butyl acetate. As can be seen by comparing the $E_{\text{paper}}/E_{\text{metal}}$ ratios, significant differences exist between relative evaporation rates when the solvents evaporate from filter paper and the corresponding relative rates when the same solvents evaporate from a smooth metal surface in the same instrument at the same settings.

The most notable differences between E_{paper} and E_{metal} occur with faster evaporating solvents and with water and alcohols. In the case of evaporation from filter paper, the ratio of surface area to volume is much higher than in the case of the evaporation from the metal. Therefore, at first solvents evaporate more rapidly from filter paper, resulting in a sharp drop in temperature, which leads to a decrease in vapor pressure that slows evaporation. In the case of evaporation from a metal surface, the surface area is much smaller and the thermal conductivity is much higher. Both factors minimize the temperature drop, leading to less decrease in vapor pressure and evaporation rate. The difference is greater with fast evaporating solvents such as *n*-pentane and acetone than with *n*-butyl acetate, which evaporates more slowly, resulting in their low ratios of E_{paper} to E_{metal}. The experimental temperature was 25°C, but that is the air temperature. What controls the rates of evaporation and hence the relative rates is the actual temperature(s) of the surfaces.

TABLE 18.5. Volume-Based Relative Evaporation Rates at 25°C

Solvent	E_{paper}	E_{metal}	Ratio
n-Pentane	12	38	0.32
Acetone	5.7	10	0.55
Ethyl acetate	4.0	6.0	0.67
Methyl ethyl ketone	3.9	5.3	0.74
n-Heptane	3.6	4.3	0.83
Toluene	2.0	2.1	0.92
Ethyl alcohol	1.7	2.6	0.65
Methyl isobutyl ketone	1.7	1.7	1.0
Isobutyl acetate	1.5	1.5	1.0
n-Butyl acetate	1	1	1
sec-Butyl alcohol	0.93	1.2	0.81
m-Xylene	0.71	0.71	1.0
n-Butyl alcohol	0.44	0.48	0.92
2-Ethoxyethanol	0.37	0.38	0.98
Water	0.31	0.56	0.56
Methyl *n*-amyl ketone	0.34	0.35	0.96
2-Ethoxyethyl acetate	0.20	0.19	1.1
n-Decane	0.18	0.16	1.1
2-Butoxyethanol	0.077	0.073	1.1
Isophorone	0.023	0.026	1.0
Diethylene glycol monoethyl ether	0.013	0.014	0.99

The $E_{\text{paper}}/E_{\text{metal}}$ ratios are also low for water and alcohols. This results from the greater extent of hydrogen-bond interaction of the hydroxyl groups with the very large surface area of cellulose of the paper compared with the smooth aluminum surface. This retards evaporation of water and alcohols relative to *n*-butyl acetate. Note that relative to *n*-butyl acetate, *sec*-butyl alcohol evaporates more rapidly from the smooth metal surface and more slowly from the filter paper.

When formulating baking coatings for spray application, it is common to use a mixture of fast and very slow evaporating solvents. A significant fraction of the fast evaporating solvent evaporates before the spray droplets reach the object being coated, raising viscosity and reducing the tendency of the coating to *sag*, while the slow evaporating solvent keeps the viscosity low enough to promote *leveling* and to minimize the probability of *popping* when the coated object is put into a baking oven. (See Chapter 23 for a further discussion of sagging, leveling, and popping.) In selecting slow evaporating solvents, formulators have generally used tables of relative evaporation rates at 25°C and boiling points, which are available for a large number of solvents. Evaporation rate data have been published for only a limited number of slow evaporating solvents over the range of 75 to 150°C [18]. The rates were determined using a thermogravimetric analyzer (TGA) isothermally at a series of furnace temperatures. The rate relationships can be quite different at different temperatures. For example, at 25°C, the evaporation rate for a commercial mixture of the dimethyl esters of succinic, glutaric, and adipic acids is about five times slower than for isophorone. However, at 150°C, their evaporation rates are approximately equal.

Which evaporation rate data are "correct"? All of them are; they depend on the particular circumstances under which they were determined. However, we do not apply coatings to filter paper (or to aluminum balance pans or to TGA pans), nor do we dry them in a Shell Evaporometer (or a TGA furnace). The rates at which solvents evaporate in actual use depend on the particular situation. Solvents evaporate more rapidly from coatings applied by a spray gun than from coatings applied by roller coating. The type of spray gun can make a substantial difference. Other significant variables include the rate of air flow through the spray booth, the shape and mass of the object coated, the film thickness applied, the flash-off time before entering an oven, and the way that heat is zoned in the oven.

18.3.3. Evaporation of Mixed Solvents

Evaporation of solvent blends rather than pure solvents adds further complications. In *ideal* homogeneous solutions, vapor pressure is governed by Raoult's law, which predicts that the vapor pressure P_{i} of the *i*th component of the solution is reduced from the vapor pressure of the pure liquid P_{i}^0 in proportion to its mole fraction x_{i}:

$$P_{\mathrm{i}} = x_{\mathrm{i}} P_{\mathrm{i}}^0$$

Since the vapor pressure of each solvent in the blend is different, the composition of the solvents that evaporate is different from that of the solvent blend. Therefore, the partial vapor pressures change continuously as solvent evaporates from a mixture. Raoult's law provides a good approximation for many combinations of solvents, especially when structures are similar and intermolecular interactions are minimal. However, other solvent mixtures are *nonideal* as a result of interaction effects. These effects change as ratios of solvents change. The vapor pressure P_{total} of any mixture of miscible solvents can be calculated by the following equation, where χ represents an empirical adjustment factor for the interaction effects, usually given the more dignified-sounding title of *activity coefficient*:

$$P_{\mathrm{total}} = P_1 + P_2 + \cdots + P_{\mathrm{i}} = \chi_1 P_1^0 x_1 + \chi_2 P_2^0 x_2 + \cdots + \chi_{\mathrm{i}} P_{\mathrm{i}}^0 x_{\mathrm{i}}$$

Activity coefficients for many solvents have been evaluated and incorporated into computer programs that can calculate partial vapor pressures of each solvent in a mixture throughout its evaporation. One such program is called UNIFAC [19]. Results of such calculations are often presented as the partial vapor pressures at each 10% interval through the evaporation. Several assumptions are involved in calculating vapor pressures, and in order to relate vapor pressure to evaporation rate, it is assumed that all other factors (temperature, surface/volume ratio, and air flow) affecting evaporation rate are fixed. Thus, the results of such calculations are only approximations. However, in view of the uncertainties of relative evaporation rates, a high level of accuracy is not needed. The evaporation of solvent blends is discussed in an extensive review paper [20].

Relative evaporation rates of mixed solvent compositions can be determined experimentally in an evaporometer. The relative evaporation rate of a mixed solvent E_{T} is calculated from volume fractions *c*, activity coefficients *a*, and relative evaporation rates *E* of the individual solvents [21]:

$$E_{\mathrm{T}} = (caE)_1 + (caE)_2 + \cdots + (caE)_{\mathrm{n}}$$

Such calculated E_{T} values are of dubious accuracy: The composition changes over time, so the value of E_{T} changes. The difference between experimental and calculated relative evaporation rates is especially large when comparing a solvent mixture with a narrow range of E values with another with a wide range of E values. For example, one could calculate E_T for a mixture of two solvents with high and low E values that would be equal to the E value of a single solvent with an intermediate E value. However, it is evident that the mixed solvent would actually have a smaller relative evaporation rate than the single solvent since after the fast evaporating solvent was gone, the slow evaporating solvent would evaporate more slowly than the single intermediate E value solvent.

This description makes it sound almost impossible to formulate a satisfactory solvent mixture for a coating. However, formulation does not start in a vacuum of knowledge. Experience with other formulations that proved useful under somewhat similar circumstances provides guidance. Using such formulations together with any reasonable table of relative evaporation rates, one can make a first attempt at a new formulation. The coating is then applied under the particular circumstances, and adjustments are made as needed. The final adjustment is almost always made by an experienced person in the user's factory with production spray guns and operating conditions. The use of relative evaporation rate tables assists development of a formulation that is in the ball park of what is needed; because final in-factory adjustments are needed anyway, it may not matter much which relative evaporation rate table was used.

Evaporation rates of water–organic solvent mixtures require special consideration for at least four reasons. First, strong interactions often cause deviations from Raoult's law. Second, relative humidity (RH) affects the evaporation rate of water but has little or no effect on the evaporation rates of organic solvents. Third, azeotropic effects may occur. Fourth, the heat capacity and heat of vaporization of water are unusually high.

The humidity effect is illustrated by the fact that the relative evaporation rate (E) of water at 0 to 5% RH and an air temperature of 25°C is 0.31; but at 100% RH, E is 0. If a solution of 2-butoxyethanol ($E = 0.077$) in water evaporates at low RH, water evaporates more rapidly, and the remaining solution becomes enriched in 2-butoxyethanol. At high RH, 2-butoxyethanol evaporates more rapidly and the remaining solution becomes enriched in water. At some intermediate RH, the relative evaporation rates of water and 2-butoxyethanol are equal. When an aqueous solution evaporates at this RH, the composition of the remaining solution is constant. This RH has been called the *critical relative humidity* (CRH) [22]. The CRH for 2-butoxyethanol solutions in water is estimated at about 80%. If the relative evaporation rate of the solvent were larger than that of water, even at 0 to 5% RH, there would be no CRH, since the solvent would evaporate more rapidly than water at any RH. At the other end of the scale, if the relative evaporation rate of the solvent were very low, the CRH would approach 100%.

Azeotropic behavior is likely to occur with water solutions. Rocklin has studied the role of azeotropy in speeding up water–solvent evaporation in humid air [23]. He reports development of a computer model, the AQUEVAP program, that permits calculation of the fastest evaporating water–solvent blends at various RH values. For example, at 40% RH, the time required for 90% evaporation of a 20 wt% solution of 2-butoxyethanol in water is 1820 seconds compared with 2290 for water alone. Thus, co-evaporation of water and 2-butoxyethanol accelerates evaporation.

The high heat capacity and heat of vaporization of water can also affect the evaporation rates of water and water–solvent blends in an oven. For example, the times for 99% weight loss of 2-butoxyethanol (bp 171°C), water, and a 26 : 74 blend of 2-butoxyethanol/water in a TGA when room temperature samples were put into the furnace at 150°C were 2, 2.6, and

2.5 minutes, respectively [24]. While the air temperature in the furnace was 150°C, the samples took some time to heat up. The higher heat of vaporization of water (2260 J g^{-1} at its boiling point) compared to 2-butoxyethanol (373 J g^{-1} at its boiling point) slowed the rate of heating of the water and water–solvent blend enough to more than offset the expected evaporation rates based on boiling points or E values.

18.3.4. Evaporation of Solvents from Coating Films

Except in high-solids coatings (Section 18.3.5), the resin or other coating components have little effect on the initial rate of solvent evaporation when coating films are applied. Initial rates of evaporation of solvent from resin solutions are, within experimental error, the same as or close to the rates of evaporation of the solvents alone under the same conditions. Such observations are not inconsistent with Raoult's law, which predicts that dissolved resins will have little effect on vapor pressure because of their high MWs. However, as solvent loss from a coating continues, a stage is reached at which the rate of evaporation slows sharply. As the viscosity of the remaining coating increases, availability of free volume decreases and the rate of solvent loss becomes dependent on the rate of diffusion of solvent through the film to the surface rather than on the rate of evaporation from the surface. The solids level at which the transition from evaporation rate control to diffusion rate control occurs varies widely but is often in the range 40 to 60 NVV.

Hansen described the situation as first stage and second stage losses of solvent [25]. In the first stage, the rate is governed by the factors that govern evaporation of solvent mixtures: vapor pressure, surface temperature, air flow over the surface, and surface/volume ratio; at this stage, there is a first-power dependence on wet film thickness. After a transitional stage, evaporation slows and the rate of solvent loss becomes dependent on the rate of diffusion of the solvent molecules through the film. During this stage, the evaporation rate depends on the square of film thickness. In line with the changes in viscosity, the first stage is sometimes called the *wet stage* and the second stage, the *dry stage*. An example of a plot of weight of solution remaining as a function of time for evaporation of MIBK from a soluble vinyl chloride copolymer resin solution is shown in Figure 18.1.

During the second stage, the diffusion rate is controlled primarily by free volume availability. That is, the solvent molecules move through the film by jumping from free volume hole to free volume hole. The most important factor controlling free volume availability is $T - T_g$. If solvent evaporation is occurring at a temperature well above the T_g of the solvent-free resin, diffusion rate will not restrict the rate of solvent evaporation at any stage in drying. If the T_g of the resin is above the temperature at which drying is occurring, solvent evaporation will become diffusion rate controlled as $T - T_g$ becomes small. No experimental data are available as to the values of $T - T_g$ when diffusion rate control becomes important; such values are probably system dependent.

When the second stage is reached, the rate of evaporation becomes dependent on how fast the solvent molecules get to the surface, not on their vapor pressure. As solvent loss continues, concentration of the remaining resin solution increases, and therefore T_g increases and the rate of diffusion slows further. If the T_g of the resin is sufficiently higher than the temperature of the film, the rate of solvent loss will, in time, approach zero. Years after films have been formed, there will still be residual solvent left in the film. If solvent must be essentially completely removed in a reasonable time, the film

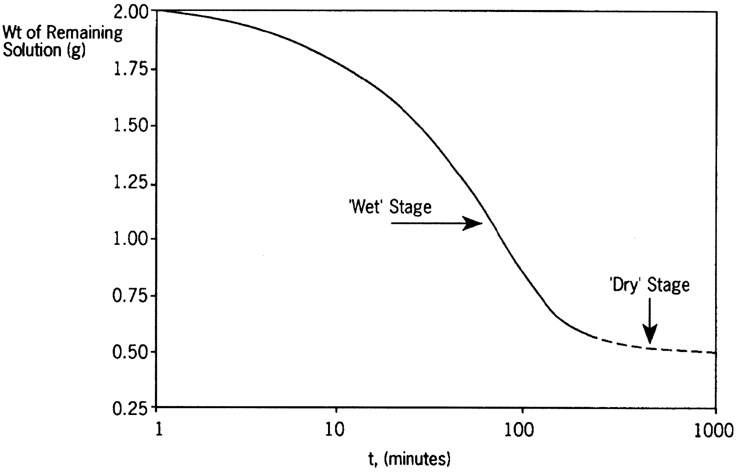

Figure 18.1. *Two-stage release of solvents MIBK in Vinylite VYHH at 23°C, initially at 20 wt% polymer. (From Ref. [26], with permission.)*

must be baked at a temperature above the T_g of the solvent-free resin. It is a common mistake for novice polymer chemists to think that the rate of solvent loss from polymer samples can be increased by drying under a vacuum at temperatures below T_g. Since the rate of solvent loss has reached a stage at which it is independent of the vapor pressure of the solvent, it is also independent of atmospheric pressure above the sample.

Solvent evaporation is affected by the addition of a plasticizer. The concentration of solvent at which solvent loss becomes diffusion controlled decreases as plasticizer concentration increases. The amount of solvent retained after some time interval decreases as plasticizer concentration increases. Perhaps, less obviously, in the case of mixed-solvent systems, the ratio of slow to fast evaporating solvent retained in the film increases as plasticizer concentration increases.

There have been many attempts to quantify the diffusion of solvents from coating films during solvent evaporation, but success has been limited [27,28]. Some of the problems are discussed in Ref. [29], and possible approaches to modeling the diffusion through scaling analysis are suggested. As a broad generalization, small molecules tend to evaporate faster than large molecules in both the first and second stages because small molecules tend to be more volatile in the first stage and to diffuse faster in the second stage. However, other factors are involved. One is molecular configuration. Since the molecules must jump from hole to hole, the smaller the size of the solvent molecule, the greater its chance of finding sufficiently large holes. Even though its relative evaporation rate is higher, cyclohexane is retained in films to a greater degree than toluene because cyclohexane has a higher molar volume.

Figure 18.2 shows the results of an experiment illustrating the effect of cross-sectional size. Nitrocellulose and acrylic lacquers were made at 20 wt% solids in 60 : 40 isobutyl acetate (IBAc) and *n*-butyl acetate (BAc), and the ratios of the two solvents remaining in the films were monitored. Like other branched-linear isomeric pairs, the relative evaporation rate of branched IBAC is higher than that of linear BAC. Thus, the ratio of IBAc to BAc remaining in the film decreased during the first, wet stage of solvent loss, reaching a minimum of about 35 : 65. During the second, dry stage, the linear compound

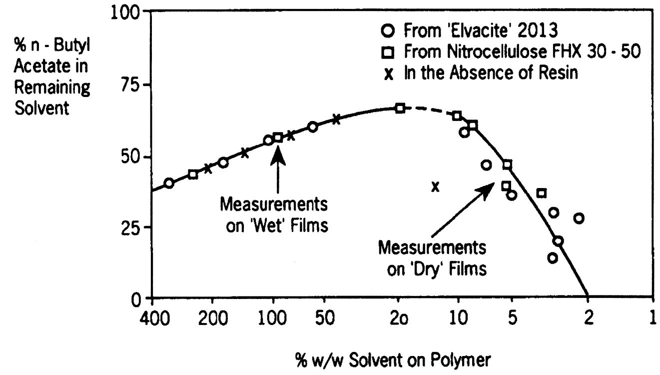

Figure 18.2. *Changes in remaining solvent concentration during wet and dry stages of solvent evaporation at 23°C from films of an acrylic resin (Elvacite 2013) and nitrocellulose, each initially in 60 : 40 IBAc to Bac. (From Ref. [26], with permission.)*

diffused more rapidly, so the ratio of IBAc to BAc remaining in the film increased and approached 90 : 10 [26]. Equations have been developed that model the effect of solvent size on diffusion based on the free volume of polymers [30].

In air dry coatings, T_g often increases to a level above ambient temperature, while significant amounts of solvent remain in the film. When this happens, solvent evaporation becomes extremely slow, and detectable amounts of volatile solvents may remain in the film for years. Residual solvent has been shown to affect adversely film properties such as corrosion and moisture resistance (Section 7.3.1.1). Thus, selection of solvents that have minimal detrimental effects may be a factor in optimizing long-term film performance.

18.3.5. Evaporation of Solvents from High-Solids Coatings

Generally, it is more difficult to control sagging of spray applied high-solids coatings than of their lower solids counterparts (Section 24.3). Although other factors may be involved, there is considerable evidence that high-solids formulations lose much less solvent than are lost by conventional coatings while atomized droplets are traveling between a spray gun and the object being coated [31,32]. As a result, there is less increase in viscosity and therefore a greater tendency to sag. Explanations for this decreased solvent loss do not appear to be adequate. One factor is the colligative effect of the lower mole fractions of solvent(s) in high-solids coating. A sample calculation illustrates this difference. If the vehicle of a conventional coating consists of a 30 wt% solids solution of a resin with an $\bar{M}_n$ of 15,000 in 70% of a solvent mixture with an $\bar{M}_n$ of 100, the mole fraction of solvent is 0.997. However, if a high-solids coating has 70% solids of a resin with an $\bar{M}_n$ of 1000 and 30% of a solvent mixture with an $\bar{M}_n$ of 100, the mole fraction of solvent is 0.811. Although this difference is in the direction of slowing solvent evaporation from the high-solids coating, it does not seem large enough to account for the large differences in solvent loss that have been reported.

It was suggested without experimental evidence that high-solids coatings may undergo transition from first-stage to second-stage solvent loss with relatively little solvent loss compared to that for conventional coatings [33]. The reasoning was that the T_g of the solution in a high-solids coatings could change more rapidly with concentration, hence reach a stage of free volume limitation of solvent loss after only a little loss of solvent. Consistent with this hypothesis, Ellis found that high-solids polyester coatings were formulated at concentrations that were already above the transition concentration where the solvent loss rate becomes diffusion controlled [34]. He also found that the transition points occur at higher solids with linear molecules, such as *n*-octane versus isooctane, and *n*-butyl acetate compared to isobutyl acetate. Further research is needed to fully understand the reasons for slower loss of solvents from high-solids coatings; meanwhile, slower solvent loss can be a serious problem for the application of high-solids coatings. More detailed discussion of sagging and sag control in high-solids coatings appears in Sections 24.3 and 25.2.2.

18.3.6. Volatile Loss from Waterborne Coatings

For solventborne coatings, the formulator has available a variety of solvents having a wide range of properties and volatility. But for waterborne coatings, the major volatile component is water, which comes with only one vapor pressure–temperature curve, one heat of vaporization, and so on. Furthermore, the relative humidity at the time of application and drying of the coatings can have a major effect on rates of volatile losses from waterborne coatings. Formulators use limited levels of organic solvents to modify evaporation rates; however, future regulations can be expected to reduce the levels permitted.

A major class of waterborne coatings is based on water-reducible resins, which are not soluble in water (Section 8.3). A salt of the resin, dissolved in an alcohol or an ether alcohol, is diluted with water. During dilution, the resin forms aggregates that are swollen with solvent and water, dispersed in a continuous aqueous phase that also contains some solvent. The relative evaporation rate of water is affected by the relative humidity; so with solvents such as 2-butoxyethanol, there is a critical relative humidity (CRH) (Section 18.3.3). It has been found that the CRH is different for coatings than for water–solvent blends without resin. For example, CRH is 65% for 10.6 wt% (based on volatile components) 2-butoxyethanol in a coating, in contrast to 80% calculated for the same concentration of a 2-butoxyethanol–water blend without resin [35]. A possible explanation of the difference in CRH is that the concentration of 2-butoxyethanol in the continuous water phase is below the average and the solvent–water ratio inside the aggregates is above the average. This type of distribution and its effect on the composition of vapor above a model aggregate system using a more volatile solvent, *t*-butyl alcohol, has been demonstrated [36]. Such effects can be critical in controlling sagging and, particularly, popping of such waterborne coatings (Sections 23.3, 23.7, and 26.1).

The other major class of waterborne coatings uses latexes as the principal binder. Evaporation of water from a drying latex paint film resembles first-stage drying throughout most of the process; it is controlled by temperature, humidity, evaporative cooling, and rate of air flow over the surface [37]. After most of the water has left, evaporation slows as a result of coalescence of a surface layer through which water must diffuse. In latex paints to be applied by brush or roller, it is desirable to retard the development of a partially coalesced surface layer to permit lapping of wet paint on wet paint. This generally requires the presence of a slow evaporating solvent such as propylene glycol. The presence of these solvents does not affect the initial rate of water loss, but does slow the development of a surface skin [38]. The presence of such a water-soluble solvent also facilitates the loss of coalescing solvent. Use of both types of solvents is discussed further in Chapter 31.

18.4. VISCOSITY EFFECTS

Solvent selection can have a major effect on the viscosity of resin solutions. This results from two factors: the viscosity of the solvent itself and the effect of solvent–resin interactions. The direct effect of solvent viscosity on solution viscosity can be seen in equations that relate viscosity and resin concentration. Even the simplest relationship, which is valid over only a narrow range of concentration of solutions with viscosities in the approximate range 0.1 to 10 Pa•s, shows this dependence on solvent viscosity:

$$\ln \eta_{\text{solution}} = \ln \eta_{\text{solvent}} + K(\text{conc})$$

For example, a difference of viscosity of 0.2 m Pa•s between the viscosities of two solvents (1.0 and 1.2 m Pa•s) may appear trivial but can cause a difference of 2000 m Pa•s in the viscosity of a 50 wt% solution of a resin (10 Pa•s versus 12 Pa•s) [39]. The relationship between concentration and viscosity of resin solutions is discussed in more detail in Section 3.4.3.

One must be careful when comparing viscosities of solutions. There are data in the literature that make comparisons based on weight relationships, volume relationships, weight of solvent per volume of coating, and weight of resin per volume of solution. One must decide what type of comparison is appropriate for a particular purpose. Most commonly, weight ratios are used when considering the viscosity of resin solutions, but they can be misleading because air pollution regulations are based on weight of solvent per volume of coating. If one compares the viscosity of resin solutions with different solvents on a weight basis, one might make the wrong choice in trying to minimize the weight of solvent per volume of coating. Since flow is generally related to volume considerations, use of volume fraction comparisons might seem desirable, but polymer solutions are seldom ideal, creating uncertainty about the significance of volume fraction numbers.

An example of the effect of solvent choice on viscosity of an acrylic solution containing 400 g L^{-1} of solution of the various solvents is given in Table 18.6. For comparison purposes, the densities and viscosities of the solvents alone are also given. The data in Table 18.6 illustrate the substantial effect that solvent selection can have on the solution viscosity of a given polymer. The weight concentrations of these solutions are not constant; it would have been interesting to compare also the viscosities of equal-weight-ratio solutions. The data suggest that solvents with low density and low viscosity tend to give low solution viscosity, as predicted by theory. However, other factors are involved.

Another factor that is sometimes important is the effect of solvent–solvent interactions on the viscosity of solvent mixtures. In general, these effects are small except for mixtures that include alcohols or water. When relatively small (generally, $<40\%$) amounts of alcohols are mixed with other solvents, they do not increase the viscosity of the solution proportionally to their relatively high neat viscosities [41]. This results from reduced multiple hydrogen-bond interactions between the alcohol molecules in the presence of other solvents. The effects are larger and less obviously predictable in the case of solutions of solvents in water.

TABLE 18.6. Viscosities at 25°C of Solutions of a High-Solids Acrylic; Solvent Concentration 400 g L^{-1} Solution

Solvent	Solvent Viscosity (m Pa·s)	Solvent Density (g ML^{-1})	Solution Viscosity (m Pa·s)
Methyl propyl ketone	0.68	0.805	80
Methyl isobutyl ketone	0.55	0.802	110
Ethyl acetate	0.46	0.894	121
Methyl amyl ketone	0.77	0.814	147
n-Butyl acetate	0.71	0.883	202
Toluene	0.55	0.877	290
Isobutyl isobutyrate	0.83	0.851	367
Xylene	0.66	0.877	367

Source: Ref. [40].

Large viscosity effects can result from solvent–resin interactions. To distinguish these effects from the effects of solvent viscosity discussed previously, it is common to compare relative viscosities (η/η_s) of solutions. The effects of interactions are complex and not fully understood in even relatively simple systems. At least two factors play a role. First, most resins used in coatings have polar and hydrogen-bonding substituents, such as hydroxyl groups or carboxylic acid groups, that tend to associate with polar groups on other molecules, often substantially increasing viscosity. Solvents that can prevent or minimize such interactions by interacting with the polar groups tend to reduce viscosity. Polar solvents with single hydrogen-bond acceptor sites are effective in minimizing relative viscosity; examples are ketones, ethers, and esters. Water can also serve to reduce the viscosity of oligomers with hydrogen-bond interactions. It has been shown that up to 20% (depending on the formulation) of water can dissolve in solvent-free coatings and that adding water, usually 5 to 15%, reduces viscosity by 40 to 60% [42].

A second factor is the effect of a given solvent on the hydrodynamic volume of the individual resin molecules with their closely associated solvent molecules. If the interaction between resin and solvent molecules is strong, the chains of the resin molecules become extended and their hydrodynamic volume increases. If the interaction is not so strong, the molecules contract and the hydrodynamic volume becomes smaller. Relative viscosity tends to be directly related to hydrodynamic volume. However, if solvent–resin interaction is so weak that there can be resin–resin interaction rather than only resin–solvent interaction, clusters of resin molecules form and relative viscosity and viscosity increase. In the majority of coating applications, especially high-solids coatings, which use low-MW resins, resin–resin interactions are the stronger of the two effects, although hydrodynamic volume effects can be significant. Thus, most high-solids formulations include hydrogen-bond acceptor solvents. The situation with mixed solvents is more complex. We are aware of only one publication on viscosity effects with solvent mixtures. In a study involving a limited number of systems, Erickson and Garner [43] found that relative viscosity was dominated by the effect of the solvent that interacted most strongly with the resin.

A word of caution: Relative viscosities can be useful for understanding the factors affecting viscosity, but the viscosities important in applying coatings are not relative viscosities. A solvent giving a comparatively high viscosity solution could give a relatively low relative viscosity solution. The viscosity of resin solutions is discussed further in Section 3.4.

Solvent selection can also affect storage stability. Inclusion of alcohols in formulations containing melamine–formaldehyde resins can increase storage life by minimizing cross-linking during storage (Section 11.3.3). Polyesters can transesterify with primary alcohols during storage; this can be a problem especially with water-reducible polyesters (Section 10.5). Alcohols can react slowly with epoxy resins during storage. Hydrogen-bond acceptor solvents can extend the pot life of epoxy–amine coatings (Section 13.2.5). Reaction rates of isocyanates with hydroxyl groups are reduced in H-bond acceptor solvents, extending pot life (Section 12.4 and Ref. [44]). Urethane-grade esters and ketones that contain no more than traces of alcohols or water are available.

18.5. FLAMMABILITY

Fires and explosions of flammable coating solvents can inflict terrible burns. Many tragic accidents have occurred in which people were killed or severely burned. Sadly, these accidents could have been prevented. Most solvents used in coatings are flammable. Care should be exercised when working with solvents in the laboratory, in the coatings factory, and in end use environments. Flammability depends on structure and vapor pressure. Generally, there is both an upper and a lower level of vapor concentration that limit flammability or explosion. If the partial pressure is low enough, not enough energy is released during burning to maintain the vapor–air mixture above the ignition temperature of the system. If the partial pressure of the solvent is high enough, there is insufficient oxygen for explosion or fire. Tables of upper and lower explosive limits of many solvents are available. A full container of solvent may present less of a fire risk than a recently emptied container; the vapor phase in the former might have the solvent at concentrations above the upper explosive limit, whereas the "empty" container may have a concentration in the explosive range.

The most common cause for fires in coating factories has been static electricity. Solvent flowing out of one tank and into another tank by gravity can pick up enough electrostatic charge to cause a spark, which can set off a fire or explosion. To avoid such charge accumulation, all tanks, pipes, and so on, used in handling solvents and solvent-containing mixtures should be grounded electrically at all times. A second cause is sparking of electric motors or faulty electrical connections. Factories and laboratories should be equipped with explosion proof electrical installations. One should never try to bypass these installations. Also, of course, smoking is a potential ignition source.

There are two main types of flammability tests: *open cup* and *closed cup*. Both measure a *flash point*, the minimum temperature at which solvent can be ignited by a hot wire. ASTM specifies standard conditions for both tests. Generally, open cup testers give results more appropriate for indicating the degree of hazard of a mixture when exposed to air, as during a spill. The closed-cup flash point more nearly describes the fire hazard of a liquid enclosed in a container. U.S. Department of Transportation regulations for shipment of flammable liquids are based on closed cup tests. Transportation costs can be affected substantially by the flash points of the material being shipped. A closed cup flash point is lower than an open cup flash point. Solvents used in architectural paints should have closed cup flash points over 38°C. Extensive tables of flash points of solvents are available. Different sources sometimes disagree on flash point values. Variations are not surprising for solvents such as naphthas and mineral spirits that are variable mixtures, but variations are also found with single component solvents such as *n*-butyl acetate.

The ASTM methods are said to be accurate to ±2.5°C. Reproducibility is poorer at temperatures below 0°C.

Many coatings contain a mixture of solvents. It is safest to determine flash points of mixtures experimentally. The factors affecting flash points, including molecular interactions in blends, have been discussed by Ellis [45]. It has been reported that good predictions of closed cup flash points for mixed solvents can be made by a UNIFAC computer program that requires only flash points and molecular structures of the pure components [46]. The best results were reported using UNIFAC group interaction parameters derived from flash points of binary solvent mixtures. Calculation of useful approximations of flash points of mixed solvents with simpler equations has been reported [47].

Risk of fire or explosion can be eliminated by meeting either of two conditions. If solvent vapor concentrations in air are kept well outside the concentration range within which ignition is possible or if all sources of ignition are eliminated, there can be no fire. Unfortunately, many accidents have occurred because neither of these conditions were satisfied. Because it is difficult to be certain that either of these conditions can be met in all circumstances, prudent practice dictates that all possible steps should be taken to meet both conditions, providing redundancy. The importance of good ventilation cannot be overemphasized, especially since the vapors of solvents, especially relatively dense ones, may stratify in stagnant air. As a result, solvent vapor concentrations can be higher in the lower part of the workspace, perhaps high enough to explode even when the average concentration is below the lower explosive limit.

18.6. OTHER PHYSICAL PROPERTIES

Density can be an important variable. It can have a major effect on cost. Most solvents are sold on a weight basis, but the critical factor and, correspondingly, the critical cost in almost all cases in the coatings field is the cost per unit volume. Most U.S. air pollution regulations are based on weight of solvent per unit volume of coating, which also favors the use of low density solvents in formulations (Section 18.9).

Conductivity can affect solvent choice. As discussed in Section 23.2.3, the use of electrostatic spray guns requires control of the conductivity of the coating. In general, formulations that have appreciable but low conductivity work best. The conductivity of hydrocarbon solvents is too low to permit pickup of adequate electrostatic charge. Alcohols, nitroparaffins, and small amounts of amines are common solvents or additives to increase conductivity to a desired range. The conductivity of waterborne coatings can pose problems for electrostatic application, such as the need to insulate the spray apparatus and relatively fast loss of charge from spray droplets. Additives can minimize the latter problem. For example, inclusion of glycol ethers improves the sprayability of waterborne coatings, apparently by reducing the surface conductivity of water. Presumably, the alkyl groups of the ethers orient quickly to the surface of the droplets.

Surface tension can be another important factor influencing solvent selection (Section 24.1). Solvent can affect the surface tension of coatings, which, in turn, can have important effects on the flow behavior of coatings during application, as discussed at length in Chapter 24. Solvent selection can also be a factor affecting the development of surface tension differentials across the surface of a drying film during application and film formation; these differentials can affect flow behavior [48,49]. Since surface tensions depend on the temperature and concentration of resins in solution, solvent volatility can have a large effect on the development of surface tension differentials. For a coating to wet a substrate, the surface tension of the coating must be lower than that of the substrate. Solvent selection can be a factor, particularly in aqueous systems. Although surface tension of aqueous systems can be reduced by adding surfactant, it is often more desirable to accomplish the same purpose with a solvent such as 2-butoxyethanol. Solvent evaporates, whereas surfactant leaves residues in the final film that may be detrimental to properties such as adhesion and humidity resistance.

18.7. TOXIC HAZARDS

In considering the toxic risks of volatile solvents, the extent of exposure must be considered in combination with toxicity data. All solvents are toxic at some level of exposure. Obviously, one should avoid ingesting them. The hazard from skin contact can be controlled by wearing protective clothing. Generally, the greatest potential risk comes from inhalation.

Three general types of toxicity data are important. Acute toxicity indicates the level of intake in single doses that can be injurious or lethal, information that can be particularly important in cases of accidental ingestion or spills. A second type of toxicity data concerns the level of exposure that is safe when people are going to be exposed 8 hours a day for long periods of time. This type of data is used, for example, to set the upper concentration limit for solvent in a spray booth. A third type is risk of exposure over periods of years to low levels of materials, which can increase health risks such as cancer. When it is found, usually by animal tests, that a solvent may be carcinogenic, very low levels of permissible exposure are set. The levels are frequently too low to be controlled by economically feasible methods. The effect is that carcinogenic solvents are banned. For example, benzene has not been used in coatings for many years for this reason. Although most solvents used in large quantities in coatings have been tested and are thought to be noncarcinogenic, it is prudent for the user to be aware of current knowledge of the materials that he or she is using and to minimize inhalation and contact with all solvents.

Extensive tables of all three types of data are available. In formulating coatings it is also necessary to consider the clientele who will use them. Although coatings sold to retail consumers are carefully labeled to include application cautions, one must assume that many people will not read the labels. When selling to a large corporation, it is reasonable to assume that the Material Safety Data Sheets will be read and appropriate practices will be established. But when selling to small industrial customers such as automobile repair shops, one cannot assume that the customer will pay attention to precautions. It may be ethical to sell a coating with a somewhat toxic solvent to one class of customer but unethical (although perhaps legal) to sell it to another class of customer. A common difficulty is to know what the level of exposure will be. Reference [50] describes an approach to assessing possible exposures when retail consumers apply coatings in a room.

In 1990 the U.S. Congress listed hazardous air pollutants (HAP) for which use is to be reduced [51]. Among those of importance in the coatings field are methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), *n*-hexane, toluene, xylenes, methyl alcohol, ethylene glycol, and ethers of ethylene glycol. The U.S. EPA Hazardous Air Pollutants Strategic Implementation Plan describes regulatory efforts [52]. The first step was a voluntary program aimed at reducing emissions of 17 chemicals, including methanol, MEK, MIBK, isophorone, toluene, and xylene, by 50% (of 1988 levels) by 1995. Mandatory HAP limits are included in EPA's Unified Air Toxics Regulations, issued for all major categories of coatings users in 1995–1999; for an example, see Ref. [53]. Compliance is required within three years of the issue date. Mono- and diethers of ethylene glycol, diethylene glycol, and triethylene glycol are listed on the HAP list, but ethers of propylene glycol are not. *t*-Butyl acetate and 2-butoxyethanol (monobutyl ether of ethylene glycol) have been removed from the HAP list. The present HAP list motivates replacement of listed solvents with solvents not on the HAP list. Such substitutions may do little or nothing to reduce hazards or to improve air quality if the unlisted solvent is as hazardous as the listed one.

18.8. ATMOSPHERIC PHOTOCHEMICAL EFFECTS

Since the 1950s, it has been realized that the presence of organic compounds in the atmosphere can lead to serious air pollution problems. Terminology can be confusing; in the older literature, such compounds are referred to as "hydrocarbons," meaning any organic compound, not just unsubstituted hydrocarbons. More recently, they have been termed *volatile organic compounds* (VOC). The terms *reactive organic gases* (ROG) and *reactive organic compounds* (ROC) are also used. Particularly in Europe, solvents are classified by their *photochemical ozone creation potential* (POCP). Three end effects of VOC emissions into the atmosphere are important: formation of eye irritants, formation of particulates, and formation of toxic oxidants, especially ozone.

Although all of these factors are important, the most critical for coatings is ozone. Ozone is a naturally occurring component of the atmosphere but is toxic to plants and animals. When you go up in the pine forests in the Rocky Mountains and smell the wonderful "fresh air," the odor is ozone. Pine and oak trees emit substantial quantities of VOC into the atmosphere, the UV level increases with altitude, and as a result, ozone generation is high. Plants and animals, including humans, evolved in the presence of some ozone and can tolerate its presence up to a point. However, with the rapid growth of VOC emissions from human-made sources, ozone levels on many days of the year in many parts of the world, especially in and around cities, have exceeded the levels that many plants can withstand and increased risks to human health, especially of susceptible individuals.

The EPA reports that man-made VOC emissions in the United States peaked in 1970 at about 33.7 million short tons/year and have been declining fairly steadily ever since, reaching about 16 million short tons/year by 2004 [54]. This >50% reduction is a major accomplishment, especially during a period when the U.S. GDP increased 187% and vehicle miles traveled increased 171%. Since 1970, coatings emissions decreased roughly in proportion, accounting for 11 to 14% of total manmade emissions throughout the period. For perspective, highway vehicles emitted about 5.9 million short tons in 1998 and 4 million short tons in 2003. In recent years, emissions from coatings have been on the order of 2 million short tons/year, enough to be an important target for future regulation. The coatings industry has done a lot to reduce VOC emissions, but it will be asked to do a lot more.

There is not general agreement on the level of ozone that is considered safe. From 1978 to 1997, the U.S. National Ambient Air Quality Standard for ozone allowed no more than a 1-hour period per year (averaged over three years) when the concentration of ozone in the air exceeded 0.12 ppm. Many urban areas in the United States have had trouble meeting this standard. In 1997, the EPA reduced the standard to 0.08 ppm. For this standard to be attained, the three-year average of the fourth-highest daily maximum 8-hour average of continuous ambient air monitoring data over each year must not exceed 0.08 ppm [55]. It is estimated that 47 of the 50 states have some areas that do not comply with the new standard. (See Ref. [55] for further information on ozone regulations.)

Photochemical reactions in the atmosphere are complex and depend on many variables in addition to the amount and structure of VOCs, especially the concentrations of various nitrogen oxides. Full discussion of the reactions is beyond the scope of this book. References [56–58] provide brief and more detailed reviews on the state of the science. Probably, the principal pathways leading to the generation of ozone are by way of hydrogen abstraction from the VOC compounds. Some of the reactions that have been proposed to explain ozone generation are shown in Scheme 18.1, in which RH represents a VOC compound.

Note that nitrogen oxides (NO_x) participate in the ozone-forming reaction sequence shown in Scheme 18.1. A 1991 study by the National Research Council concluded that in many areas of the United States, substantial reductions of ozone can be accomplished only by reducing NO_x levels in addition to or instead of reducing VOC [59]. Coatings emit almost no NO_x; the main sources are electricity generation and transportation.

An important variable in the rate of ozone generated from VOCs is the ease of abstraction of hydrogens from reactive organic gases by free radicals, such as the hydroxyl free radicals shown in the first equation of Scheme 18.1. Data are available on the rate constants for a wide variety of organic compounds [58]. In general terms, compounds with hydrogens on carbon atoms alpha to amines or ethers, hydrogens on tertiary carbon atoms, allylic hydrogens, and benzylic hydrogens are examples of easily abstractable hydrogens (Section 5.1). POCP values are determined by rates of reaction of hydroxy free radicals with the various solvents.

Scheme 18.1

$$\mathrm{RH} + \cdot\mathrm{OH} \longrightarrow \mathrm{H_2O} + \mathrm{R}\cdot$$

$$\mathrm{R}\cdot + \mathrm{O_2} \longrightarrow \mathrm{ROO}\cdot$$

$$\mathrm{ROO}\cdot + \mathrm{NO} \longrightarrow \mathrm{RO}\cdot + \mathrm{NO_2}$$

$$\mathrm{NO_2} + h\nu \longrightarrow \mathrm{NO} + \mathrm{O}$$

$$\mathrm{O_2} + \mathrm{O} \longrightarrow \mathrm{O_3}$$

In early investigations of the effects of VOC on air pollution, organic compounds were divided by rabbit eye irritation tests into photochemically active compounds of high and low reactivity. It was proposed that if the emission of the highly reactive compounds could be limited, the less reactive ones could dissipate and avoid high local concentration of pollutants. This led to the establishment of a definition of *photochemically reactive solvents* in *Rule 66* of the Los Angeles Air Control District. After some years of experience, it was realized that most organic compounds are photoreactive and that the extent of dissipation in the atmosphere after local emission had been overestimated. Changing from highly reactive compounds to less reactive compounds might diminish the air pollution effects near the scene of emission in exchange for increasing air pollution down-wind from the emission site. Furthermore, the coatings industry objected to having to use different solvent combinations in different parts of the country. This situation led to the conclusion that it would be best to limit the emission of almost all organic compounds into the atmosphere.

In establishing future regulations, there is a difference of opinion as to whether all solvents should be considered as equally undesirable in the atmosphere, as they are now. The present approach is simpler to enforce. However, it may well be that using less reactive solvents to replace more reactive ones would be advantageous by allowing at least some opportunity for dissipation in the atmosphere to minimize the probability of local excess ozone concentrations. In Europe, some regulations are based on the *photochemical ozone creation potential* (POCP) of individual solvents. A list of POCP values and examples of reformulation of solvents to minimize POCP emissions may be found in Ref. [58]. The POCP values have been calculated by computer modeling, using reaction kinetic data to assess changes in ozone formation and checked in smog chambers [56]. Values for about 200 VOCs are available. Xylene and related aromatic hydrocarbons have particularly high POCP values. There are no exempt solvents.

California has established regulations covering solvents used in aerosol spray cans based on limiting the permitted level of solvents based on the grams of ozone generated in the atmosphere per gram of product. The levels permitted vary based on the product in the aerosol can as well as the individual solvents contained in the formulation. (See Ref. [60] for the California regulation and tables of products and reactivity.) In this new system all solvents are classified as *reactive organic compounds* (ROC), including those that have been established as exempt from VOC regulations. A book describing the derivation of regulations for aerosol coatings has been published by California Air Resources Board (CARB), it is available on the Web site of the American Solvents Council [61]. CARB states that this new approach to regulation replacing VOC limits with reactivity-based limits can achieve equivalent air quality while providing manufacturers with more flexibility and that it may result in a more effective and cost efficient control strategy.

It was found that the effect of hydroxy free radicals on ozone production used in POCP depended on the ratio of NO_x to ROC. Therefore, a new system of rating the effect of solvents on ozone was developed. In a smog chamber filled with a base reactive organic gas mixture and NO_x appropriate to the area for which regulations are to be applied, a reactive solvent was added and the incremental reactivity on ozone generation is calculated by dividing the maximum amount of ozone generated by the addition by the amount of compound added. Table 18.7 gives the maximum incremental reactivity values (MIR) for some of the solvents tested. (See Section 18.9.2 for a discussion of aerosol regulations.)

An ingenious approach to VOC reduction is use of supercritical carbon dioxide as a component in a solvent mixture [62], detailed in Section 23.2.5. A formula used to calculate VOC is given below at the beginning of Section 18.9.1 and is discussed further there. The units used in most U.S. regulations are weight of solvent per unit volume of coating as applied, excluding water and exempt solvents.

VOC emissions can be affected substantially by the *transfer efficiency* in spray applied coatings. When a coating is sprayed, only a part of the coating is actually applied to the object being coated. Transfer efficiency represents the percentage of the coating used that is actually applied to the product. As the transfer efficiency increases, the VOC

TABLE 18.7. MIR Values of Selected Solvents, m($g_{ozone}/g_{solvent}$)

Methyl acetate	0.07
PCBTF	0.11
t-Butyl acetate	0.22
Acetone	0.43
n-Butyl acetate	0.89
Odorless mineral spirits	0.91
2-Butanol	1.60
1-Methyl-2-propyl acetate	1.71
VM&P Naphtha	2.03
Toluene	3.97
Methyl isobutyl ketone	4.31
Mixed xylenes	7.37

emissions decrease, since less coating is used. Transfer efficiency depends on many variables, particularly the type of spray equipment utilized (Section 23.2). In some cases, regulations have been established requiring certain kinds of spray equipment or setting a lower limit on transfer efficiency, such as 65%.

Besides reducing the VOC content of coatings and increasing transfer efficiency, there are two other broad approaches to minimizing VOC emissions: solvent recovery and incineration. In some cases it is feasible to recover the solvent used in coatings. One can pass the air flowing out of a drying chamber through activated carbon beds where the solvent is adsorbed. After the surface of the carbon is saturated with solvent, the material is heated to distill and recover the solvent. Alternatively, the solvent-laden air can be passed through condensers cooled with liquid nitrogen; the nitrogen that is vaporized is fed into the drying chamber, reducing the oxygen content and, hence, permitting higher concentrations of solvent without exceeding the lower explosive limit. Solvent recovery is desirable when it is feasible, but feasibility is limited by low solvent concentration in the air stream needed to stay safely below the lower explosive limits. In the case of effluent air from spray booths, it must be below concentrations that could have toxic hazards; the solvent concentration is generally too low to permit economic recovery of the solvent.

Minimizing VOC emissions by incineration involves heating the effluent solvent laden air stream in the presence of a catalyst to a temperature high enough to burn the solvent. As with solvent recovery, this approach is economically feasible only when solvent concentrations are relatively high. Incineration has been found to be particularly applicable in coil coating (Section 30.4). In this case, most of the solvent is released in the baking oven. Part of the effluent air from the baking oven is recirculated back into the oven; the amount of air recirculation is limited so that the solvent content does not approach the lower explosive limit. The balance of the effluent air is fed to the gas burners that heat the oven. The solvent in the air is burned along with the gas; the fuel value of the solvent reduces the gas requirement. Thus, VOC emission is minimized and the fuel value of the solvent is used.

Between 1970 and 1995, VOC emissions from typical auto assembly plants were reduced by 70 to 80% by the combination of reduced VOCs, improved transfer efficiency, and incineration [63]. Further reductions have probably been achieved since then.

18.9. REGULATION OF SOLVENT EMISSIONS FROM COATINGS

In the United States, the EPA establishes regulations regarding emission of VOC and HAP solvents into the atmosphere. States or other subdivisions are allowed to have more restrictive regulations than the national regulations. The European Union has also established regulations.

18.9.1. Determination of VOC

VOC values at for waterborne or solventborne coatings are calculated by the following formula:

$$\mathrm{VOC} = \frac{(\text{wt\% of all volatiles} - \text{wt\% of water} - \text{wt\% of exempt solvent})(\text{density of coating})}{\text{liters of coating} - \text{liters of water} - \text{liters of exempt solvents}}$$

This definition of VOC as weight/volume follows from the conventions that air pollution data are based on weights of pollutants and that coatings are sold and applied on a volume basis. Regulatory limitations are based on VOC content of the coating “as applied.” If, as is very common, the user is to add solvent to the coating after receiving it from the coating manufacturer, the VOC is based on the coating after this solvent has been added. The exclusion of water is to prevent circumventing regulations by developing coatings with low solids that are diluted with water but still have high VOC contents relative to the dry film thickness that has to be applied.

The amount of VOC emitted by a coating is not easily determined. In most cases, only approximations of potential VOC emissions can be calculated, even when the exact formulation of a coating is known. Solvent can be retained in films for very long periods of time. In latex paints, coalescing solvents are used that are only slowly released from the coating. In cross-linking coatings, volatile by-products may be generated by the reaction. For example, MF cross-linking leads to the evolution of a molecule of volatile alcohol for each co-condensation reaction, and in self-condensation reactions, there can be emission of alcohol, formaldehyde, and methylal. The amount released depends on curing conditions and the amount of catalyst used. On the other hand, when slow evaporating glycol ether solvents are used in an MF cross-linking system, it is probable that some of the glycol ether transetherifies with the MF resin and is not emitted from the film. Amines used in “solubilizing” water-reducible coatings may volatilize to different extents, depending on conditions and amine structure [64,65]. With high-solids two package coatings, the amount of volatile material can be affected by many variables, most obviously by the time interval between mixing the two packages and application. Very high solids coatings use low MW oligomers; particularly when baked, some of the oligomer may volatilize.

Experimental measurement of VOC is not straightforward, either. The amount of VOC released depends on conditions under which the coating is used. Time, temperature, film thickness, air flow over the surface, and in some cases, the amount of catalyst are among the variables that affect the results obtained. Although it would seem that determination under the conditions of actual use would be most appropriate, this is not easy to do. For air dry coatings, the time required for the determination would be very long. For baking coatings, there can be differences in conditions for use of the same coating. It is generally agreed that it would be desirable to have a standard method for determining VOC emissions. However, there is little agreement as to what that standard method should be; in view of the effect of application variables, it is doubtful if a single appropriate standard method will ever be developed.

Methods for determination of VOC and other useful information were collected by Brezinski in 1993 [66]. Improved methods are needed. For example, a round robin study of ASTM D-2369-89 (the standard method for measuring volatile content) gave results 5 to 34% higher than expected, with large standard deviations for two component coatings; results with one component coatings correlated better [67]. An updated ASTM method, D-2369-95, uses similar procedures; its reproducibility ranges from ± 3.4 to 5.3%, with little difference between one- and two-component coatings. The standard method for determining VOCs is ASTM D-3960-96; in a round robin test of solventborne automotive coatings, its reproducibility was 2.96%.

Measuring VOC of waterborne coatings is made more complex by the need to determine water content, and water analysis methods are surprisingly poor. A standard gas chromatography method, ASTM D-3792-99, is only reproducible to 5%. A rather complicated Karl Fischer procedure (ASTM D-4017-02) is only reproducible to 5.5%, and this was an improvement over earlier versions of the procedure. A round robin test of waterborne automotive coatings by ASTM D-3960-96 had a reproducibility of only 9.75%, with most of the poor reproducibility attributable to the water analysis methods. Note that in the formula above, as the ratio of water to regulated solvent increases, errors in water analysis are magnified in calculation of VOC.

Current U.S. EPA regulations treat most solvents useful in coatings [except water, acetone, *t*-butyl acetate, CO_2, 4-chlorobenzotrifluoride (PCBTF), methyl acetate, perchloroethylene, and certain silicone fluids and fluorinated solvents] as equally undesirable. In establishing future regulations, there is a difference of opinion as to whether all solvents should be considered as equally undesirable in the atmosphere, as they are now. The present approach is simpler to enforce. However, it may well be that using less reactive solvents to replace more reactive ones would be advantageous by allowing at least some opportunity for dissipation in the atmosphere to minimize the probability of local excess ozone concentrations. CARB has begun to depart from the present approach. As detailed in Section 18.9.2, new regulations for solvents used in aerosol spray cans are based on the grams of ozone generated in the atmosphere per gram of product, not on total solvent. The levels permitted vary based on the product in the aerosol can as well as the individual solvents contained in the formulation. (See Ref. [68] for the California regulation and tables of products and reactivity.)

An alternative to VOC analysis is to calculate VOC based on the formulation of the coating. This calculation requires knowledge of the solvent content of all coating components and assumptions about what fraction of the solvents are actually emitted and about how much additional VOC is produced by chemical reactions such as cross-linking. Even so, calculated VOC values may be more reliable than measured values in many cases, especially for waterborne coatings with very low VOC, in which the error of water analysis is magnified.

18.9.2. Regulations

Regulators recognize that for adequate performance, some coatings require higher VOC levels than others. The EPA assessed the most advanced technology for each end use and established different maximum VOC guidelines for major applications. States and localities within the United States may enforce more rigorous guidelines. California has done so for many years, and in 2005 six northeastern states began enforcing stricter limits. During the 1990s, the EPA guidelines ranged from 150 to 780 g L^{-1} (1.9 to 6.5 lb/gal). Tighter EPA guidelines are expected.

Examples from the 1999 EPA VOC emission standards are 450 g L^{-1} for architectural enamels, 250 g L^{-1} for exterior and interior flat paints, and 150 g L^{-1} for traffic-marking paint [69]. EPA regulations for automobile refinish coatings permit: wash primer, 780 g L^{-1}; primers and primer–surfacers, 580 g L^{-1}; primer–sealer, 550 g L^{-1}; single-/two-step top coats, 600 g L^{-1}; top coats of three or more steps, 630 g L^{-1}; and multicolor top coats, 680 g L^{-1} [70].

In 1995 the U.S. EPA revised their wood furniture coatings regulation after extensive discussions with the industry. It was agreed that regulations should be expressed as pounds of VOC per pound of coating solids on the wood surfaces. The overall limits were set at 2.3 lb of VOC including a maximum of 1.0 lb of HAPs per pound of solids. In new plants or finishing lines, HAP emissions are limited to 0.8 lb per pound of solids. For specific coatings the following maxima were set: waterborne top coats, 0.8 lb; higher solids solvent borne sealers, 1.9 lb; top coats, 1.8 lb; and acid-cured alkyd amino vinyl sealers, 2.3 lb [71].

In some cases, such as automotive assembly plants, regulations are based on total volatile emissions from a factory rather than individual coatings.

The automotive refinish coating limits apply to the entire country as the maximum levels permitted, but states or regions are free to set more restrictive limits. In most other applications the emission limitations apply only in regions that do not meet national levels of ozone concentrations.

CARB frequently sets more restrictive regulations than the EPA. For example, CARB 2002 regulations [72] for architectural and maintenance coatings limit high gloss paints to 250 g L^{-1} rather than the 450 g L^{-1} allowed by EPA for high gloss enamels. Not only is CARB often more restrictive than the EPA, but the South Coast Air Quality Management District (southwestern California) often sets limits more restrictive than CARB. Effective July 1, 2006, the VOC limits are 100 g L^{-1} for chemical storage tank coatings, essential public service coatings, industrial maintenance coatings, primers, sealers, and undercoats, recycled coatings, rust preventive coatings, and specialty primers. In addition, as of July 1, 2008, the limit for flat paints will be 50 g L^{-1}. South Coast regulations can be accessed on the Internet [73].

CARB has established regulations controlling solvents (and propellants) used in aerosol coatings based on MIR values of incremental ozone production ($g_{ozone}/g_{solvent}$) (Table 18.7) rather than the total solvent. MIR values can then be used to calculate the MIR values of any mixture of solvents, which in turn permits the calculation of the MIR per gram of coating. The emissions of reactive organic compounds (ROC) from aerosol coatings in California was estimated to be 26.5 tons/day, with the capacity to produce 56.3 tons of ozone per day. Table 18.8 gives the regulatory limits for grams of ozone per gram of product for some of the 35 types of aerosol coatings.

More restrictive regulations are also being developed by the Ozone Transport Commission (OTC) covering the 17 northeastern states, and six of these began enforcing tighter limits in 2005. For examples of OTC regulations and comparisons with EPA, CARB, and California South Coast regulations, see Ref. [74].

The limit on HAP emissions at any facility has been set by the EPA at 10 tons per individual HAP per year, and a total of 25 tons per year for all HAPs. Lower limits are

TABLE 18.8. MIR Limits (g L^{-1}) for Selected Aerosol Coatings

Flat paints	1.21
Non-flat paints	1.40
Primers	1.11
Auto body primers	1.57
Automobile top coats	1.77
Auto bumpers and trim	1.75
Traffic paint	1.18
Marine spar varnish	0.87

set for individual chemicals thought to be more dangerous. The following solvents and plasticizers are on the HAP list: benzene, di-2-ethyhexyl phthalate, dibutyl phthalate, dimethylformamide (no more than 1 ton per year), dimethyl phthalate, dioxane, ethylene glycol, mono and di alkyl and aryl ethers of ethylene glycol (except the butyl ether of ethylene glycol), diethylene glycol, triethylene glycol, hexane, methoxyethanol, ethoxyethyl acetate, isophorone, methyl ethyl ketone, methylene chloride (no more than 4.0 tons per year), 2-nitropropane (no more than 1.0 ton per year), cresols and phenol, toluene, triethylamine, and xylenes.

A 2004 European Directive covering decorative, functional, and protective coatings mandates strict VOC limits to take effect in 2007, with further tightening in 2010 [74].

A paper is available that urges the establishment of more uniform international regulations of emissions of VOCs from coatings, using automotive refinish coatings as an example [75]. The authors point out that as the globalization of industry proceeds, large inefficiencies result from having different requirements in different countries for similar coatings.

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19

Color and Appearance

Color and the interrelated topic of gloss are important to the decorative aspects of coatings and sometimes, to their functional aspects. Although we have all experienced color since we were babies, but most people have little understanding of it. Many technical people think of color as an aspect of physics dealing with the distribution of visible light. Although that is a factor, color is a psychophysical phenomenon. The difficulty of understanding color can be grasped by considering its most rigorous definition: *Color* is that characteristic of light by which an observer may distinguish between two structure-free fields of view of the same size and shape. In effect, it says that color is what is left to distinguish between two objects when all other variables have been removed—not a very satisfying definition.

Color has three components: an observer, a light source, and an object. (The single exception is when the light source is the object being viewed.) There is no color on an uninhabited island. This is not just a semantic statement; color requires an observer. There is no color in the absence of light; in a completely darkened room there is no color, not because you cannot see it, but because it is not there. There must be an object; if you look out the window of a spaceship without looking at a planet or star, there is no color—there is an observer, there is light, but there is no object.

Another major factor affecting appearance is surface roughness. If a surface is very smooth, it has a high gloss; if it is rough on a scale below the ability of the eye to resolve the roughness, it has a low gloss. If, however, the roughness can be resolved visually, a film may exhibit scratches, brush marks, orange peel, texture, and so on. Furthermore, there can be a combination of small scale and larger scale roughness, so films can, for example, have low gloss and brush marks or high gloss and orange peel. The eye can resolve irregularities in surface smoothness of approximately 25 μm, depending on the

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Organic Coatings: Science and Technology, Third Edition, by Zeno W. Wicks, Jr., Frank N. Jones,
S. Peter Pappas, and Douglas A. Wicks

distance from the object. Adding to the complexity, color and gloss interact—changing either one changes the other.

19.1. LIGHT

Light is electromagnetic radiation to which our eyes are sensitive. The range of visible wavelengths varies somewhat among individuals, but in most cases is 390 through 770 nm. The sensitivity of the eye varies as a function of wavelength, as shown in Figure 19.1. The figure also shows the response of photomultiplier tubes and silicon photodiodes. The eye is relatively insensitive to the shorter and longer ends of the range. The response of our eyes depends on the distribution of wavelengths of light emitted by the light source. In the case of monochromatic light sources, the colors we see range from violet through blue, green, yellow, and red with increasing wavelength. We see different colors as the ratios of wavelengths in polychromatic light sources change. If we look at a light source with nearly equal content of all wavelengths, we see white.

Sunlight is considered the standard light, but sunlight varies depending on the time of day, latitude, season, cloudiness, and so on. When work toward understanding color began, light from overcast north sky (in the northern hemisphere) was accepted as standard. Based on many measurements of energy distribution, a light source designated as D_{65} was adopted as a standard related to average daylight. The mathematical description of a light source is called an *illuminant*. A graph of standard illuminant D_{65} is shown in

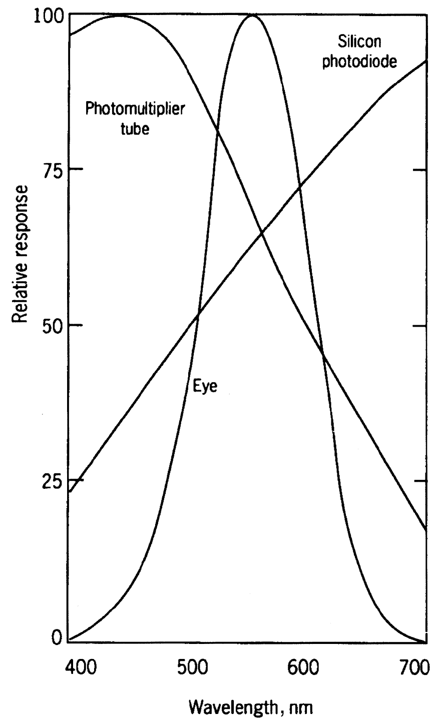


Figure 19.1. Sensitivity of the eye, photomultiplier tube, and silicon photodiode as a function of wavelength. (From Ref. [1], with permission.)

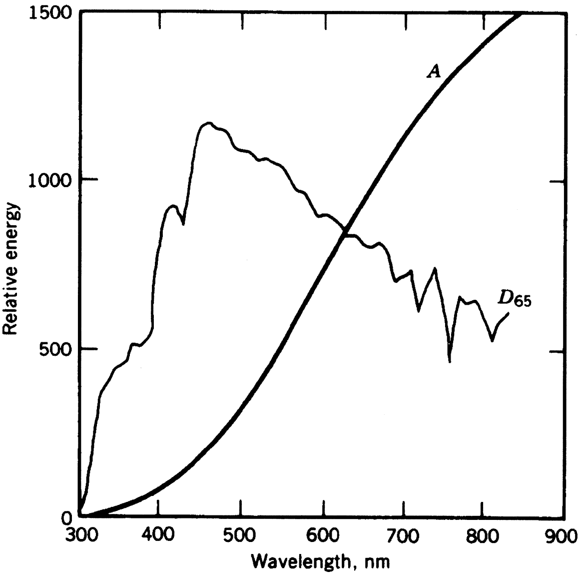


Figure 19.2. Relative spectral power distributions of CIE standard illuminants A and D_{65}. (From Ref. [2], with permission.)

Figure 19.2. Tables giving energy distributions as a function of wavelength for various bandwidths from 1 to 20 nm wide are available [3].

The energy distribution from tungsten lights is different. Another standard light source, *A*, is a carefully specified tungsten light operated under specified conditions. A graph of illuminant *A* is also shown in Figure 19.2, and tables of its energy distributions are available. Fluorescent lights are another type of light source, and many types are available. As shown in Figure 19.3, they exhibit a continuous energy distribution with peaks at a series

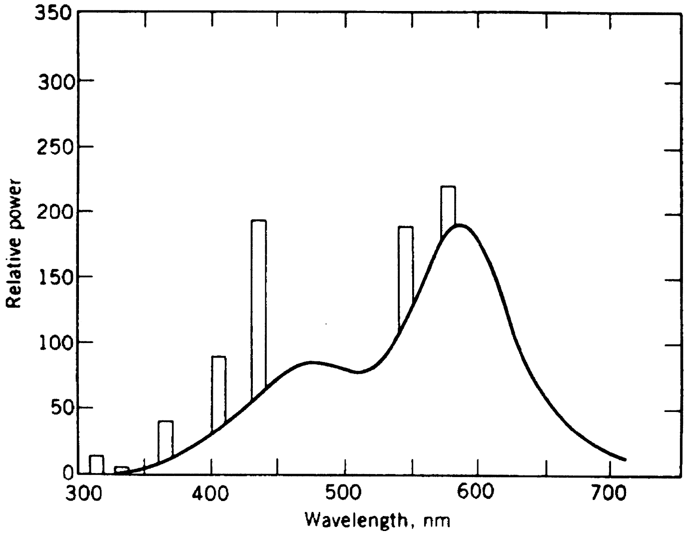


Figure 19.3. Spectral power distribution of a cool white fluorescent lamp (IES 1981). (From Ref. [1], with permission.)

of wavelengths. Even if the underlying continuous spectrum were the same as D_{65}, the peaks would lead to changes in colors when these lights are used as a light source in comparison with daylight.

19.2. LIGHT–OBJECT INTERACTIONS

An important factor that affects color is the interaction between the light and the object being viewed.

19.2.1. Surface Reflection

When a light beam is directed at a surface, some light is reflected at the surface and some passes into the object. As shown in Figure 19.4, if the surface is optically smooth, light is reflected at the same angle (r) as the angle of incidence (i) [4]. This kind of reflectance is called *specular* (mirror-like) *reflectance*. By convention, an angle of incidence normal to the surface is designated as 0° and the grazing angle is 90°. The fraction of light reflected (R) varies with angle of incidence and difference in refractive index (n) between the two phases. If there is no difference in index of refraction, no light is reflected at the interface; as the difference increases, the fraction of light reflected increases. For angles of incidence near 0°, the fraction reflected can be calculated using the following equations given in both the general form, Eq. 19.1*a*, and where the first medium is air ($n_1 = 1$), Eq. 19.1*b*:

$$R = \left(\frac{n_2 - n_1}{n_2 + n_1}\right)^2 \tag{19.1a}$$

$$R = \left(\frac{n - 1}{n + 1}\right)^2 \tag{19.1b}$$

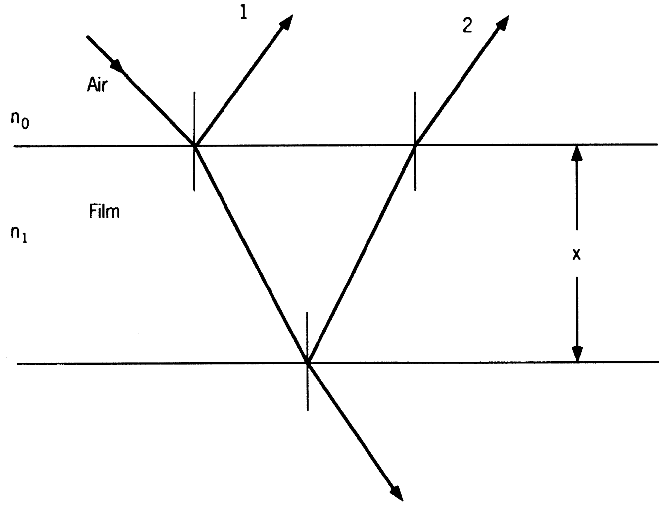


Figure 19.4. *External and internal reflection and refraction of light by a nonabsorbing film (refractive index, n_1, thickness, x) with optically smooth parallel surfaces. (From Ref. [4], with permission.)*

Most resins have refractive indexes of about 1.5; Eq. 19.1*b* shows that approximately 4% of incident light is reflected when the angle of incidence is near 0°. The dependence of reflection on angle of incidence is illustrated in Figure 19.5; reflectance approaches 100% as the angle of incidence approaches 90°. The family of curves in Figure 19.5 illustrates the combined effects of refractive index difference and angle of incidence.

Light not reflected at the surface enters the object. When a light beam enters an object, it is *refracted*; that is, it is bent, also shown in Figure 19.4. The angle of refraction varies with the ratio of the refractive indexes of the two media:

$$\sin r = \frac{n_1}{n_2} \sin i \tag{19.2}$$

When light passes from air into a nonabsorbing plastic film with parallel, optically smooth surfaces and an index of refraction of 1.5, the angle of refraction is smaller than the angle of incidence (Figure 19.4). If the angle of incidence is near 0°, the fraction reflected at the first surface is 0.04, and 0.96 is transmitted into the film. If there is no absorption, 0.96 reaches the second film/air interface. There, 0.96 × 0.96 of the original light is transmitted into the air on the other side of the film, being refracted so that the angle of refraction is equal to the original angle of incidence. There is also reflection at the second surface, and 0.04 × 0.96 is reflected back toward the first surface. Again, there is reflection of 4% and transmission of 96% at the back of the first surface. As a result, $(0.96)^2 \times (0.04)$ of the original light is transmitted out of the film at an angle equal to the original angle of incidence, and $(0.96) \times (0.04)^2$ is reflected back into the film. This bouncing back and forth continues, if there is no absorption, until the total transmission equals 0.92 and total reflectance equals 0.08.

When a light beam passes from a medium of higher refractive index to one of lower refractive index, the angle of the beam increases. If the angle of incidence is high enough, all light is reflected back and none is transmitted out. If the refractive indexes

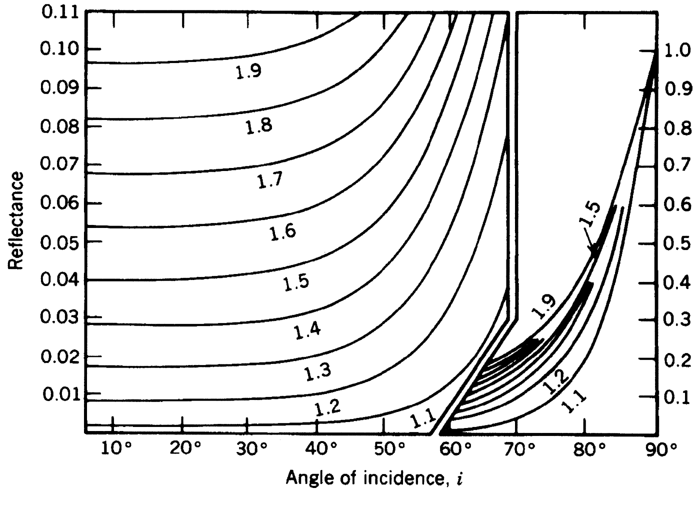


Figure 19.5. *Fraction of light reflected from a smooth surface as a function of the angle of incidence* i *with various differences in refractive index. (From Ref. [5], with permission.)*

are 1.5 and 1, the critical angle (at which all the light is reflected) is calculated to be 41.8°. Total reflection is the basis for optical fibers. If light enters the end of a nonabsorbing fiber in which there are no bends, such that the angle of incidence with the inner surface of the fiber is less than its critical angle, all of the light will follow the fiber, even all the way across an ocean.

If the thickness of a film is small (60 to 250 nm), interference colors will be seen. The intensity of some wavelengths of reflected light are enhanced, and others are transmitted selectively. With a refractive index of 1.5 in air, at a film thickness of 66 nm, bluish-white color is reflected and yellowish-white color is transmitted; as thickness is increased, other colors are preferentially reflected. The colors seen are affected by the angle of incidence of the light.

19.2.2. Absorption Effects

In almost all coatings, the color we observe is affected by differential absorption of various wavelengths of light. Colorants, dyes, pigments, and to a degree, some resins, absorb some wavelengths of light more strongly than others. These absorptions are controlled by the chemical structures of the colorants. First, we consider the absorption effects in transparent systems, that is, systems in which the colorant is in solution or is so finely divided that it does not significantly reflect light at the colorant–resin interface. The extent of absorption depends on chemical composition, wavelength, particle size, optical path length (film thickness), concentration, and media–colorant interactions.

Each colorant has an absorption spectrum that controls the absorption of various wavelengths of light. Chemists generally speak of molar absorptivities, ε, in units of Lmol^{-1} path length^{-1}, corresponding to the absorbance per molar concentration of a substance. Physicists generally speak of absorption coefficients, K, in units of path length^{-1} mass^{-1}, corresponding to the absorbance per unit mass of the system.

The smaller the particle size, the greater the fraction of light absorbed by the same quantity of a colorant. The highest molar absorptivities are exhibited by individual molecules in solution. In the case of pigments, the smaller the particle size of a pigment, the greater the absorption. The longer the path followed by a beam of light through a medium containing absorbers, the greater the degree of absorption. In transmission of a beam of light at 0°, the optical path equals the film thickness. At any other angle, the optical path length is greater than the film thickness. If, in passing through a unit path length, one-half of the light of a particular wavelength is absorbed and one-half is transmitted (ignoring surface reflection), on passing through two units of path length, three-fourths is absorbed and one-fourth is transmitted. Mathematically, this relationship is expressed by an exponential equation, as shown in Eqs. 19.3*a* and 19.3*b*, in which X is path length, I is intensity of light transmitted, and I_0 is the original light intensity. Chemists commonly use base 10 (Eq. 19.3*a*), and physicists base e (Eq. 19.3*b*):

$$\frac{I}{I_0} = 10^{-\varepsilon X} \tag{19.3a}$$

$$\frac{I}{I_0} = e^{-KX} \tag{19.3b}$$

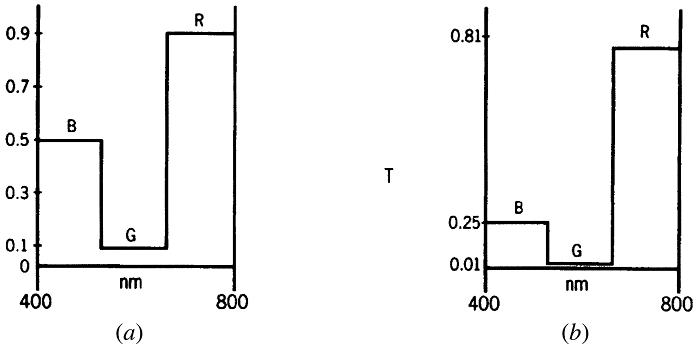


Figure 19.6. *Transmission spectra of idealized magentas: (a) path length = x; (b) path length = 2x.*

Ideally, the same relationship holds when the concentration of the colorant in the medium is changed:

$$\frac{I}{I_0} = 10^{-\varepsilon CX} \tag{19.4}$$

Equation 19.4 holds only over a limited range of concentrations; the width of the range is system dependent. When absorbers are in solution, there are less likely to be intermolecular interactions between molecules in dilute solutions than in more concentrated solutions. In the case of pigment dispersions, concentration effects are likely to be larger. Another complication is possible interactions with the media. In the case of solutions, a change in solvents can sometimes lead to association of molecules effectively increasing particle size and hence reducing absorption. There can also be effects of hydrogen bonding between a soluble dye molecule and different solvents. This changes the structure, leading to a change in absorption spectrum. In dispersions of pigments, changes in the medium, such as dilution with solvent, can lead to flocculation (agglomeration) of pigment particles; this causes a larger particle size and hence reduced absorption.

Figure 19.6 shows transmission spectra of idealized reddish magentas. Spectra (*a*) and (*b*) result from transmission of light through the same transparent coating of path length X and $2X$, respectively. (Surface reflection effects are ignored.) The fraction of light of all wavelengths transmitted through the thicker coating, shown in spectrum *b*, is less. But also, the relative transmissions of the blue (B), green (G), and red (R) parts of the spectra are different. The color seen in case *b* would be a redder purple than in case *a*. The composition is the same but the shade of the color is affected by path length. The same type of change takes place if the concentration is doubled at the same film thickness. This is an idealization of a real situation. One of the inks in four color process printing that permits printing of multicolored pictures is a reddish magenta. The film thickness of magenta ink affects the color of the magenta print and hence the combined color picture.

19.2.3. Scattering

Scattering is another phenomenon that can occur during the passage of light through a film. If there are small particles dispersed in the film that have a different refractive index than the medium, light is reflected and diffracted at the interfaces between the particles and the medium. The physics involved in scattering is complex and beyond the scope of this brief presentation, but the results can be stated in a simplified manner. When a beam of light passes through a film containing nonabsorbing particles, the light is internally reflected in all directions, so it changes from a beam to diffuse illumination inside the film. Light that reaches the back of the top surface at angles greater than the critical angle is reflected back into the film; part of the light reaching this surface at angles less than the critical angle leaves the film. If the film is thick enough, no light can pass through it completely; all the light is reflected back out of the top surface. The reflection is, however, not just at the specular angle, but at all angles; that is, this light is diffusely reflected even though the top surface of the film is optically smooth. The extent of light scattering by nonabsorbing particles depends on refractive index difference between particles and medium, particle size, film thickness, and particle concentration.

The greater the difference in refractive index, the greater the degree of light scattering. The degree of scattering increases steeply as the difference in refractive index increases (Figure 19.7). The degree of scattering is the same whether the particles have a higher or lower refractive index than the medium. For example, water droplets in air (fog) scatter light as efficiently as air droplets of the same size at the same concentration in water (foam). An ideal white pigment would absorb no light and have a very high refractive index, so the difference in refractive index from that of binders would be large. Rutile TiO_2 comes close to meeting these specifications; it has an average refractive index of 2.73, but it absorbs some light below about 420 nm. Another crystal type of TiO_2, anatase, absorbs less light, but its refractive index is lower, 2.55. The smaller index of refraction difference leads to less efficient scattering.

Scattering is affected by particle size (Figure 19.8). For rutile TiO_2 in a resin with a refractive index of about 1.5, the scattering coefficient for 560-nm light increases with particle size to a maximum at 0.19-μm diameter, then drops off steeply [6]. Commercial TiO_2 has a range of particle sizes. Since efficiency drops off more rapidly on the small diameter size side of the maximum, TiO_2 pigments are produced with an average particle diameter somewhat over 0.2 μm. See Ref. [7] for calculations showing the effect of particle size distribution and particle agglomeration on scattering. The particle diameter with

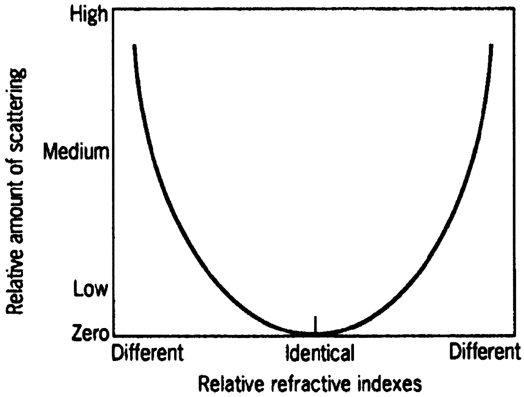


Figure 19.7. Scattering as a function of refractive index difference; particles have higher refractive indexes than the media on the right-hand part of the curve and lower values on the left. (From Ref. [1], with permission.)

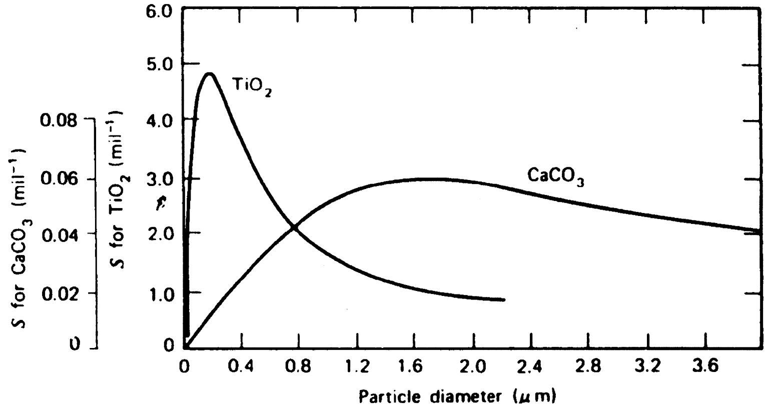


Figure 19.8. Scattering coefficients as a function of particle size for rutile TiO_2 and $CaCO_3$. (From Ref. [6], with permission.)

maximum scattering depends on refractive index difference. For calcium carbonate ($n = 1.57$), the scattering coefficient goes through a maximum at about 1.7 μm. As expected from the small difference in refractive index, scattering by even optimum particle size is low.

The extent of light scattering is affected by film thickness. If no absorption occurs, the light that is not reflected back out of the top surface is transmitted unless the film thickness is great enough so that all the light is reflected back. Scattering is also affected by concentration. At low concentrations of particles, such as rutile TiO_2, transmission through a film (neglecting surface reflection) follows a relationship similar to that for absorption:

$$\frac{I}{I_0} = e^{-ScX} \tag{19.5}$$

As concentration increases, however, scattering efficiency reaches a maximum, then decreases. In the case of rutile TiO_2 pigmented coatings, the efficiency decreases so much that finally, the fraction of light transmitted increases and the fraction reflected decreases. The result can be seen in a plot of scattering coefficient S as a function of pigment volume concentration (PVC) of rutile TiO_2 in dry films [6] (Figure 19.9). PVC is defined as the volume percent pigment in a ***dry*** film of coating. In commercial practice, the cost effectiveness of pigmenting with TiO_2 drops off sufficiently at PVCs above about 18% that it is not generally economically sound to use a higher PVC of TiO_2. The optimum value varies somewhat from system to system; it depends on how well the pigment is dispersed in the film and on the TiO_2 content of the particular TiO_2 pigment, which may vary from grade to grade by more than 10% (Section 20.1.1).

19.2.4. Multiple Interaction Effects

The effects of surface reflection, absorption, and scattering are interdependent. Light sources generally are not narrow beams, but relatively broad beams or diffuse sources. Surfaces are not often optically smooth; in some cases, we strive for surface roughness. In coatings, we seldom deal with pigments or pigment combinations that only absorb or

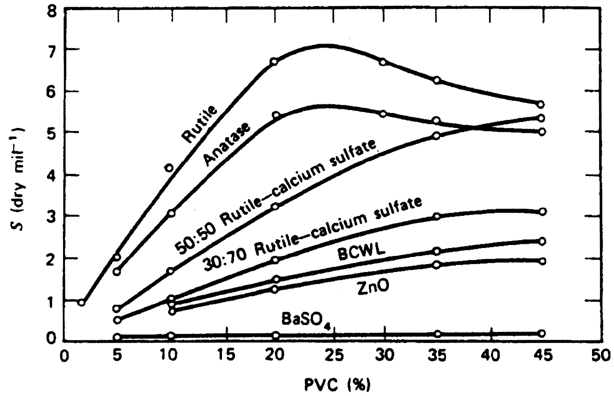


Figure 19.9. *Experimental plots of scattering coefficients versus PVC for selected pigments in a dry acrylic lacquer. BCWL is basic carbonate of white lead. (From Ref. [6], with permission.)*

only scatter light; commonly, both occur simultaneously. We are seldom interested in free films, but rather in films on a substrate so that the reflectance at the bottom surface of a film is not the same as that of the top surface of the film. The eye does not distinguish between the light reaching it that has been reflected from the top surface, from within the film, or from the bottom surface of a film. The combined light from all three sources is integrated when the eye responds.

Surface reflectance increases as the angle of incidence increases (Figure 19.5). If a panel of a high gloss (smooth surface) blue paint illuminated with a beam of white light is observed at any angle other than the specular angle, one sees a comparatively dark blue color, resulting from the diffuse reflectance back out of the film. If the angle of incidence approaches 90°, one sees a very light blue color at the specular angle because the observed light contains a high fraction of surface reflected light and only a little light from within the film. If the illumination is diffuse instead of a beam, the color is a lighter blue from most angles of observation because one sees a higher fraction of surface reflected light. If the blue paint is low gloss (rough surface) with exactly the same composition as in the earlier example, a lighter blue color is seen under diffuse illumination at most viewing angles compared with the high gloss paint. This results from a greater ratio of surface reflected light reaching the eye. The color is darkened at most viewing angles by wetting the surface with water, since the water fills in the surface roughness.

The effects of pigment concentration and film thickness on coatings that absorb or weakly scatter light without rescattering the primary scattered light can be modeled by simple equations. However, interactions resulting from both absorption and multiple scattering together are more complex, and equations that model reflection and transmission are more complex. Figure 19.10 gives a set of Kubelka–Munk equations that model reflectance, R_1 and transmittance T_1 of a translucent or opaque film or slab of material of thickness X containing light absorbers and scatterers. The observer is viewing the sample in air, while the absorbers and scatterers are embedded in a medium such as plastic or resin.

The Kubelka–Munk reflectance R and transmittance T of the film in the absence of a refractive index boundary include the effects of absorption K, scattering S, and film thickness X. The boundary reflections from both sides of the top surface r_1, and the inner and bottom sides of the film r, as well as the corresponding boundary transmittances t_1 and t influence the reflectance R_1 and transmittance T_1 seen by the observer viewing the sample

$$R_1 = r_1 + \frac{t_1 t[R(1 - rR) + rT^2]}{(1 - r_1 R)^2 - r^2 T^2}$$

$$T_1 = \frac{t_1 t T}{(1 - r_1 R)^2 - r^2 T^2}$$

$$t_1 = 1 - r_1; \qquad t = 1 - r$$

$$R = \frac{\sinh bSX}{a \sinh bSX + b \cosh bSX}$$

$$T = \frac{b}{a \sinh bSX + b \cosh bSX}$$

$$a = 1 + \frac{K}{S}; \qquad b = (a^2 + 1)^{1/2}$$

For completely opaque slabs or films, simplified equations can be used.

$$\frac{K}{S} = \frac{(1 - R_\infty)^2}{2R_\infty}; \qquad R_\infty \text{ is the reflectance at complete hiding}$$

Surface reflection must be corrected for using Saunderson's equation:

$$R_1 = r_1 + \frac{t_1 t R_\infty}{1 - rR_\infty}$$

Assumptions

1. The equations apply to a single wavelength at a time.
2. K and S are the same throughout the film.
3. Pigment particles are randomly oriented.
4. The internal radiation flux is perfectly diffuse.
5. Edge effects are ignored.

Figure 19.10. *Kubelka–Munk equations and assumptions.*

in an air medium. Two boundary reflectances r_1 and r are required because light normally incident on the film from air has a reflectance value of 0.04, while diffuse light incident on the boundary from inside the resin has a reflectance value of 0.596 for a material of refractive index about 1.5. The differences between R_1 and R, as well as those between T_1 and T, in the case of typical plastics and resins are very significant. Other Kubelka–Munk equations are available that permit calculations when the reflectances at the inner side of the top and bottom sides of the film are different [8].

19.3. HIDING

Color is affected by reflectance back through the film of light reaching the substrate to which the coating is applied. It is common to compare the colors of a coating applied over a striped black and white substrate. If one can see the pattern of the stripes through the coating, the coating is said to exhibit poor *hiding*. The difference results from the reflection of light reaching the white stripes compared with absorption of light reaching the black stripes. The effect is as if some black pigment was put in the coating above the black stripes. If all light entering the film is absorbed or scattered back out of the film prior to reaching the substrate, there is no effect of substrate on color; hiding is complete. Simplified Kubelka–Munk equations can be used for such opaque films (Figure 19.10).

Hiding is a complex phenomenon and is affected by many factors. Hiding increases as film thickness increases. Low hiding coatings require thicker films; that is, coverage decreases; the area covered (hidden) by a liter of coating is less and the cost is higher. Hiding increases as the efficiency of light scattering increases; that is, hiding is affected by the refractive index differences, particle sizes, and concentrations of scattering pigments present. Hiding increases as absorption increases. Carbon black pigments, which have high absorption coefficients for all wavelengths, are particularly effective. Colorants also increase hiding but not as much as black. Surface roughness increases hiding; a larger part of the light is reflected at the top surface, reducing the differences of reflection resulting from differences in the substrate to which a coating is applied.

An important factor affecting hiding, sometimes forgotten in testing coatings, is uniformity of film thickness. Application of coatings commonly results in nonuniform thickness. Coatings are generally formulated to level, that is, to flow after application to make the film thickness more uniform (Section 24.2). Leveling is often incomplete, however, and there can be effects on hiding. Consider a poor leveling coating where an average film thickness of 50 μm of dry coating has been applied, but there are brush marks remaining, so adjacent to each other are lines with film thicknesses of 65 and 35 μm. If the hiding at 50 μm is just adequate, hiding will be inferior at 35 μm. The difference in color is emphasized by the thin layers of coating being right next to the thick layers. The contrast results in a poorer rating in hiding by the uneven film than by a uniform 35-μm film of the same coating. Further complicating hiding is the variation of substrates over which the coating is applied. Hiding of a white coating applied over a white surface might be rated as excellent, but hiding of the same coating over a black surface might be rated poor.

There are quality control tests that compare hiding of batches of the same or similar coatings, but no test is available that can provide an absolute measure of hiding [9]. The only way to establish covering power of a coating is to apply it to an appropriate large surface with a film thickness that gives adequate hiding and then calculate the actual coverage in $m^2\,L^{-1}$ or ft^2/gal.

In some cases, hiding is not desired; an example is a coating for metallized plastic Christmas tree ornaments. One wants transparent red, green, blue, and so on, coatings. Preparation of a transparent coating requires that there be no light scattering within the film; therefore, the particle size of colorant particles must be very small.

19.4. METALLIC AND INTERFERENCE COLORS

Metallic coatings are widely used on automobiles. They are made with transparent colorants together with *nonleafing* aluminum pigment (Section 20.2.5). These metallic coatings exhibit unusual shifts in color as a function of viewing angle (Figure 19.11). When an observer looks at a metallic film from an angle near the normal, the path length of light through the film is short because it is reflected back by the aluminum. On the other hand, from a greater viewing angle, the observer sees light that has been reflected back

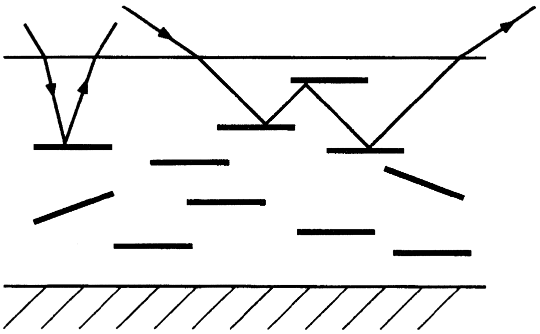


Figure 19.11. Idealized diagram of the reflection of light in a metallic coating.

and forth within the film so that the path length is longer and the color is darker. Metallic coatings are lighter in color when viewed near the normal angle (the *face color*) and darker when viewed from a larger angle (the *flop color*). It is desirable to achieve a high degree of *color flop*, that is, a large difference between face and flop colors. To do so requires a smooth surface (high gloss), a transparent film having very little light scattering from the resin or color pigment dispersion, and parallel alignment of the aluminum flake particles to the surface of the film. (See Section 30.1.2 for a discussion of possible mechanisms for orientation of aluminum during film formation.)

Pigments that produce colors by interference are also used in automotive coatings, sometimes in combination with metallic flake. They are often called *effect pigments*. Three types of such pigments that are used commercially are described in Section 20.2.5.

19.5. THE OBSERVER

The third critical aspect of color is the observer; both the eye and the brain are involved. The retina of the eye has two types of photodetectors, rods and cones. These detectors are stimulated by light photons to send signals through the optic nerves to the brain. At low levels of illumination, rods are sensitive to all wavelengths of light and become insensitive as the level of illumination increases. Cones are insensitive at low levels of illumination but are sensitive at higher levels. The response of cones is wavelength dependent, having three ranges of sensitivity that overlap. One peaks in the blue region of the spectrum, another in the green, and the third in the red region. These overlapping ranges lead to complex signals to the brain, which integrates the signals so that we can see thousands of different colors. At low levels of illumination, we see only with rods, and vision is limited to shades of gray. At intermediate levels of illumination, there are responses from both rods and cones; hence, one does not see bright colors, only grayish ones. At higher levels of illumination, the rods are inactive and we see a full range of colors from the responses of cones.

The mechanism of color vision is complex, only partly understood, and beyond the scope of this book. There are variations from person to person in the degree of response to the three ranges of sensitivity. As a result, colors seen by different observers are not identical. Usually, the differences are small, but in some cases they are large. In extreme cases, some people are *color blind*. There are different types of color blindness; the most common is red–green color blindness.

To specify color and predict responses to mixtures of colorants, a mathematical model of a *standard human observer* was established by an international committee of experts known by the acronym of its French name as CIE. Figure 19.12 shows a graph of three functions that model color vision. At any given wavelength, the standard observer has the same response to the ratio of the values of $\bar{x}$, $\bar{y}$, and $\bar{z}$ at that wavelength as to the monochromatic light of that wavelength. Tables of *CIE Color Matching Functions* are available as a function of wavelength with bandwidths of 1, 10, and 20 nm [3].

Within the range of higher illumination, the eye adapts to changes in levels of illumination. For example, if an area of white is surrounded by black, the white looks whiter than if the black were not present. The eye adapts to the level of light reflected by the combined black and white and responds more to the white in the presence of the black. Similar effects occur when two strongly colored fields of view are adjacent to each other. Yellow surrounded by blue–green looks more orange than if the blue–green were absent. In general, if one looks at color chips when selecting a coating, the color is different than if that coating is applied to a large surface because of the effect of the surrounding area on the color. Many other effects result from such interactions between the eyes and combinations of colors on a surface. (See Ref. [5] for further discussion.)

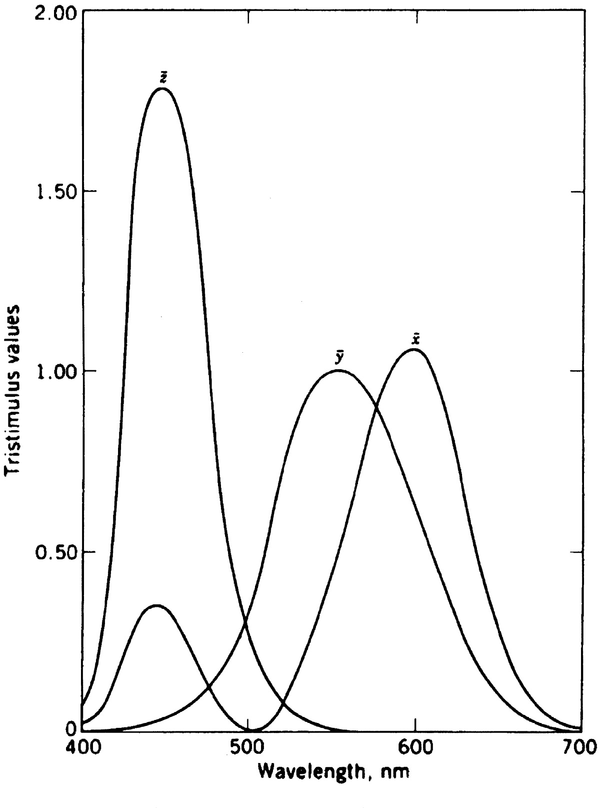


Figure 19.12. *CIE color matching functions, $\bar{x}$, $\bar{y}$, and $\bar{z}$, for equal energy spectra. (From Ref. [1], with permission.)*

19.6. INTERACTIONS OF LIGHT SOURCE, OBJECT, AND OBSERVER

Color depends on the interaction of three factors: light source, object, and observer. If any factor changes, the color changes. If we observe an object under a light source with the energy distribution of illuminant *A* (Figure 19.4) and shift to a different illuminant, for example, illuminant *C* (similar to D_{65}), the color changes. Light source *A* has relatively lower emission in the blue end of the spectrum and relatively higher emission in the red end. The light reaching the eye when the object is illuminated with source *A* has more red light and less blue light than the light reflected from the same object illuminated

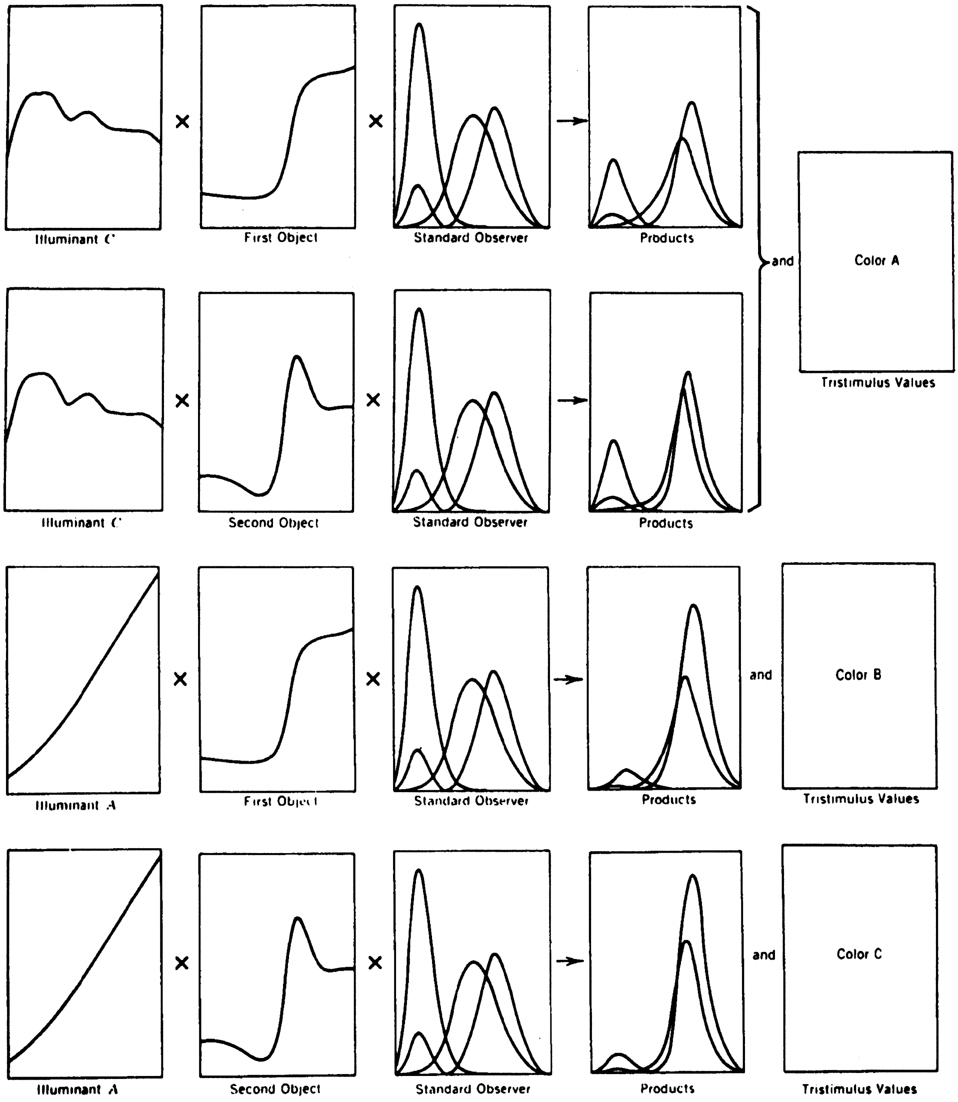


Figure 19.13. Light source effects and metamerism. (From Ref. [1], with permission.)

with source *C*. The color is different. The situation is illustrated in spectral sets *a* and *b* in Figure 19.13, which shows the different responses as product spectra of light source × object × observer for an object with illuminants *A* and *C*.

The only way to be sure that a pair of coatings will match under all illuminations is to use colorants with identical chemical composition and physical states. If the chemical composition and physical state of the colorants in two coatings are the same, their reflectance spectra are identical, and the coatings match under any light source unless there are differences in pigment distribution within the coatings. It is possible for two materials with different colorant compositions, and hence different reflectance spectra, to result in the same color under a light source. However, such a pair will not match under light sources with different energy distributions. This phenomenon is called *metamerism*. In a spectral match, the two panels change color with a new light source, but it is the same change in both cases. In a metameric pair, the color is the same with one light source; the colors of both panels also change when the light source is changed, but the extent of change is different between the two panels. This situation is illustrated in Figure 19.13, which shows responses of a second object with illuminants *C* (spectral set *c*) and *A* (spectral set *d*). The first and second objects (a metameric pair) are identical under illuminant *C*, but their colors are different under illuminant *A*.

19.7. COLOR SYSTEMS

The human eye can discriminate thousands of colors. However, it is difficult for a person to tell another person what colors he or she sees. A color description such as "light grayish blue–green" illustrates this difficulty. Many systems have been developed to permit definitive identification of colors. There are two types of systems: one that uses color samples in specific arrangements and one that identifies colors mathematically. All color systems have at least three dimensions, to include all the possible colors.

The most widely used visual color system in the United States is the *Munsell Color System*, in which carefully prepared and selected color chips are classified in a three-dimensional system. The dimensions of the Munsell System are called *hue*, *value*, and *chroma*. *Hue* refers to the dimension of color, described as blue, blue-green, green, greenish-yellow, yellow, yellowish-red, red, reddish-purple, purple, purplish-blue, and back to blue. The *value* dimension characterizes the lightness of a color as compared to a series of gray samples, a *gray scale*. The value 0 is assigned to pure black and the value 10 to pure white. A light blue has a high value, whereas a dark blue of the same hue has a low value. The *chroma* dimension refers to the difference between a color and a gray of the same value and hue. A bright red has a high chroma, whereas a grayish red of the same hue and value has a low chroma.

The color chips in the Munsell System are prepared so that there are equal visual differences between all pairs of adjacent chips. The chips are labeled systematically; for example, a chip labeled G5/6 is a green with a value of 5 and a chroma of 6. One can look at a set of Munsell chips and know the color that someone meant when they made such a designation. There are two limitations to this statement. The light source must be specified. Chip G5/6 gives a different color under source *A* than under source D_{65}. Second, surface roughness affects color, so comparisons have to be made at equal gloss levels. Two sets of Munsell chips are available: one with high gloss and the other with low gloss. Significant errors can result in comparing either of these with materials that are semigloss. In Europe, a different color chip system, the Natural Color System, is most widely used [10].

The mathematical color system is the *CIE Color System*. It is based on mathematical descriptions of light sources, objects, and a standard observer. Light sources are specified by their relative energy distributions, objects are specified by their reflectance (or transmission) spectra, and the observer is specified by the CIE standard human observer tables. For color analysis, the light reflected (or transmitted) from (or through) an object is measured with a spectrophotometer. Since in most cases, the reflection is diffuse, it is essential to use a spectrophotometer with an integrating sphere so that all of the light being reflected is sampled, not just that at some narrow angle. For the most accurate data, reflectance measurements are taken at each wavelength and the values over the range 380 to 770 nm would be used in the summation. For most purposes, the accuracy is sufficient using 16 measurements at 20-nm intervals from 400 through 700 nm.

To identify the color resulting from the interaction of a light source, an object, and a standard observer, one uses the data for these three dimensions to calculate the *tristimulus values* X, Y, and Z using Eqs. 19.6*a*, *b*, and *c*.

$$X = \sum_{380}^{770} \bar{x}_\lambda E_\lambda R_\lambda \tag{19.6a}$$

$$Y = \sum_{380}^{770} \bar{y}_\lambda E_\lambda R_\lambda \tag{19.6b}$$

$$Z = \sum_{380}^{770} \bar{z}_\lambda E_\lambda R_\lambda \tag{19.6c}$$

Tristimulus values are different for the same object and the same observer when the energy distribution E of a different illuminant is used. This is as it should be, since we know that colors change as the light source changes. The tristimulus values uniquely and unequivocally define colors. For example, $X = 14.13$, $Y = 14.20$, and $Z = 51.11$ is a definitive description of a color, but what color? Unfortunately, even experts often cannot say by looking at the numbers. This set of tristimulus values is for a blue, but few people could look at them and tell you it is a blue, much less whether it is a grayish-blue and approaches being a purplish-blue, which it happens to be.

The X and Y tristimulus values can be converted to *chromaticity values* x and y by normalization:

$$x = \frac{X}{X+Y+Z} \qquad y = \frac{Y}{X+Y+Z} \tag{19.7}$$

If one has a metameric pair of coated panels, the tristimulus values and the chromaticity values are the same with the light source under which the panels match. They are not the same, however, if calculated with the energy distributions from another light source. When the light source changes, the X, Y, and Z and the x and y values of both panels change, but the changes are to different degrees.

The chromaticity values of each wavelength of the spectrum can be calculated and plotted against each other to form the *CIE spectrum locus* (Figure 19.14). The ends of the locus are connected by a straight line called the *purple line*. There are no purples in

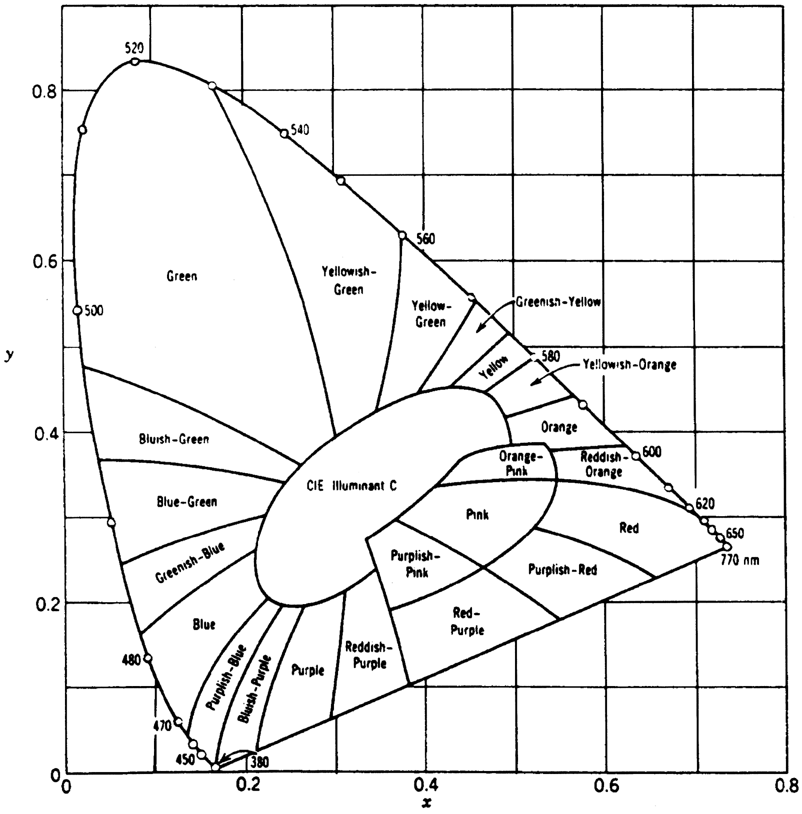


Figure 19.14. CIE chromaticity diagram showing the location of various hues. (From Ref. [1], with permission.)

the spectrum; in CIE color space, hues of purple lie along this line. As shown, the plot can be divided into color areas, so one can look at the x and y values and have a reasonable idea of the shade of a color. The third dimension rises vertically from the plot; it is the Y tristimulus axis, *luminance*; $Y = 100$ (or 1, in some conventions) at the x, y values of the light source. The Y at the spectrum locus line approaches 0. At x, y points between the spectrum locus and the point of the source, Y is always less than 100. As the value of Y gets larger, the gamut of possible colors narrows (Figure 19.15).

If one draws a line from the point of the source through the point of a sample extended out to the spectrum locus, the wavelength at the intercept is called the *dominant wavelength* of the color. This dimension corresponds to the hue dimension in the Munsell System, but the scale is different. If this extrapolation intercepts the purple line, the line is extrapolated in the opposite direction, and the intercept with the spectrum locus is called the *complementary dominant wavelength*. If one divides the distance from the source point to the sample point by the total distance from the source point to the spectrum locus (some workers express it as a percentage), one obtains the *purity*. Purity is the same dimension as chroma in the Munsell System, but the scale is different. The vertical Y dimension is a gray scale, as in the Munsell value dimension, but again, the scale is different.

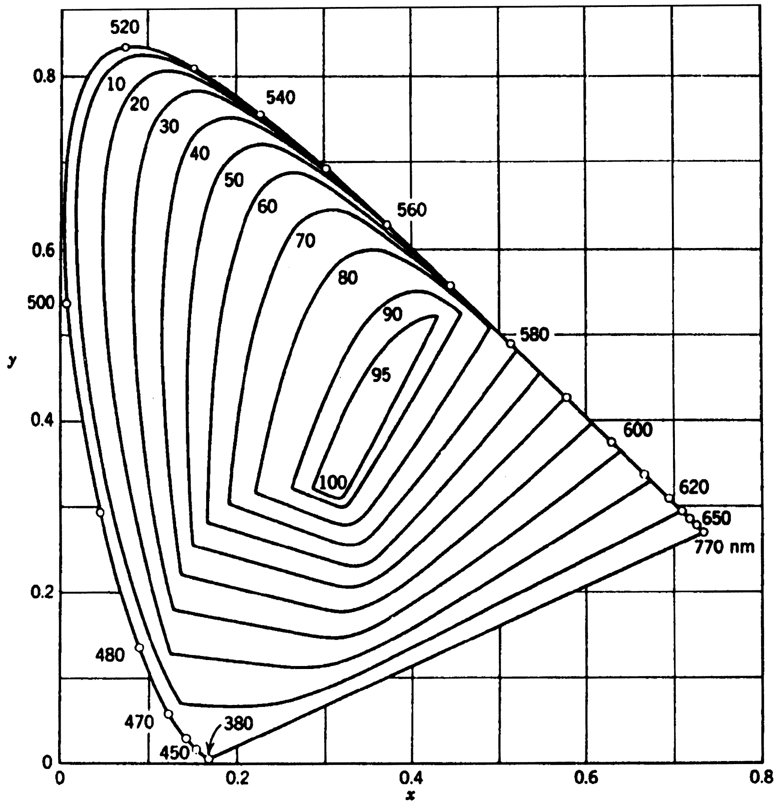


Figure 19.15. Topographical diagram of a three-dimensional CIE color space with illuminant C. *(From Ref. [1], with permission.)*

Figure 19.15 shows a topographical diagram of three-dimensional CIE Color Space with illuminant *C*. All real colors that can be seen with light source *C* fall inside this color space. In the Munsell system, the boundaries are limited not by reality of color, but by the color purity of the available pigments to make the reference chips. CIE color space is not visually uniform (Figures 19.14 and 19.15). For example, a small difference in x and y in the blue part of the color space represents a substantial difference in color, whereas in the green part of color space, the same difference in x and y values represents little difference in color. In this sense, Munsell color space is preferable, since the differences are visually uniform. However, color calculations of the types needed for instrumental color matching are feasible with CIE color space, but not with Munsell space. If the comparisons are to be visual, one commonly uses the Munsell system. If the comparisons are to be mathematical and include all possible color space, one uses the CIE system.

There have been many attempts to transform CIE color space mathematically to a visually equal color space; then differences could be used as meaningful measures for specification purposes. Some progress has been made, and color differences (ΔE) can be calculated using the CIE 1976 $L^*a^*b^*$ equations. L^* represents lightness, a^* redness–greenness, and b^* yellowness–blueness. These quantities are calculated from tristimulus values by the following equations:

$$L^* = 116\left(\frac{Y}{Y_n}\right) - 16$$

$$a^* = 500\left[f\left(\frac{X}{X_n}\right) - f\left(\frac{Y}{Y_n}\right)\right]$$

$$b^* = 200\left[f\left(\frac{Y}{Y_n}\right) - f\left(\frac{Z}{Z_n}\right)\right]$$

In these equations, X, Y, and Z are the tristimulus values of the sample; X_n, Y_n, and Z_n are the tristimulus values of the light source; $f(Y/Y_n) - (Y/Y_n)^{1/3}$ for values of $(Y/Y_n) > 0.008856$; $f(Y/Y_n) = 7.787(Y/Y_n) + 16/116$ for values of Y/Y_n equal to or less than 0.008856; and the functions $f(X/X_n)$ and $f(Z/Z_n)$ are similarly defined.

The classical equation for CIELAB color difference is

$$\Delta E(L^*a^*b^*) = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$$

These equations still do not represent fully uniform color space. If specifications are written for a line of colors specifying a fixed ± range for ΔE for the entire series, the requirements will be more stringent for some colors than for others. Even if color difference equations were available that were visually uniform, their use would still be limited for specifications. The color would be permitted to vary equally in any direction from the central standard. However, it is common for people to be more concerned about deviations in one direction in color space than in other directions. For example, there is commonly a greater tolerance for whites to be off in the blue direction than for them to be off in the yellow direction.

CIE has developed a series of improvements over the CIELAB color-difference formula, most recently CIEDE2000 [11]. Implementation of this system requires a 22-step calculation [12]: easy with computers but beyond the space limits of this book. A recent evaluation of 128 pairs of samples concluded that the "CIEDE2000 formula outperformed CIELAB and it is also more accurate than a panel of observers" [13].

19.8. COLOR MIXING

There are two types of color mixing: additive and subtractive. In *additive mixing*, the primary colors are red, green, and blue. Additive mixing is involved in theatrical stage use of overlapping colored spot lights, as well as in color television, where three colors of dots (red, green, and blue) are projected near each other on the screen. The lights from nearby dots are "added" when we look at them to give colors, which depend on the ratio of the three colors in nearby dots. In additive color mixing, equal amounts of blue and green light give blue–green (*cyan*); similarly, blue and red light give purple (*magenta*); green and red light give *yellow*; and equal addition of all colors gives white light. With appropriate light sources, lights of all colors can be made. Note that we see as yellow the combination of all wavelengths in the green, yellow, orange, and red segments of the spectrum.

In almost all cases, however, color mixing encountered in coatings is not additive but *subtractive mixing*. We use colorants that absorb (subtract) some of the light of some wavelengths from white light. If we add a second colored pigment to a coating containing

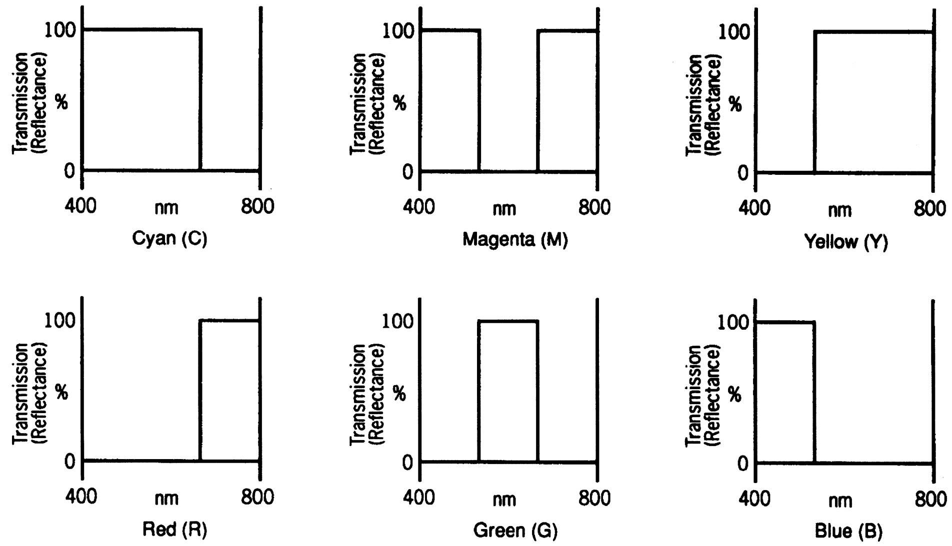


Figure 19.16. Transmission (or reflectance) spectra of cyan, magenta, and yellow colorants, together with their complementary colors.

colored pigment, we subtract more; we cannot add back any intensity of wavelengths by using an additional further colorant. The primary colors in subtractive mixing are cyan, magenta, and yellow. If we mix equal quantities of an ideal cyan and an ideal magenta, the result is blue. That is, the cyan absorbs red and the magenta absorbs green, so blue remains. Similarly, cyan and yellow yield green, magenta and yellow yield red, and a mixture of equal amounts of all three ideal absorbing colorants absorbs all light and yields black. Idealized transmission (or reflectance) spectra of the primary colors, which illustrate their complementary nature, are provided in Figure 19.16.

19.9. COLOR MATCHING

A large fraction of pigmented coatings is color matched. The customer originally chose some color for a refrigerator, automobile, or other product, and a coating formulator was given a sample of a material with this color and was asked to match the color using a coating formulation appropriate for the end use. After the formulator establishes the appropriate ratio of the appropriate pigments and after the customer approves the color match, the factory must color match batch after batch of the coating to meet this standard. Sometimes the formulator develops the formula first, and the color is accepted by the customer.

19.9.1. Information Requirements

Before starting the initial laboratory color match, the color matcher needs a substantial amount of information.

1. *Metamerism.* Is a spectral (nonmetameric) match possible? That is, can exactly the same colored pigments (including white and black) be used to establish the match as were

used to make the customer's sample? If not, the customer must realize that any match will be metameric; that is, the colors will match under some light source but not under others. For example, if the sample is a dyed fabric, the color of the textile cannot be matched exactly under all lights by any coating, since the colorants cannot be identical. If, as another example, the customer has been using a coating made with one or more pigments containing lead compounds and wishes to have a lead-free coating, only a metameric match is possible.

2. *Light sources*. If the match is to be metameric, the customer and the supplier must agree on the light source(s) under which the color is to be evaluated. If there is to be more than one light source, a decision should be made as to whether it is more desirable to have a close match under one light source without regard to how far off the match might be under other light sources, or to have a fair color match under several light sources but not a close match under any individual light source.

3. *Gloss and texture*. The color of a coating depends on its gloss and texture. Some of the light reaching the eye of an observer is reflected from the surface of the film and some from within the film. The color seen by the observer depends on the ratio of the two types of reflected light. At most angles of viewing, more light is reflected from the surface of a low gloss coating than from the surface of a high gloss coating. It is impossible to match the colors of a low gloss and a high gloss coating at all angles of viewing. There must be agreement as to the gloss of the coating, and if the gloss of the standard is different from the gloss desired for the new coating, the angles of illumination and viewing must be agreed on. It is impossible to make even a metameric match of the color of a fabric sample with a paint at all angles of viewing, since both the colorants and the surface textures have to be different. When paint manufacturers advertise on TV that their paint stores can do this, they are engaging in misleading advertising.

4. *Color properties*. Colorants have to be chosen that permit formulation of a coating that can meet the performance requirements. Need the coating have exterior durability, resistance to solvents, resistance to chemicals such as acids and bases, resistance to heat, meet some regulation for possible toxicity, and so on?

5. *Film thickness and substrate*. Since in some cases, the coating will not hide the substrate completely, the color of the substrate can affect the color of the coating applied to it, and the extent of that effect will vary with the film thickness. This variable is particularly important in applications such as can coatings and coil coatings, for which relatively thin coatings are applied (<25 μm in the case of can coatings). A thin coating that was color matched over a gray primer will not match over a red primer. A coating set up for one coat application on aluminum will not match the color standard if it is applied over steel.

6. *Baking schedule*. Since the color of many resins and some pigments are affected by heating, particularly at high temperatures, the color of a coating can be affected by the time and temperature of baking. It is also necessary to specify what the color requirements are for overbaking.

7. *Cost*. The color matcher should know the cost limitations. There is no sense in making an excellent color match with pigments that are too expensive for a particular application.

8. *Tolerance*. How close a color match is needed? Coatings for exterior siding or automobile top coats require very close color matches. For many others, close matching is unnecessary, but some customers, in their ignorance, set tight tolerance limits. Overly tight tolerances raise cost without benefiting performance. For coatings that are going

to be produced over time with many repeat batches, the most appropriate way to set color tolerances is to have an agreed on set of limit panels. For example, for a deep yellow coating, these would be the limits of greenness and redness, brightness and darkness, and high and low chroma. Since panels can change with age, spectrophotometric measurements should be made of the standard and the limit panels, and CIE tristimulus values calculated. The customer would then agree to accept any batch of coating having a color within this volume of color space. As mentioned earlier, while ΔE color differences, calculated from the 1976 CIELAB Color Difference Equations, have been used to set color tolerances, they have limitations. It is undesirable to use them as a general statement of tolerance for a series of colors. Furthermore, they permit variation equally in any direction from the standard color, which is frequently undesirable.

19.9.2. Color Matching Procedures

There are two approaches to matching colors: visual and instrumental. In visual color matching, experienced color matchers examine the sample to be matched, and from their experience select a combination of pigment dispersions that they think will permit matching the color. A formulation is mixed and the coating applied; since gloss affects color, the gloss must first be compared with the standard and adjusted if needed. The color matcher looks at the resulting color in comparison to the standard and decides what further addition of either one or more of the same pigment dispersions, or perhaps dispersions of different pigments, are needed to adjust the color match.

Spectrophotometric curves of the original standard sample can be used in an analytical mode to help identify component colorants in the standard, thereby simplifying pigment selection for visual matching. Organic pigments can often be identified by examining the absorption spectra of solutions of colorants from a sample of coating [14]. The process continues until a satisfactory combination of pigment dispersions has been selected. Color matching must be based on dry films. It can be useful to compare samples of wet coatings to estimate progress toward a match, but since color changes considerably during application, film formation, and drying, decisions have to be based on dry films prepared under conditions approximating the way in which the coating will actually be used. When matching a new color, even a highly experienced color matcher seldom matches a color in less than three *hits*, and commonly, it takes several more hits, sometimes requiring changes in one or more of the original choices of pigments.

The visual color matcher not only has the responsibility of selecting the colorants and their ratios to make a color match, but he or she must also attempt to make the color match so that it will be as easy as possible to produce batch after batch efficiently in the factory. It is not economically feasible for pigment manufacturers to produce successive batches of color pigments that are exactly the same color and color strength. Furthermore, there will be batch to batch variation in dispersions made from these pigments. The formulation should be set up so that it can be adjusted in the factory to permit matching the color standard despite these variations. It is desirable to use four pigments (counting black and white, but not inerts) to make the original match. This provides the four degrees of freedom necessary to move in any direction in three-dimensional color space. Sometimes use of single pigments cannot be avoided, but it is undesirable especially in applications in which close color matches are needed. Sometimes, more than four pigments are needed, but this adds to the complications of production and should be avoided, if possible. The factory should not make any changes in the pigments in the formulation, which would result in a metameric match.

Visual color matching is a highly skilled craft requiring years of apprenticeship to master. It is still practiced and still important, but the trend is toward computerized instrumental color matching. Instrumental color databases, along with computer programs, can be used to select colorants and their ratio both for original color matches in the laboratory and to provide information as to the amount of the various pigment dispersions to be added in the factory to match production batches. Establishing such a program requires a major effort. The database must be set up carefully. The pigments must be made into dispersions; and multiple single color coatings with different concentrations of color pigment dispersion in a series of appropriate white coatings must be made and applied. The reflectance values must be measured at 16 wavelengths; for critical matches, values at 35 wavelengths may be needed. (See Ref. [10] for further discussion of the creation of the pigment database.)

Analysis of computer color matching is beyond the scope of this book. References [10] and [15] (and the general references cited) review computer color matching and provide detailed discussions. Solid color coatings at complete hiding can be accurately color matched by current computer color matching software. The basis for these programs is the Kubelka–Munk theory outlined in, Figure 19.10. These programs attempt to achieve a tristimulus match between the sample and standard or object to be color matched. The mathematics of this operation is complicated by the nonlinear nature of the relation between the colorant concentrations in the sample and the tristimulus values of the sample and standard.

Typical color measurements consist of either 16 or 35 reflectance measurements at a set of wavelengths in the visible region. To utilize these data for color matching, the reflectances must be corrected for boundary reflections by means of Saunderson's equation to give Kubelka–Munk reflectances, Figure 19.10. These reflectances can be used to calculate the ratio K/S for the sample to be matched at each wavelength. The K and S values are assumed to be linear functions of the pigment concentrations chosen to match the sample. In the case of a four pigment match:

$$K = k_1c_1 + k_2c_2 + k_3c_3 + k_4c_4$$
$$S = s_1c_1 + s_2c_2 + s_3c_3 + s_4c_4,$$
$$((K/S)s_1 - k_1)c_1 + ((K/S)s_2 - k_2)c_2 + \cdots + ((K/S)s_4 - k_4)c_4 = 0$$

for each of the 16 (35) wavelengths, since the measured K/S ratio and k_i and s_i values for the individual pigments are different at each wavelength. In addition, the pigment concentrations are usually expressed as percentages to satisfy the equation

$$c_1 + c_2 + c_3 + c_4 = 100$$

It would seem easy to select three wavelengths to give three equations that combined with the last equation would give four linear equations with four unknowns that on solution would give the required pigment concentrations to match the sample. Unfortunately, this is not the case in practice. Even using all 16 (35) K/S equations and using various estimates such as tristimulus weighted averaging or least squares solutions of the determined set of 17 (36) equations in four unknowns does not in most cases give, a close tristimulus color match. Allen devised a method that is used by most commercial software to obtain a tristimulus match [16]. Starting from an initial estimate of pigment concentrations obtained using the K/S ratios and tristimulus weighting, these concentrations are refined iteratively to approximate a tristimulus match.

The ΔX value is the difference between the measured X value of the object to be matched and the X value of the match calculated from the initial concentrations. The partial derivatives of X with respect to concentration are calculated from the initial match concentrations. The values for Y and Z are calculated in the same fashion. The details of these calculations can be found in the cited references. The resulting four equations are solved for the four unknown Δc_{i} values, and a new set of match concentrations are calculated by adding the Δc_{i} values to the initial estimate of c_{i} values used to set up these equations. The process is repeated until a tristimulus match or no further improvement in the match is obtained. Usually, the best tristimulus match with the four chosen pigments is obtained in less than three iterations.

If the four colorants chosen are close to or identical with the colorants in the object to be matched, a nonmetameric match results. If the degree of metamerism as judged by the variation in color difference between the object and match for two or more illuminants is unacceptable, different four pigment combinations can be tried until an acceptable match is attained.

Matching of metallic colors has been more difficult to computerize because the colors have to match at multiple *aspecular angles*, angles with differences between the angle of illumination and the angle of viewing. The reflectances of the samples and all of the colorants in the database must be determined at multiple angles. Instruments are now available that measure at a variety of aspecular angles. The angle of illumination is fixed and the angle of viewing can be set at different angles. In the United States, the accepted aspecular angles are 15°, 45°, and 110°. (See ASTM E-12.12, Standard Practice for Multiangle Measurement of Metal Flake Pigmented Materials.)

Matching colors with pearlescent flakes, interference, and cholesteric pigments is further complicated by changes in hue as a function of angle of illumination and angle of viewing (Section 20.2.5). Instruments are now available that have three illuminating angles (i.e., 25°, 45°, and 75°) with viewing angles for each of the illuminating angles of $+15^\circ$ and -15°, but research continues, and more elaborate geometries may be needed [17].

Other information on the colorants, such as cost, properties, regulatory restrictions, and so on, can be built into the database. The computer can then calculate a series of alternative colorant combinations selected for lowest cost, least degree of metamerism, excluding pigments with inadequate exterior durability, and so on. The formulator can then choose the most appropriate combination for the particular color-matching assignment. The formulator then makes up an experimental batch of paint, applies it to the appropriate substrate, bakes or dries it, and measures the reflectance values. The result is seldom a satisfactory color match on the first attempt. Reflectance values of the first hit are compared instrumentally with those of the standard, and the computer calculates the amounts of the various colorants needed so that the color will match. The number of hits required to make color matches has been found to be significantly less using computer color matching than the number required by even experienced visual color matchers.

The same program is used in production of factory batches of colored coatings. The colorants to be used have already been selected and must not be changed. The laboratory formulation is used for the initial mix, but a fraction of each of the colorants is held back.

(Otherwise, if the factory batch of some pigment dispersion were stronger than standard, too much of that colorant would be put in.) The batch is mixed, a panel is coated, and its reflectance is measured. The data are then used to calculate what additions have to be made to the batch to obtain a color match. If necessary, the process is repeated. The savings in time and hence in cost using computer color matching can be large, but the cost of establishing and maintaining the database is substantial. Since the colors of pigment dispersions vary from batch to batch of pigment and of pigment dispersion, measurements of each batch usually have to be made for comparison with the standard database values. Computer programs can be written to correct for small differences in the colors from batch to batch.

19.10. GLOSS

Gloss is a complex phenomenon. Individuals frequently disagree on the visual assessment of gloss and generally do not have in mind a clear definition of gloss, partly because there are several types of gloss. *Specular* (mirror-like) *gloss* is the type most often considered in coatings. A high gloss surface reflects a large fraction of the light that is reflected from the surface at the *specular angle*, that is, the angle of reflected light equal to the angle of the incident light beam. Lower gloss surfaces reflect a larger fraction at nonspecular angles. When considering gloss, people visually compare the amount of light reflected at the specular angle with the amounts reflected at other angles. If the contrast in reflection is high, gloss is said to be high. Note that gloss is ***not***, as seems to be commonly assumed, directly related to the fraction of light reflected from the surface. The fraction of light reflected at a surface increases as the angle of illumination increases (Figure 19.5). At most angles of illumination, surface reflection from a low gloss surface is greater than from a high gloss surface. Surface reflection at the specular angle increases as the refractive index of an object increases (Figure 19.5).

If a surface is rough on a micro scale, the angle of incidence of a beam of light is not the same as the geometric angle of the surface with the light beam. Light is reflected at specular angles between the light beam and individual rough facets of a surface. If a surface has many small facets oriented at all possible angles, a beam of light is reflected in all directions. Such a surface is a *diffuse reflector* and has a low gloss; it is called *matte* or *flat*. *Flat* is unfortunate terminology, since a perfectly smooth (flat) surface gives high gloss, whereas a microscopically rough surface gives what we call a *flat surface*. At intermediate surface roughness, the gloss is intermediate and is called *semigloss*, *eggshell*, *satin*, or a variety of other terms.

A phenomenon related to specular gloss is *distinctness-of-image* (DOI) *gloss*. A perfect specular reflector is a perfect mirror with an image that exactly mimics the original. If a surface has perfect diffuse reflection, no mirror image can be seen. At intermediate stages, the image is more and more blurred as the ratio of specular to diffuse reflection decreases. Furthermore, larger surface irregularities lead to distortion of the image. Commonly, one sees some degree of both blurring and distortion.

Sheen, as the term is used in the coatings industry, refers to reflection of light when a low gloss coating is viewed from near a grazing angle. A high gloss coating reflects a high fraction of light whose angle is near grazing. Reflection from most low-gloss surfaces is low at a grazing angle. A low gloss coating is said to have a high sheen if there is significant reflection at a grazing angle. The effect is easy to see but difficult to describe; there is not a glare (as when a glossy surface is illuminated and viewed at a grazing angle) but a "soft," relatively high reflection.

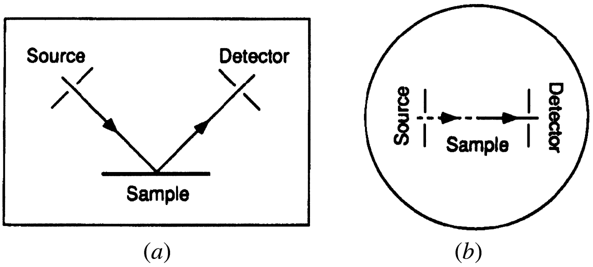
Luster is another type of gloss effect. (To illustrate the problem of defining gloss, a dictionary definition of luster is: gloss, sheen.) Luster is directional gloss. For example, some woven fabrics are much glossier when viewed parallel to the warp than when viewed parallel to the woof. Such fabrics exhibit variations in gloss looking at folds in a draped fabric. If the contrasts are great, the fabric is said to have a high luster. Similar effects can sometimes be observed in textured coatings.

Haze can be said to be a form of gloss. When light enters a hazy film, it is scattered to some degree, causing some diffuse reflection to reach the eye of the observer. The result is similar to having some of the light reflected at nonspecular angles at the surface. The contrast between the fractions of light reflected at specular and nonspecular angles is reduced. In pigmented coatings, it may be difficult to distinguish visually between gloss reduction resulting from haze and from scattering of light by a pigment. It is always desirable for a formulator to make a batch of coating with no pigment to check the clarity of a dried, cross-linked, pigment-free film.

Bloom gives a similar effect to haze. If a liquid component of a coating film is not soluble in the resin binder, it can separate from the body of the film in small droplets. These can come to the surface, making it uneven, diffusing light beams striking the surface and reducing gloss. In contrast to haze, bloom can be wiped off a surface with a cloth damp with solvent for the blooming material; commonly, bloom reappears.

19.10.1. Variables in Specular Gloss

Some of the variables of specular gloss can be visualized by use of schematic diagrams based on hypothetical measurements by an idealized goniophotometer. A goniophotometer is an instrument in which a beam of light can be directed at a surface at any angle of incidence and can measure the amount of light reflected at any angle in the same plane as the incident beam. A schematic representation of an idealized instrument is shown schematically in Figure 19.17. Figure 19.17(*a*) shows a cross section through the plane of the beam of light. Figure 19.17(*b*) shows a schematic view looking down on the instrument. The drawing shows that the only light detected by the photometer is that reflected in the plane of the beam of light. No instrument can measure light reflected at all angles in all planes. Also, there is no way to build an instrument that would measure light reflected at 90°. In this idealized instrument, the beam of light is narrow enough so that only a point on the surface is illuminated, and the photometer can detect a reflected beam with a beam width approaching zero.



(*a*) (*b*)

Figure 19.17. Simplified representation of a goniophotometer.

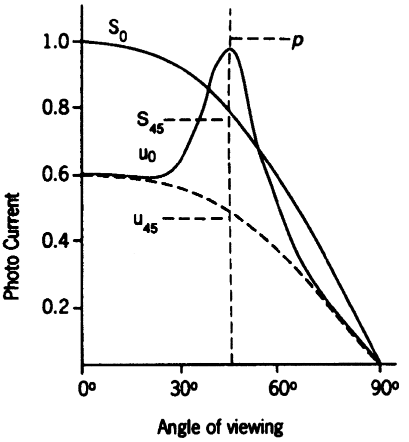


Figure 19.18. Schematic representation of the photocurrent reflected as a function of angle of viewing. (From Ref. [18], with permission).

All light reflected from a perfect mirror is at the specular angle and in the same plane as the beam of light. From a perfect diffuse reflector, light is reflected at all angles in all planes. Line S_0 in Figure 19.18 shows photocurrent as a function of angle of viewing from a perfect diffuse reflector illuminated at 45°, as measured by an ideal goniophotometer [18]. At first glance, the results do not seem rational, but it must be recalled that the photometer can measure all the light reflected at 0° and only a fraction approaching zero of the light reflected in all planes at 90°.

Also shown in Figure 19.18 is the idealized response curve u for a semigloss white coating. Comparison of these two curves illustrates three factors important in considering specular gloss. First is the *relative brightness* A of the sample compared to that of the diffuse reflector. Here A is the ratio of light intensities in the perpendicular direction u_0/S_0. Second is *height-of-gloss*, h, which is calculated from the *peak height*, p:

$$h = \frac{P - u_{45}}{S_{45}} = \frac{p}{S_{45}} - \frac{A}{100} \tag{19.8}$$

Third is the *distinctness-of-image* aspect of gloss δ: as defined by Eq. 19.9, in which P is the total area under the sample curve, U is the area of diffuse background reflection from the sample, and S is the area under the standard diffuse reflector curve.

$$\delta = \frac{h}{F} \qquad F = \frac{P - U}{S} \tag{19.9}$$

If A is large, an observer will consider the gloss of a sample to be lower than that of a sample with lower A. If h is small, the gloss of a panel will be lower than that of a sample with higher h. It is instructive to compare a white gloss coating with a black gloss coating. A is larger and h is smaller for the white coating because white scatters light that enters a film, resulting in a high extent of diffuse reflection. On the other hand, a black coating absorbs almost all the light entering its film, so there is little diffuse reflection from within the film. If the surfaces of the two films are equally smooth, the surface reflection is equal, but the black coating will be seen as glossier, even though it reflects less of the incident light. It is impossible to make a white coating with as high a gloss as that of a high gloss black coating. The possible gloss of colored coatings is intermediate; the darker the color, the higher the potential gloss. We saw in Section 19.2.4 that gloss affects color; now we see that color affects gloss. If the value of δ is high, the surface acts as a mirror, giving a clear image. As the value of δ decreases, there is more and more blurring of the specular image.

One must be careful when comparing these values with observer evaluation of gloss. As has already been stated, different observers rate the gloss of pairs of panels differently. Intensity of reflection (peak height) is not a major factor in an observer's evaluation of gloss; the principal factors are the contrast between reflection at the specular angle and the distinctness of image. Gloss is also affected by the distance between the observer and an object. An observer who is close enough to resolve irregularities on the surface visually will say that a surface is a rough, high gloss surface. On the other hand, one observing the same surface at a greater distance, which does not allow visual resolution of the irregularities, will say that it is a smooth, low gloss surface.

The major factor controlling gloss of coatings is pigmentation. As a film shrinks with volatile loss, pigment particles can cause irregularities in the surface. Roughness of the surface varies with the ratio of pigment volume concentration (PVC) to the critical pigment volume concentration (CPVC) in the dry film (Section 22.1). (The effect of pigmentation on gloss as solvent evaporates is discussed in Ref. [19].)

In solventborne high gloss coatings, the pigment concentration in the top micrometer or so of a dry film contains little, if any, pigment. This pigmented-depleted layer results from the motions within a film as solvent evaporates. Initially, convection currents are set up within the film; and both resin solution and dispersed pigment particles move freely. As solvent evaporates, the viscosity of the film increases and movement of pigment particles is slowed. Movement of resin solution continues longer, so the top surface contains little pigment. Application of a clear top coat over a pigmented base coat can increase gloss.

As PVC increases, the amount of pigment at the surface increases, decreasing gloss. Particle size of the pigment affects gloss; if aggregates of pigment are not broken up in the dispersion process, gloss will be lower. Flocculated pigment systems have a lower CPVC, so at the same PVC there will usually be a greater likelihood of low gloss. However, since large particles stop moving before small ones, flocculated particles will stop moving sooner than well stabilized ones, which can lead to increased gloss in low-PVC coatings. (The effects of pigment particle size and clear-layer thickness on specular gloss are discussed in Refs. [20] and [21].)

In some coatings (e.g., furniture lacquer), it is desirable to have a low gloss but still a high degree of transparency. This is accomplished using a small quantity of very fine particle size silicon dioxide as a pigment. The combination of small particle size and low refractive index difference results in minimal light scattering as long as concentration is low. When solvent evaporates from such a lacquer, the SiO_2 particles keep moving until the viscosity of the surface of the film becomes high. The result is a higher than average concentration of pigment in the top of the film, reducing gloss at relatively low PVC.

Poor leveling can reduce gloss. If the irregularities are large, as is commonly the case with brush marks, the surface is seen as a glossy, but wavy surface. However, if the irregularities are small, as is commonly the case with orange peel, gloss will be rated as lower. An irregular surface can result from poor leveling over a smooth surface but can also be the result of applying a coating over a rough substrate. It has been shown that smoothness and gloss are affected by the extent of roughness of a substrate, film thickness, and viscosity [22]. (See Section 24.2 for further discussion of leveling.)

Wrinkling affects gloss. If the surface of a film cross-links before the lower layers of the film, wrinkling is likely to occur (Section 24.6). When the lower layers cross-link, shrinkage occurs, causing the top of the film to pucker up in wrinkles. If the size of the wrinkles is small enough, gloss will be low, but looked at in a microscope, the surface can be seen to be an irregular glossy surface.

Since the fraction of light reflected at a surface increases as refractive index increases, gloss of high gloss coatings tends to increase as refractive index of a coating increases, since the contrast between reflection at the specular angle and other angles is greater. Refractive index differences between different binders are small, so although detectable, this effect is generally small compared to surface roughness [17,18]. Refractive indexes of pigment can also have an effect.

Latex coatings generally exhibit lower gloss than solventborne coatings at equal levels of pigmentation in dry film (Section 32.3). There are several reasons for this:

1. Latex coatings have both resin and pigment particles as dispersed phases. During drying of a latex paint film, there is not the same opportunity for separation to give a pigment-depleted thin layer at the top of the film as in a solvent coating. Latexes with smaller particle size give somewhat higher gloss films than do larger particle size latexes. Some difference in segregation may occur, since large particles stop moving first as a film dries.
2. Pigment-free dry films of many latexes are not transparent; they are hazy, reducing gloss. The haze is due to the presence of dispersants and water-soluble polymers that are not completely soluble in the latex polymer.
3. Fairly commonly, surfactants bloom to the surface of a latex coating, reducing gloss.
4. It is generally more difficult to achieve good leveling with latex coatings. Surface roughness such as brush marks reduce gloss. The effect of brush marks depends on how close an observer is to the surface. If one is close enough to resolve the brush marks visually, the coating can look like a wavy, gloss surface. From a greater distance, the gloss appears to be low.

Gloss can change during the life of an applied film. In some cases the surface of the film embrittles and then cracks as the film expands and contracts. Generally, this mechanical failure is progressive, and after initial loss of gloss, there is film erosion. In other cases, especially clear coats, erosion occurs first, and loss of gloss is evident only after erosion is deep enough to cause protrusion of pigment particles of the base coat. Erosion of binder in pigmented films can proceed to a stage in which pigment particles are freed from binder on the surface and rub off easily; this phenomenon is called *chalking*. Chalky surfaces have dramatically lower gloss, and the color therefore, changes to a lighter color. Loss of gloss can also result from loss of volatile components after a film is exposed; this causes film shrinkage and increases surface roughness [23]. (An excellent review of durability and gloss appears in Ref. [23].)

In some cases, the gloss of a low gloss surface increases with use. It is fairly common for the gloss of flat wall paints to increase if rubbed, for example, near a light switch. This increase in gloss is called *burnishing*.

19.10.2. Gloss Measurement

No fully satisfactory method for measuring gloss is available, and no satisfactory rating scale for visual observation of gloss has been developed. Although all people will agree as to which film is glossier if the gloss difference is large, they frequently disagree in ranking if the difference is small. Even the same observer experiences difficulty in consistently ranking a series of panels if the differences in gloss are small.

Caution must be exercised in using instruments that measure gloss. In Section 19.10.1 we discussed an idealized goniophotometer. In practice, one has to accept less than this ideal. The beam diameter cannot actually approach zero because there must be sufficient light intensity reflected from all angles to give a measurable response on available photodetectors. In real instruments there is a light source shining on a slit aperture at a fixed distance from a sample surface. The reflected light goes through another slit aperture at a fixed distance to a photodetector.

Specular gloss meters are widely used, but correspondence between meter readings and visual comparisons is limited. Such instruments give significantly different readings with differences in intensity of reflected light, but observers are relatively insensitive to such differences. Furthermore, the aperture of the slit in a gloss meter is about 2°, whereas the limit of resolution of a human eye is about 0.0005° of arc [19]. A gloss meter is therefore less sensitive to distinctness-of-image than the eye (when the observer is close to the object). The distance between the aperture and a panel is fixed in a gloss meter, whereas a person can view a panel from any distance.

The most widely used gloss meters, also called reflectometers, are simplified goniophotometers in which one measures a response only at the specular angle. Those most commonly used in the coatings industry can make measurements when the angles of incidence and viewing are 20°, 60°, and 85°. A schematic drawing is shown in Figure 19.19. The first step for using a gloss meter is to calibrate the instrument with two standards: one with high gloss and the other with a lower gloss. If the second standard does not give the standard reading after the instrument is set with the first standard, something is wrong; most commonly, one or both of the standards is dirty or scratched. Other possible problems include panel misalignment, deterioration of the light source, or a malfunction of the photometer. One must use the standard that has been calibrated at the angle selected. Black and white standards are available. Reflection at the specular angle is not the

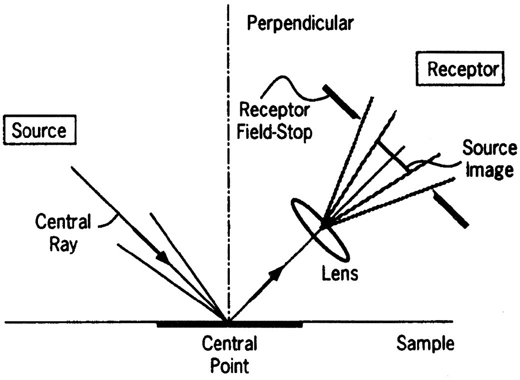


Figure 19.19. Gloss meter. (From Ref. [18], with permission.)

same from a white and a black standard with equal surface roughness (Section 19.10.1). It is not feasible to have standards of all different colors; white standards are used for light colors and black standards for dark colors. (One should always report which set of standards is used.) Standards are standardized by NIST using a research goniophotometer, as described in Ref. [24]. In contrast to gloss meters, such research instruments allow both angles of illumination and viewing to be varied independently; but they are expensive and relatively difficult to maintain.

In normal practice, one first measures at 60°. If the reading obtained is over 70, readings should be made at 20° rather than at 60° since precision is higher nearer the midpoint of the meter reading. It is common to read low gloss panels at both 60° and 85°. Readings at 85° may have a relationship to sheen. It is essential to report the angle at which readings are made. Multiple readings should be taken and analyzed statistically. This reduces the probability that local surface irregularities or dirt particles are affecting the meter reading. It has been said that slight brush marks do not affect readings if the direction of the brush marks is parallel to the plane of incidence. If results are to be compared between two laboratories, it is essential to check the compatibility of their instruments. This is best done by measuring at least three black and three white standards on each instrument. Readings are reproducible on carefully calibrated instruments to ±3%, but it is better to express error in terms of units, such as ±2 gloss units [25]. This is a high percentage of error in the low gloss range.

Gloss meters give results in numbers between 0 and 100, but there is confusion as to what the numbers mean. Commonly, though undesirably, they are expressed as percentages. It is better to call them gloss units or just meter readings. They are ***not***, as some people seem to believe, the percentage of light reflected at the surface. They are closer to being the percentage of light reflected at that angle compared to the reading that would be obtained if a perfectly smooth surface were measured. As noted previously, the total reflection from a black matte surface is much higher at most angles of illumination and viewing than that from a high gloss black surface. The point can be emphasized by comparing meter readings of the same panels at 20° and 60°. Meter readings are lower for the same panel when the setting is 20° than when it is 60° [26] (Figure 19.20).

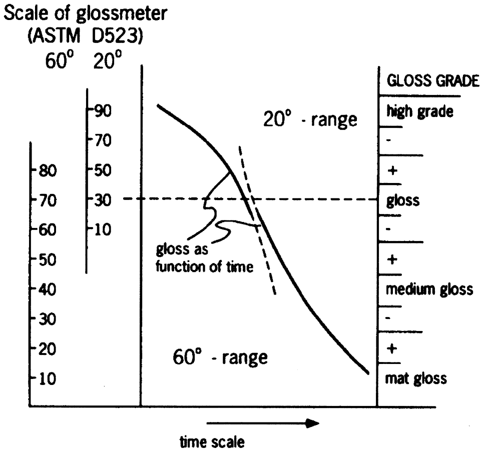


Figure 19.20. *Transition of gloss readings according to Freier [26]. (From Ref. [18], with permission.)*

With sufficient care, the instruments can be used for quality control comparisons of lots of the same or very similar coatings and for following loss of gloss on aging. For specification purposes other than quality control, specular gloss meters are not appropriate, and one must rely on standard visual panels. The customer selects three panels of each color, one with the desired gloss and the others representing the upper and lower acceptable limits.

Figure 19.20 also illustrates a procedure to follow loss of gloss when a high gloss panel is exposed to exterior weathering. Initial readings were taken at 20°, then after some exposure, at both 20° and 60°, then for panels that have shown considerable loss of gloss only at 60°. Different scale units in the 20° and 60° readings (left) provide for a continuous slope at the transition point. The right scale designates gloss grade as observed visually.

Distinctness-of-image (DOI) meters rely on using the sample as a mirror (Figure 19.21). The reflection of a grid on the surface of the panel is compared visually to a set of photographic standards ranging from a nearly perfect mirror reflection to a blurred image in which the grid cannot be detected. One reports a comparison of the degree of blurring and also a qualitative statement about distortion. Correspondence with visual assessment in the high gloss range is better than that with specular gloss meters. Instruments are available to make comparisons based on optical density rather than relying on visual comparisons.

Newer instruments with linear diode array detectors are being made which permit multiple measurements of light reflected at small angle increments without using an aperture in front of the detector [27]. Computerized instruments make multiple measurements of reflectance from small areas (approximately 100 μm in diameter) over a 10 cm^2 area. This permits separation of the reflection from micro roughness and macro roughness, thus giving a numerical rating for gloss and a separate measurement of macro roughness, such as orange peel or texture.

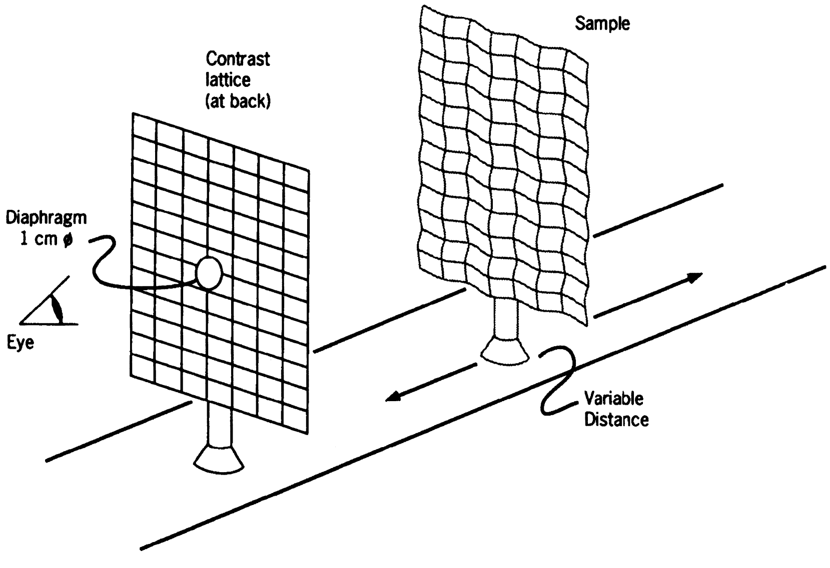


Figure 19.21. DOI meter. (From Ref. [18], with permission.)

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20

Pigments

Pigments are insoluble fine particle size materials used in coatings for one or more of five reasons: to provide color, to hide substrates, to modify the application properties of a coating, to modify the performance properties of films, and/or to reduce cost. Pigments are divided into four broad classes: white, color, inert, and functional pigments. Pigments are insoluble materials used as colloidal dispersions. Dyes are soluble colored substances; they are used in only a few specialized coatings, such as stains for wood furniture (Section 31.1.1). Some pigments are called *lakes*. The original meaning of *lake* was a dye that had been converted into a pigment by irreversible adsorption on some insoluble powder. The term *lake* is now sometimes used when a colored pigment is blended with an inert pigment. When the pigment is essentially all color pigment, it is sometimes called a *toner*.

Particle size affects color strength, transparency or opacity, exterior durability, solvent resistance, and other properties of pigments. For any given pigment, the manufacturer selects the most appropriate compromise for the particle size and designs the process to produce that average particle size consistently. The manufacture of most pigments involves precipitation from water; the process conditions determine the particle size. Many pigments are surface treated during or after precipitation. The precipitated pigment is filtered and the filter cake is dried. During drying, pigment particles become cemented together in aggregates. The coating manufacturer generally receives pigment from the pigment manufacturer as a dry powder of aggregates and must disperse these aggregates to break them up to their original particle size and make a stable dispersion (Chapter 21).

Organic Coatings: Science and Technology, Third Edition, by Zeno W. Wicks, Jr., Frank N. Jones,
S. Peter Pappas, and Douglas A. Wicks

20.1. WHITE PIGMENTS

A large fraction of coatings contain white pigment. White pigments are used not only in white coatings, but also in a substantial fraction of other pigmented coatings to give lighter colors than would be obtained using color pigments alone. Furthermore, many color pigments give transparent films, and the white pigment provides a major part of the hiding power of the coating. As discussed in Section 19.2.3, the ideal white pigment would absorb no visible light and would have a high scattering coefficient. Since a major factor controlling scattering efficiency is the difference in refractive index between the pigment and the binder, refractive index is a critical property of a white pigment. Reference [1] is a monograph on white pigments.

20.1.1. Titanium Dioxide

The most important white pigment used in coatings is TiO_2. Purchases of TiO_2 by U.S. coatings companies in 2002 were $868 million [2]. The technology of TiO_2 pigments is reviewed in Refs. [1] and [3]. The factors affecting the hiding power of TiO_2 are discussed in Refs. [1] and [4]. Two different crystal types are used: *rutile* and *anatase*. Rutile is used in larger volume primarily because it gives about 20% greater hiding power than anatase; the average refractive index of rutile is 2.73, compared to 2.55 for anatase. On the other hand, rutile absorbs some violet light, whereas anatase absorbs almost no visible light (Figure 20.1). Whereas a coating pigmented with only rutile looks white, it looks yellowish alongside a coating pigmented with anatase.

The color of rutile TiO_2 coatings can be adjusted by tinting. If one adds a small amount of a dispersion of a violet pigment, such as carbazole violet, the white coating obtained is less yellow. The violet pigment strongly absorbs wavelengths other than violet and

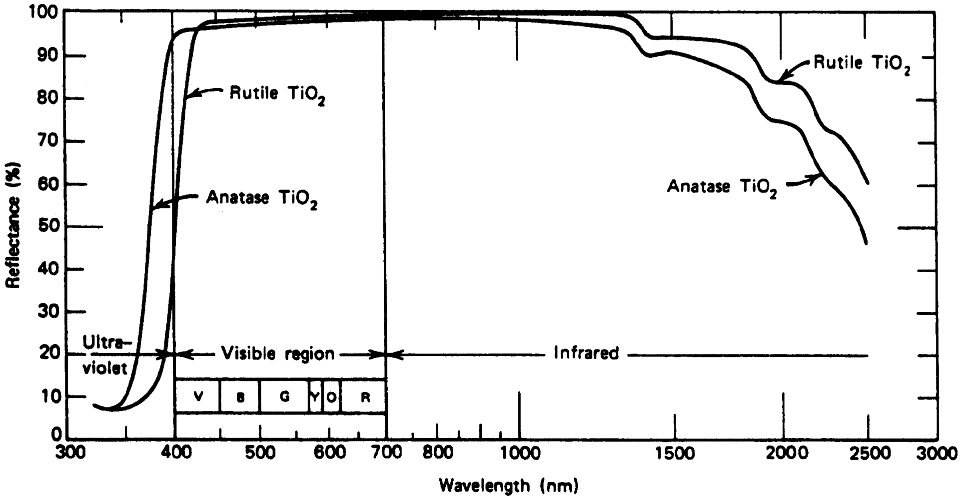


Figure 20.1. Reflectance spectra of rutile and anatase and anatase TiO_2 coatings. (From W. A. Kampton in Ref. [5a], Vol. I, p. 2, with permission.)

reduces the difference in reflection of the violet wavelengths compared to the others. This makes the coating a light gray, but unless there is a higher reflectance white present for comparison, it is seen as white, not gray. At the same time, there is the added advantage that hiding power is increased due to the additional light absorption. Phthalocyanine blue is also used as a tinting pigment. Phthalocyanine blue does not give as "white a white" as carbazole violet, but it is less expensive and gives slightly improved hiding. The most common tinting pigment used in whites is carbon black. Carbon black is less expensive than either violet or blue pigments, and gives a greater increment to hiding. Since carbon black absorbs all wavelengths of light, it does not reduce the yellowness of the white but provides a lower cost method of increasing hiding. "Transparent TiO_2" (i.e., very fine particle size TiO_2) is used in metallic automotive coatings to give a frosted effect.

In white pigmented UV cure coatings, the lower absorption of near UV radiation by anatase TiO_2 is an advantage over rutile, since there is less interference with absorption of UV radiation by photoinitiators. Another difference between rutile and anatase TiO_2 is in their photoreactivity. Anatase pigmented coating films fail more quickly on outdoor exposure by *chalking* than do rutile pigmented films. Chalking is the formation of loose particles on the exposed coating surface resulting from the erosion of binder by photodegradation (Section 5.2.4). Chalking is usually undesirable, although *self-cleaning* white house paints are deliberately formulated with anatase TiO_2, so they chalk readily. When the surface of the film erodes away, dirt accumulation is also removed, so that the paint surface stays whiter.

In most exterior applications, chalking must be minimized, and rutile TiO_2 is used. However, although rutile is less photoreactive than anatase, it is still sufficiently reactive to reduce exterior durability. The problem is minimized by treating the surface of the TiO_2 particles during pigment manufacture [1,3]. The most common surface treatments are silica (SiO_2) and/or alumina (Al_2O_3); a variety of other metal oxides are also used with silica and/or alumina. A typical surface treatment for exterior grades of rutile is about 6 wt% silica and 4 wt% alumina. An ideal surface treatment would be a continuous shell on all TiO_2 particles to prevent contact between the TiO_2 and the binder. Perfection has not been achieved, but the best chalk-resistant grades of rutile with a shell of SiO_2 show little acceleration of degradation. The best treated anatase pigments accelerate chalking more than do treated rutiles, but much less than does untreated anatase pigment. Since TiO_2, especially rutile, absorbs UV strongly (Figure 20.1), it competes with the binder in a coating for UV absorption. If chalk-resistant grades are used, the reduced UV absorption by the binder tends to enhance exterior durability.

Surface treatment also affects other properties of the pigments. Alumina treatments improve dispersibility in solventborne coatings. However, alumina can partly neutralize acid catalysts, such as those used with coatings containing Class I MF resins, reducing cure rates (Section 11.3.1). Specially treated TiO_2 pigments permit production of more stable dispersions in waterborne coatings. TiO_2 dispersions in water, called *slurries*, are used in the manufacture of latex paints (Section 21.3). The slurries are manufactured by the TiO_2 producer and shipped in tank cars or trucks to replace dry pigment. The price on a pigment basis is about the same, but the slurry is a pumpable liquid, and aggregation of pigment particles is minimized, so there are substantial savings in material handling and dispersion costs.

A variety of TiO_2 pigments is offered by each TiO_2 manufacturer. Formulators need to be aware of the differences among the types. Some are designed for maximum exterior durability, some to provide maximum gloss, some are more easily dispersed in water systems, and others are more easily dispersed in solvent systems. The TiO_2 content of the various types of pigments varies from as high as 98% to as low as 75%. Generally, the hiding varies with TiO_2 content, so the amount of TiO_2 needed for hiding varies with pigment type. Another consideration is the range of particle sizes; the broader the range, the larger the fraction of particles that provide less than optimum hiding. Coating performance problems and economic waste have resulted from use of the wrong type of TiO_2 and from indiscriminate substitution of one type for another.

20.1.2. Other White Pigments

Until the late 1930s, white lead [basic lead carbonate, $2PbCO_3 \cdot Pb(OH)_2$] was widely used as a white pigment. Its relatively low refractive index, 1.94, gives low hiding power, less than one-tenth that of rutile TiO_2. When TiO_2 became available, the use of white lead dropped rapidly. White lead is somewhat soluble in water and presents a toxic hazard. Many children suffer from lead poisoning attributed to eating paint containing white lead that peels from the walls and woodwork in older buildings. As a result, the lead content of any paint sold to retail consumers through interstate commerce in the United States is limited to 0.06% of the dry weight. Lead poisoning should not automatically be assumed to result from lead paint. There are other possible sources of lead exposure, including contaminated dirt.

Zinc oxide, ZnO, was formerly used as a white pigment, but because of its low refractive index, 2.02, it cannot compete for hiding power with TiO_2. As discussed in Section 20.4, ZnO is used in exterior house paints as a fungicide and in some can linings as a sulfide scavenger. About 15 million pounds of ZnO was used in coatings in 2004 [4]. Zinc oxide should not be used in primers because it is somewhat water soluble and can therefore induce blistering by osmotic pressure when water vapor penetrates through the top coats into the primer coat. Other white pigments, important at one time but largely obsolete, are zinc sulfide (ZnS), with a refractive index of 2.37, and lithopone, $ZnS/BaSO_4$.

Small air bubbles scatter light and are another white "pigment." In some cases, cost reductions are possible by taking advantage of the scattering by air bubbles in coating films. The refractive index of air, 1.00, gives a refractive index difference of about 0.50 in a typical binder. Although this difference is small compared with the difference of 1.25 between binder and rutile TiO_2, it still provides some light scattering, and hence hiding. A common way of incorporating air bubbles in a coating film is by use of such high levels of pigmentation that after the solvent evaporates, there is not enough resin to adsorb on all the pigment surfaces and to fill all the interstices between the pigment particles. The result is air voids, which increase hiding. Such coatings are said to be formulated at pigment volume levels above the *critical pigment volume concentration* (CPVC) (Chapter 22). Since interfaces between TiO_2 and air are developed, the very large refractive index difference of 1.75 is especially effective in increasing hiding. However, the voids make the film porous and reduce the protective properties of the films. In ceiling paints, advantage is taken of the added hiding, since requirements for other properties are not as important.

Particles containing air bubbles provide added hiding from the air–resin interface without imparting porosity. For example, high T_g latexes containing water trapped within the particles are available and are finding increasing use in latex paints as a partial replacement for TiO_2 [7]. The latexes are prepared by sequential emulsion polymerization [8]. Initially, a low T_g latex copolymer of acrylic acid and acrylic esters is prepared; the particles are swollen with water, especially at alkaline pHs. These core particles are encapsulated in shells of high T_g cross-linked polymer such as a styrene–divinylbenzene copolymer. When the paint is applied and the water evaporates, the conventional latex particles of the binder coalesce to form the film, but the high T_g latex particles do not coalesce. Water diffuses out of the particles, leaving air bubbles within the particles, which add to the hiding.

20.2. COLOR PIGMENTS

A wide variety of color pigments is used in coatings. References [6] and [9] provide detailed discussions of their chemistry, properties, economics, and uses, and Ref. [10] gives a more condensed coverage of organic pigments. First, it is appropriate to summarize the considerations involved for selecting color pigments for a particular coating application.

1. *Color*. The first criterion is the color of the pigment. Pigment suppliers provide technical bulletins that contain color chips showing the color obtainable with each pigment. Generally, there are two or three color chips for each pigment. The *mass tone* is displayed by a color chip in which the pigment is used as the sole pigment in the coating. Then there are one or two additional color chips showing the color obtained when the pigment is used together with TiO_2 in different ratios; these are called *tint colors*. In some cases, color chips showing the effect with added aluminum flake pigment (Section 20.2.5) are also provided.

2. *Color strength*. Some colorants are strong and others weak, corresponding to the absorption coefficients and particle sizes of the pigments. It may well be more economical to use a strong, expensive (i.e., high cost per unit volume) pigment than a weak, lower cost pigment.

3. *Opacity or transparency*. Depending on the end use, it may be desirable to use a pigment that increases hiding by both scattering and absorbing radiation, or it may be important to select pigments that scatter little, if any, light in the coating film so that a transparent color can be obtained.

4. *Ease of dispersion*. Some pigments are more easily dispersed than others. If everything else were equal, one would select the most easily dispersed pigment. Many pigments are surface treated by the manufacturers to enhance their ease of dispersion. (See Ref. [11] for a review.) Many types of surface treatment have been used, including adsorption on the surface of a molecule with a structure similar to that of the pigment, but with polar groups to enhance dispersibility; monolayers of polymers; and more recently, layers of inorganic oxides on the surface of organic pigments [12]. Pigment dispersion is a complex phenomenon involving several factors; it is discussed in detail in Chapter 21.

5. *Exterior durability*. Some pigments are more sensitive than others to photodegradation, which leads to loss of color or change of hue. Pigment manufacturers provide data that can be useful for screening pigments that may be appropriate for use outdoors. However, there can be significant variation in exterior durability, depending on the combination of pigment and resin. Therefore, for critical applications, the durability of specific

formulations must be determined. (See Chapter 5 for discussion of and testing for exterior durability.) A related property is *light fastness*. This term is usually applied to the ability of pigments to resist fading when used indoors. ASTM classes pigments in five light fastness grades, I to V. Only those classed I or II are suitable for applications where long-term color stability is critical, such as in artist paints.

6. *Heat resistance*. Coatings that are baked or exposed to high service temperatures require heat resistant pigments. A few pigments (e.g., yellow iron oxides) undergo chemical changes with heat. A more common problem is that some organic pigments slowly sublime at elevated temperatures.

7. *Chemical resistance*. In use, many coatings are exposed to chemicals, most often to acids and bases, and the pigments must resist color change under those conditions. For example, automobiles are exposed to acid rain, and home laundry machines are exposed to alkaline detergents.

8. *Water solubility*. In most applications, pigments with any significant water solubility are best avoided because they leach out of a film, resulting in loss of properties. The presence of water-soluble substances in a primer can lead to blistering of the film when water permeates through it. In latex paints, water-soluble materials can reduce the stability of the dispersion of the latex particles. The stability of colloidal aqueous dispersions can be particularly affected by the presence of low concentrations of polyvalent salts. On the other hand, pigments that help protect against corrosion by passivation (Section 20.4) must be somewhat soluble in water to be effective (Section 7.4.2).

9. *Solvent solubility*. Partial solubility of pigments in some solvents can be a problem. For example, if one is making a red coating for a bicycle that is to have a white stripe on the red coating, the red pigment must not dissolve in solvents used in the white striping coating. If the red pigment is somewhat soluble, the stripes will become pink. Such pigments are said to *bleed*.

10. *Moisture content*. Most “dry” pigments adsorb small to moderate amounts of water. The adsorbed water can cause serious problems with water-reactive binders such as polyisocyanates.

11. *Toxic and environmental hazards*. Filter face masks should always be worn when handling dry powder pigments; it is dangerous to inhale fine-particle dusts, even if they are chemically inert. In most cases, there is little or no hazard once the pigment is incorporated into a coating. However, toxicity, even in a coating film, can be important. For example, as mentioned previously, white lead is no longer permitted in architectural coatings in the United States. Lead-containing pigments are also prohibited in coatings for children’s toys and furniture. Zinc chromate pigments are generally thought to be human carcinogens. In some countries, their use in coatings is prohibited; regulations can be expected to become increasingly restrictive. Another factor that can affect pigment choice is the increasing cost of disposal of materials containing heavy metals.

12. *IR reflectance*. Inorganic pigments that reflect, rather than absorb, infrared radiation are available in a variety of colors. They are known as *complex inorganic color pigments* and as *ceramic colorants*. Many have excellent outdoor durability, and when used on building roofs and siding, their IR reflectance significantly reduces solar heating, saving energy in hot climates. Combinations of color pigments that absorb all visible wavelengths give black; thus, these pigments can be formulated to make gray paints with much less IR absorption than grays made with carbon black pigments.

13. *Cost*. Cost is important, but as noted earlier, one cannot tell which pigment is the least expensive by just looking at the price per unit weight. The critical question is: How much will the final coating cost on a volume basis? The answer is affected by color strength and density as well as price.

Purchases of inorganic color pigments by U.S. coating companies in 2002 totaled $327 million; those of organic pigments were $453 million [2].

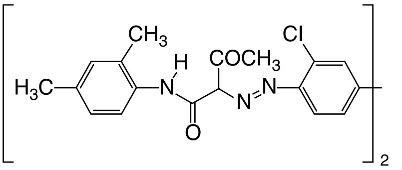
20.2.1. Yellow and Orange Pigments

20.2.1.1. Inorganic Yellows and Oranges Iron oxide yellows, FeO(OH), are low chroma brownish-yellow pigments. They give opaque films with good hiding and high exterior durability; chemical and solvent resistances are excellent. The pigments are generally easily dispersed and are comparatively inexpensive. When heated above 150°C, they gradually change color to a low chroma red because they dehydrate to form iron oxide red, Fe_2O_3. Most iron oxide yellows are made synthetically, but some natural ore ochre pigments are used. In some cases, particularly with the natural pigments, the presence of soluble iron and other metal salts can affect the stability of coatings, which cure by a free radical mechanism. Extremely fine particle size iron oxide pigments are also available; they are used when transparency is required. This effect of particle size on opacity is an excellent example of the relationship between light scattering and particle size (Section 19.2.3).

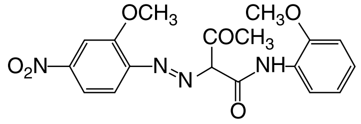
Chrome yellow pigments are bright, high chroma yellows. Medium chroma yellow pigments are predominantly lead chromate ($PbCrO_4$). Greenish-yellow colorants, called primrose yellow and lemon yellow, are co-crystals of lead chromate with lead sulfate. Redder yellows, that is chrome oranges, are co-crystals of lead chromate with PbO. Still redder oranges, molybdate oranges, are co-crystals of lead chromate with lead molybdate ($PbMoO_4$) and lead sulfate. Chrome yellows are relatively low in cost, although higher than iron oxide, at least partly because their density is higher. Chrome yellows discolor on exterior exposure to form lower chroma yellows, but their exterior durability is adequate for many outdoor uses. They are bleed and heat resistant. Due to their lead content, their use is not permitted in consumer paints in the United States. Their use in industrial applications is declining because of concern about the use of lead compounds. Their major current use is in yellow traffic striping paint. Use of chromates for this purpose has been banned in many European countries and in some U.S. states. Monoarylide yellows are their predominant replacement.

Titanium yellows are made by introducing other metal ions into the lattice of anatase TiO_2 crystals, followed by calcining to convert to the rutile crystal structure. Greenish-yellow shades are based on introducing antimony and nickel; reddish-yellow shade grades contain antimony and chromium. Their resistance to exterior exposure, chemicals, heat, and solvents is excellent. However, only relatively weak yellow colors can be produced, so the cost is high, and the range of colors that can be made is restricted. Bismuth vanadate is a yellow pigment with high brilliance and good durability that has recently been introduced.

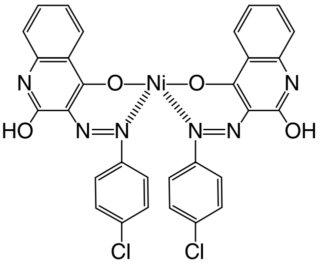
20.2.1.2. Organic Oranges and Yellows Chemical structures of representative pigments are shown in Figure 20.2. The code designations are from the Color Index



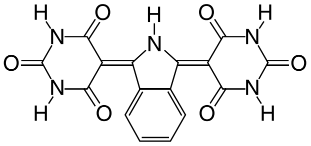
A diarylide yellow
(PY 13)



A monoarylide yellow
(PY 74)



Nickel azo yellow
(PG 10)



Isoindoline yellow
(PY 139)

Figure 20.2. Examples of organic yellow pigments.

system developed by the Society of Dyers and Colourists in the United Kingdom and the Association of Textile Chemists and Colorists in the United States. The P in the code stands for pigment, the next letter designates the hue, and the number is assigned chronologically.

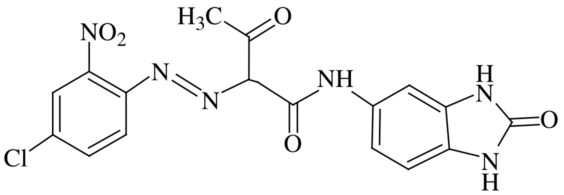
Diarylide yellows are bisazo pigments derived from 3,3′-dichlorobenzidene (e.g., PY 13), as shown in Figure 20.2. They have high color strengths and high chroma. The hue and photostability are controlled by the number, positions, and structure of substituent groups on the aromatic ring of the anilide portion of the molecule. Even the most photochemically stable diarylide yellow pigments fade on exterior exposure, especially when used in tints. On the other hand, their solvent, heat, and chemical resistance are excellent. Due to their high strength and low density, their cost is relatively low. They are used in interior coatings, for which a bright yellow color is needed in tints, and in such applications as coatings for pencils. Grades with excellent transparency can be made. Diarylide yellows are the major yellows used in printing inks, especially in yellow inks used in four-color process printing.

Monoarylide (monoazo) yellow pigments such as PY 74, also have high chromas. They have poor bleed resistance and sublime when exposed to high temperatures. However, their light fastness is better than that of diarylide yellows, although still inferior to that of inorganic yellow pigments. Some opaque grades have sufficient light resistance for use in outdoor coatings. They are replacing chrome yellows in traffic paints.

Nickel azo yellow is a relatively weak, very greenish yellow; in fact, as can be seen from the designation PG 10 in Figure 20.2, it is classified as a green. Nickel azo yellow exhibits excellent exterior durability and heat resistance. It gives transparent films and is used predominantly in automotive metallic coatings. There have been some situations in which bleeding into stripes has been reported, so specific applications must be checked for bleeding.

Vat yellow pigments, as exemplified by isoindoline yellow PY 139, give transparency with excellent exterior durability and heat and solvent resistance. They are expensive and used only when their outstanding properties are required (e.g., in automotive metallic coatings).

Benzimidazolone orange pigments offer excellent light fastness and resistance to heat and solvent. They are used as replacements for molybdate orange.



Benzimidazolone orange (PO 36)

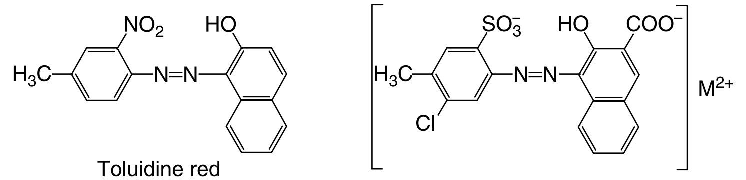
20.2.2. Red Pigments

20.2.2.1. Inorganic Reds Iron oxide (Fe_2O_3) gives the familiar barn red color. It is a low chroma red with excellent properties and low cost. In contrast to iron oxide yellows, iron oxide reds are thermally stable. When their particle size is optimal for scattering, they provide a high degree of hiding. An orange–red iron oxide is now available. There are also very fine particle grades available that provide transparent films. The excellent exterior durability makes the transparent grades suitable for use with aluminum in metallic automotive top coats. Transparent iron oxide is an excellent UV absorber and is used in transparent wood stains to protect the wood from photoxidation.

20.2.2.2. Organic Reds Toluidine red pigment, PR 3, is a moderate cost, bright red azo pigment with high color strength, good exterior durability in deep colors, good chemical resistance, and adequate heat resistance to permit use in baking enamels. As shown in Figure 20.3, it is an azo derivative of β-naphthol. Toluidine red is soluble in some solvents and gives coatings that are likely to bleed.

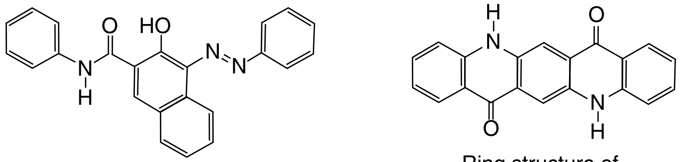
Bleed resistance with azo pigments can be achieved by the presence of carboxylic acid salts. For example, 2-hydroxy-3-naphthoic acid (BON) can be coupled with diazo compounds. Permanent Red 2B is an example of such bleed resistant high chroma red azo pigments. It is available as the calcium, barium, or manganese salt. The somewhat higher cost manganese salt shows better exterior durability than the calcium or barium salts. A variety of related azo pigments that have somewhat different shades is also available. This general class is the largest volume of organic red pigments used in coatings and inks. However, many are sensitive to bases and are not suitable for some latex paints.

Naphthol reds are a large family of azo pigments with various ring substituents (Cl, OCH_3, NO_2, etc.) in the generic structure shown in Figure 20.3. They are more resistant



Toluidine red
(PR 3)

Permanent red 2B
Ca salt: PR 48:1
Ba salt: PR 48:2
Mn salt: PR 48:4



Generic structure of napthol reds

Ring structure of quinacridone reds

Figure 20.3. *Example of organic red pigments.*

to bases, soap, and acid than are the permanent reds, and have fairly good exterior durability and solvent resistance.

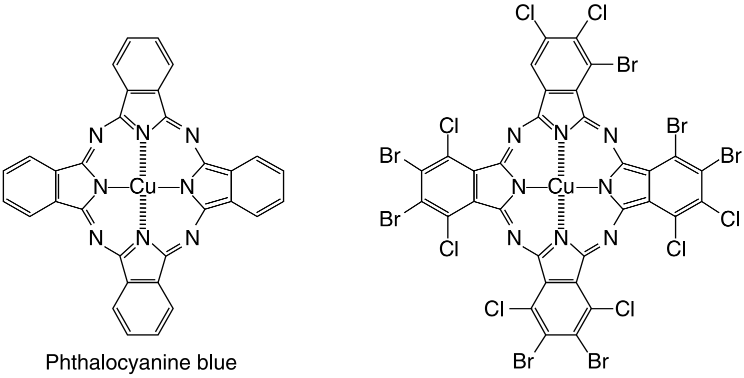
Quinacridone pigments are nonbleeding, heat and chemical resistant, and give outstanding exterior durability, even in light shades. However, their cost is high. Depending on substitution and crystal form, a variety of orange, maroon, scarlet, magenta, and violet colors are available. Large particle size grades are used when opaque pigments are needed, and fine particle size grades are available for use in metallic automotive top coats. Surface treatments are applied to increase the resistance of their dispersions to flocculation [13]. Many other high performance red pigments are available (see Refs. [6] and [8]).

20.2.3. Blue and Green Pigments

20.2.3.1. Inorganic Blues and Greens Iron blue, ferric ammonium ferrocyanide, $FeNH_4Fe(CN)_6$, is an intense reddish shade blue with fairly good properties. Historically, it was important as one of the first widely used synthetic pigments. Since the 1930s it has been supplanted increasingly by phthalocyanine blues, which have greater color strength. Co-crystals of various ratios of iron blue and chrome yellow are called *chrome greens*. The popularity of these pigments has decreased because of the high color strength of phthalocyanine green; they can no longer be used in architectural coatings in the United States because of their lead content.

20.2.3.2. Organic Blues and Greens The principal blue and green pigments are copper phthalocyanine pigments, commonly called *phthalo blue* and *phthalo green* (Figure 20.4). They exhibit outstanding exterior durability, bleed and chemical resistance, are heat stable, and have high tinting strengths. Although their cost per pound is fairly high, the high tinting strength and quite low density make their cost to use moderate.

Phthalo blues are available commercially in three crystal forms: alpha, beta, and the seldom-used epsilon. The beta form has a relatively green shade of blue and is stable.



Phthalocyanine blue
(PB 15)

Phthalocyanine green
mixed isomers

Figure 20.4. *Representative phthalocyanine pigments.*

The alpha form is redder, but not as stable; in some cases, when some grades of the alpha form are used, there can be serious problems of change of color and strength during storage of coatings or during baking. More stable alpha form pigments are available; these incorporate various additives that stabilize the crystal form and minimize problems with flocculation of dispersions. Some grades of phthalocyanine blue are slightly chlorinated; these have greener blue shades.

Phthalo greens are made by halogenating copper phthalocyanine to produce mixtures of isomers in which many of the 16 hydrogens of CPC have been replaced with chlorine or mixtures of chlorine and bromine. Phthalo greens with 13 to 15 chlorines but no bromine have blue–green shades. Partial replacement of chlorine with bromine shifts the color toward a yellow–green shade. The yellowest shades have a high ratio of bromine to chlorine, an example is PG 36, which has on average about 9 bromines and 3 chlorines.

20.2.4. Black Pigments

Almost all black pigments used in coatings are carbon blacks. They absorb UV radiation as well as light, and with most binders, black colors are the most stable on exterior exposure. Carbon blacks are made by a variety of processes of partial combustion and/or cracking of petroleum products or natural gas. Depending on the process, the particle size and therefore the degree of *jetness* (intensity of blackness) varies. High color *channel blacks* have the smallest particle sizes, with diameters of 5 to 15 nm, and have the highest jetness. They are used when intensely black, glossy coatings are desired. *Furnace blacks* have larger particle sizes, are lower in cost, and give less jet black coatings. Various grades are available, with average diameters of 50 to 200 nm. *Lampblacks* have a still larger particle size, on the order of 0.5 μm, and have lower color strengths than other carbon blacks. They are primarily used in making gray coatings. They are preferable to high-color blacks for this purpose; if a small excess of high color black is added by mistake, it may be necessary to increase the batch size 50% or more to make up for the mistake. The shade of gray obtained changes much more slowly with the addition of lampblack, making color matching easier.

Approximately 30 million pounds of all types of carbon black was used in coatings in 2004, of which about 80% was furnace black [3].

Although all carbon blacks are predominantly elemental carbon arranged in polynuclear six-member rings, the chemical structure of the surfaces varies depending on the raw material and process used in their manufacture. The surfaces are generally quite polar and in some cases are acidic. There are also variations in the porosity. Black coatings can present difficulties in formulation, especially when channel blacks are used. Due to the small particle size, the ratio of surface area to volume of the pigment particles is very high. The large surface area leads to adsorption of high ratios of resin on the pigment particles: commonly, many times their volume of polymer, increasing their volume substantially and hence giving high viscosity at relatively low pigment loading levels. Due to the polarity of the surface and the large surface area, they can selectively adsorb polar additives such as catalysts from a coating formulation. For example, in drying oil and oxidizing alkyd formulations, the metal salt driers slowly adsorb on carbon black, so that the coating dries more and more slowly as it ages.

Acetylene black pigment increases the electrical conductivity of films. Conductivity is required for coatings such as primers for plastic parts that are to be coated by electrostatic spray (Section 31.3.2.2).

20.2.5. Metallic, Interference, and Cholesteric Pigments

The most important metallic pigments are aluminum flake pigments. They are produced by milling finely divided aluminum metal suspended in mineral spirits in steel ball mills to make thin flakes. Pigments are available in a variety of particle sizes. Two major classes are used in coatings: *leafing* and *nonleafing* pigments. About 25 million pounds of aluminum pigments with a value of $150 billion were used in North American coatings in 2004 [3].

Leafing aluminum pigments are surface treated (e.g., with stearic acid) so that they have a low surface tension. When a coating containing leafing aluminum is applied, flakes orient at the surface, as a result of their low surface tension. This gives a bright metallic appearance and acts as a barrier to permeation of oxygen and water vapor through the film. As a result of barrier development, leafing aluminum pigments are used in top coats for corrosion protection of steel structures (Section 7.3.3).

Nonleafing aluminum pigments have higher surface tensions and do not come to the surface of the coating. They are used in metallic top coats for automobiles. As discussed in Section 19.4, formulations using nonleafing aluminum are designed to maximize the fraction of flakes that are oriented parallel to the film surface. Films made with transparent color pigments and nonleafing aluminum change depth of color and shade with the angle of viewing. Gold colored aluminum flakes can be made by vapor deposition of iron carbonyl on the surface of aluminum flakes, followed by oxidation to generate a thin layer of iron oxide [14]. Nonleafing aluminum pigments are surface treated to minimize their sensitivity to acid in the environment.

The aluminum pigments used in water-reducible coatings are treated to minimize the reaction of water with the aluminum (which generates hydrogen). In early work it was necessary to mix in the aluminum paste just before application. Various treatments have been developed to permit formulation of premixed coatings [15]; an example is treatment with a low acid number styrene–maleic acid copolymer.

Aluminum pigments are produced in solvent and sold as pastes so as to minimize problems of dusting and danger of explosion. But such pastes bring VOC into waterborne coatings. Aluminum pigments have been developed that are pelletized with melamine–formaldehyde resin surface coating and water stabilization treatments that can be handled easily and stirred into water–glycol ether, which in turn can be added to waterborne coatings with minimal addition of VOC [16].

Bronze, nickel, and stainless steel pigments with platelets similar to those of aluminum pigments are also available, but are used in lower volume. Bronze alloy flakes have “gold” colors; depending on the alloy composition, shades from greenish yellow to reddish gold are available. Generally, they are surface treated, so they leaf. Due to the presence of copper, on outdoor exposure, bronze alloy pigments change color to a blotchy, muddy green appearance.

Interference pigments are flake pigments that lead to color by interference (Sections 19.2.1 and 19.4). Pearlescent pigments are platelets of mica having thin surface treatment layers of TiO_2 or Fe_2O_3, which serve to give interference reflection of light striking pigment surfaces [17,18]. As a result, at some spots on the surface of the platelets, some wavelengths of light are strongly reflected and others are transmitted. At other spots, where the film thickness of the treatment layer is different, different wavelengths are reflected and transmitted. The result is a mother-of-pearl effect and an illusion of optical depth. These pigments are used in automotive coatings to give an effect related to that obtained with aluminum flake, but with the addition of hue changes with angle.

Another type of pigment that gives colors as a result of interference effects is available [19]. The pigment particles are thin (about 1 μm in thickness) flakes composed of a thin layer of reflective metal sandwiched between two layers of clear plastic, and with very thin top layers of a semiopaque, very thin metal coating on each surface. As a result of interference reflection (Section 19.4), certain wavelengths of light are reflected and others absorbed. The color obtained depends on the film thicknesses and the angles of illumination and viewing. As with other flake pigments, these flakes must be oriented parallel to the surface of the coating. North American coating consumption of pearlescent pigments in 2004 was about 4 million pounds, with a value of about $75 million.

A newer type of interference pigment, cholesteric pigments, are based on polymeric liquid crystal structures. One process for making these pigments starts with a combination of an acrylated nematic liquid crystal and an acrylated chiral compound that forms helical structures. They are dissolved in a vinyl monomer such as divinylbenzene along with a photoinitiator. The solution is coated on a polyethylene support, linear stress is applied to align the helixes, and the combination is UV cured. The film is removed from the support, milled, and classified for particle size. The resulting flakes are a translucent off-white highly cross-linked powder. The helical structure leads to interference, causing changes in color when viewed at different angles. By changing the ratio of chiral additive and liquid crystals, the wavelengths of light reflected and transmitted change. Five basic colors are commercially available. They are sensitive to UV and must be used with a benzotriazole class UVA. In waterborne automotive base coats with UVA and an adequate thickness of clear coat with UVA and HALS, they exhibit excellent durability [20]. A variety of other flake pigments for various applications are discussed in a review paper [21].

20.3. INERT PIGMENTS

Inert pigments absorb little, if any, light and have refractive indexes close enough to those of binders that they give little light scattering when used as pigments. Several synonymous terms are used: *inert pigments*, *inerts*, *fillers*, and *extenders*. Commonly, but not always, they are inexpensive and reduce the cost of a coating. The principal function of most inert pigments is often to occupy volume in a film. Other functions are to adjust the rheological properties of fluid coatings and the gloss and mechanical properties of films. As discussed in Chapter 22, many film properties are controlled by the volume of pigment in the film. The multitude of inert pigments available is discussed in Refs. [6] and [22].

Calcium carbonate ($CaCO_3$) pigments are widely used inerts. The lowest cost grades are ground limestone or mixed calcium magnesium carbonate ore (dolomite). Synthetic calcium carbonate pigments are more expensive, but they are whiter. Pigments are available with a variety of average particle sizes. In some applications, the reactivity of calcium carbonate with acids makes carbonate pigments undesirable; especially in exterior paints, degradation of film properties may be accelerated by acid rain. Calcium carbonate pigments should not be used in exterior latex paints. Water and carbon dioxide permeate through the film of a latex paint; some calcium carbonate reacts to give calcium bicarbonate, which is water soluble and permeates back out of the film. On the film surface, the water evaporates and the reaction reverses, leaving a *frosting* of insoluble calcium carbonate deposited on the film. Frosting is especially noticeable on dark color paints.

A wide range of clays (aluminum silicates) are used as inert pigments. They are available in various particle size ranges. Cost is frequently related to whiteness. As mentioned in Section 20.4, bentonite and attapulgite clays are used to modify the viscosity of coatings. Mica (aluminum potassium silicate) has a platelet structure and can be useful in reducing permeability of films to oxygen and water vapor when it is oriented parallel to the surface of the film.

Magnesium silicate minerals are also used as inert pigments. Talcs of various crystal structures affect the film strength of coatings differently. Some talcs are platey and reduce vapor permeability; others are fibrous and may be particularly effective in film reinforcing. Asbestos is a very fibrous magnesium silicate that is no longer used because it causes lung cancer when fibers are inhaled.

Silicon dioxide pigments are an important group of inert pigments. Ground natural silicon dioxide is used in a variety of particle sizes. An unusual example of an SiO_2 pigment is *diatomaceous earth*, composed of fossil skeletons of diatoms. The large ratio of surface area to volume affects film properties (Section 22.2). Very fine particle size synthetic silicon dioxide pigments are used to reduce gloss of clear coatings and to impart shear thinning flow properties to coatings, as discussed briefly in the next section. They are expensive.

Barytes (barium sulfate) has been used as an inert pigment, especially in automotive primer formulations. It is said to provide a "harder" primer. The density of barytes is high (4.5), roughly twice that of most other inert pigments. In at least some cases, it is possible that use of barytes is based on weight comparisons with other inert pigments, rather than volume comparisons, as should be done. Although barytes is not expensive on a weight basis, it is more expensive than most other fillers on a volume basis.

Although most inert pigments are inorganic minerals, organic materials can also be used as inert pigments. For example, powdered polypropylene is insoluble and acts as an inert pigment. High T_g latexes such a polystyrene latex can be used as an inert pigment in latex paints. Synthetic fibers such as aramid fibers have been shown to be effective for increasing the mechanical strength of coating films.

20.4. FUNCTIONAL PIGMENTS

Functional pigments are used to modify the application characteristics, appearance, or film properties of coatings. An important example is corrosion-inhibiting pigments. Complex zinc chromate pigments, strontium chromate, barium phosphosilicates, barium borosilicates, red lead, and zinc phosphate are used in primers to inhibit corrosion of steel by passivation of anodic areas. In contrast to other pigments, to function they must be somewhat soluble in water. Because of toxic hazards, use of chromates and red lead is decreasing rapidly. Zinc metal pigment provides corrosion protection by cathodic action and is used in a class of primers known as *zinc-rich primers*. About 70 million pounds of zinc pigment was used in North American zinc-rich primers in 2004 [3]. These pigments are discussed in Sections 7.4.3 and 33.1.2, and considerable information is provided in Refs. [6] and [23].

Flatting pigments are a type of functional pigment used to reduce gloss. Although low gloss is often attained by formulating coatings with a high volume ratio of pigment in the dry film, this is not always a desirable approach. For example, in lacquers for use on wood furniture, it is essential to have the transparency of the dry film as complete as possible so that the beauty of the wood grain is not concealed. Fine particle size silicon dioxide is widely used in such coatings as a flatting pigment.

As discussed in Section 19.10.1, during solvent evaporation from the coating film, convection currents carry the fine particles to the surface, so that the pigmentation at the surface of the dry film is high enough to reduce gloss. The combination of low total pigmentation, small particle size, and small refractive index difference gives little reduction in transparency. Silane treatment of silica is reported to improve transparency in liquid coatings, to provide excellent flatting with smooth surfaces, but to have little influence on rheology [24]. Powdered polypropylene has been used in a somewhat analogous fashion.

Some pigments are used as biocides. For example, zinc oxide is used as a fungicide. Barnacles, algae, and other organisms can grow on the outer hulls of ships; to minimize such growth, *antifouling coatings* are used. Cuprous oxide and organotin pigments have been used in antifouling coatings; although their use is now constrained by environmental concerns (Section 33.2). Finely divided silver is used in antimicrobial coatings.

Zinc oxide is used in linings for cans used for packing vegetables that evolve some hydrogen sulfide during cooking, such as corn. The ZnO reacts with the H_2S to form white zinc sulfide. This prevents the deposition of black stains that result from the formation of tin sulfide by reaction between the H_2S and the tin oxide layer on the tin surface of the tin-plated cans.

Antimony oxide (Sb_2O_3) is a white pigment with a refractive index that is too low (2.18) and a cost that is too high to use simply for hiding. It is used in fire-retardant coatings. When a combination of Sb_2O_3 and a chlorinated or brominated polymer is heated to a high temperature, combustion by-products are generated that suppress flame propagation.

Another class of functional pigments is viscosity modifiers. In general terms, these pigments increase the low shear viscosity of coatings either to inhibit pigment settling during storage of the coating and/or to reduce sagging after application of the coating. An important example used in solventborne coatings is quaternary ammonium salt–treated bentonite clay [25]. Another type of clay that is used in both solvent- and waterborne coatings is *attapulgite clay (fuller's earth)*, a fibrous clay. The fibrils of this clay associate, providing an increase in viscosity that reverses with agitation. In waterborne coatings, it also acts by absorbing water to make swollen particles that distort in shape with stress. Fine particle size silica has been used for many years as a viscosity modifier. The worldwide market for flatting SiO_2 pigments is reported to be 35,500 metric tons [24]. Fumed silica (also called pyrogenic silicon dioxide) is a fine particle-size SiO_2 that is useful to increase the low shear viscosity of coatings. It is used in both solvent- and waterborne coatings paint to give thixotropic coatings with reduced settling and with a thixotropic viscosity that allows application of thicker films without sagging. Surface treatment of SiO_2 with polydimethylsiloxane gives a pigment that is in general most suitable in solventborne coatings. In waterborne coatings it is most suitable in most cases to use the hydrophilic untreated pigment [26]. The effect of such pigments on flow is discussed in Section 3.2.

Pigments with high infrared reflectance have been used for military camouflage. Recently there is increased demand for infrared reflecting pigments for roofing and siding coatings to reduce heat absorption and hence air conditioning costs. Aluminum and white pigments have generally been used, but recently, brown, black, and brightly colored ceramic pigments with high IR reflectance have been made available [3].

20.5. NANO-PIGMENTS

Nano-pigments are pigments of very small particle size. Some authors include pigments with average particle diameters of less than 100 nm, but more commonly the term is applied to diameters below 25 nm. The term is new, but nano-pigments have been used in coatings for many years. For example, high strength channel blacks have particle diameters in the range 5 to 15 nm. Some clays can also be considered as nano-pigments, as they can be separated (*exfoliated*) into sheets on the order of 1 nm thick. A review paper on nano-material technology applications in coatings is available [27].

Compared to the effects of conventional pigments, the use of nano-pigments, especially nano-fillers, may improve resistance to scratch, mar, abrasion, heat, radiation, and swelling resistance, decrease water permeability, and increase hardness, weatherability, modulus, and strain-to-failure while maintaining toughness. These properties reflect the high surface area weight ratio of the particles. There is more surface to adsorb resin, hence a larger fraction of immobilized resin. Based on an adsorbed layer of 10 nm, the fraction of resin adsorbed on 300-nm pigment particles has been calculated to be 3%, and on 50-nm particles, to be 22% [27]. In some cases, two T_gs can be detected. When the particle size of the pigments is smaller than the wavelength of light, coatings pigmented with nano-pigments are transparent [28].

Dispersion of nano-pigments can be difficult. As particle diameters are reduced, especially below 10 nm, the physical properties of the materials change, causing various complications. As discussed in Chapter 21, conventional pigment dispersion methods are often incapable of reducing particle diameters to the nano range, but some successes have been reported [28]. In Section 21.4.4 we discuss the variables involved in selecting mills, media, and media size; pin mills are recommended. Nano color pigments for automotive metallic coatings are prepared by grinding suspensions of the conventional color pigments in butyl acetate with a commercial dispersing agent using very small high-density balls in the mill. The mill base is then used to making tinting pastes for color matching metallic colors [29]. Ball mills are used to disperse nano (aluminum silicate) in an acrylic resin with a commercial dispersing agent. The dispersion is used in making mar resistant clear coats [30].

It can also be difficult to make stable dispersions of nano-pigments. Due to their high surface energy, nano-pigments have a strong tendency to agglomerate. If there is significant agglomeration, the advantages of nano-pigments will not be realized. Various approaches have been utilized: surface treatment of the pigments, in situ polymerization in the presence of the pigments, special pigment dispersants, and ultrasonic dispersion.

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21

Pigment Dispersion

Manufacture of pigmented paints usually involves mixing liquid concentrates of dispersed pigments with the other ingredients. In this chapter we address production of these concentrates. When they are made at the paint factory, they are commonly called *mill bases*, and when they are purchased from specialist companies, they are called *dispersions* or *colorants*.

As described in Chapter 20, pigments are manufactured with the particle size distribution that gives the best compromise of properties, but the particles often become cemented together into aggregates during processing. Breaking these aggregates and forming stable dispersions of optimally sized pigment particles is a critical process in the manufacture of coatings. Making dispersions involves three aspects: (1) *wetting*, (2) *separation*, and (3) *stabilization*. Most authors agree that there are three aspects to dispersion, but different terms are used, sometimes with conflicting meanings. Be careful when reading papers to determine how an author is using the terms.

21.1. DISPERSION IN ORGANIC MEDIA

In this section we discuss dispersion in organic media, usually solutions of resins in organic solvent. Because of effects of the high surface tension and polarity of water, pigment dispersion in aqueous media is treated separately in Section 21.3.

21.1.1. Wetting

Wetting is displacement of air, and sometimes of water or other contaminants, from the surface of pigment particles and aggregates by the medium (i.e., the coating vehicle).

Organic Coatings: Science and Technology, Third Edition, by Zeno W. Wicks, Jr., Frank N. Jones, S. Peter Pappas, and Douglas A. Wicks

Wetting is an essential requirement for pigment dispersion and requires that the surface tension of the vehicle be lower than the surface free energy of the pigment. In organic media this is the case for all inorganic and most organic pigments. If a pigment has an especially low surface free energy, it is necessary to use a medium with even lower surface tension. There can be important differences in the rate of wetting. When a dry pigment is added to a vehicle to make a mill base, the pigment tends to clump up in clusters of aggregates. For wetting to occur, the vehicle must penetrate through these clusters and into the pigment aggregates. The rate of wetting is controlled predominantly by the viscosity of the vehicle; lower viscosity leads to more rapid wetting.

21.1.2. Separation

Processes are designed to separate pigment aggregates into individual crystals without grinding crystals to smaller particle size; it is generally undesirable to decrease the crystal size. Many different types of machinery are used to carry out the separation stage. Some important examples are described in Section 21.4. Dispersion machines work primarily by applying a shear stress to the aggregates suspended in the vehicle. Compressive forces resulting from impact may play a secondary role. If the aggregates are easily separated, the machinery only needs to be able to exert a comparatively small shear stress. If aggregates require a relatively large force for separation, machinery that can apply a higher shear stress is required. Pigment manufacturers have been increasingly successful in processing and surface treating pigments so that their aggregates are relatively easily separated.

Recall from Section 3.1 that shear stress is equal to shear rate times the viscosity of the mill base. The shear rate available for any particular dispersion equipment is set by machine design. The formulator must select appropriate dispersion machinery that can transfer sufficient shear stress to the aggregates and formulate a mill base for the most efficient use of the selected machinery. For the fastest rate of separation of aggregates, the mill base should have as high a viscosity as the equipment can handle efficiently. Then the highest shear stress is exerted on the pigment aggregates, and separation is accomplished in minimum time. The engineering theory and equations modeling the forces for separation are discussed in an excellent series of papers by Winkler, Dulog, and co-workers [1].

21.1.3. Stabilization

Wetting and separation are important steps in making pigment dispersions, but it is seldom a problem to carry out these two stages in organic solvent systems. On the other hand, stabilization can frequently be a serious problem and is usually the key to making good pigment dispersions. If the dispersion is not stabilized, the pigment particles will be attracted to each other and undergo *flocculation*. Flocculation is a type of aggregation, but the aggregates formed are not cemented together like the aggregates in the dry pigment powder. Although substantial shear stress is required to separate the original aggregates, flocculation can be reversed by applying relatively low levels of shear stress.

Flocculation is almost always undesirable. With light scattering pigments, the larger particle size resulting from flocculation reduces scattering and, therefore reduces hiding. With color pigments, the larger particle size reduces light absorption and thus color strength. Larger floccules in the final film affect gloss. Flocculation of pigments, including inert pigments, can change critical pigment volume concentration (CPVC) and thus affect the properties of coating films (Section 22.2). Flocculated dispersions are shear thinning and have higher viscosities at low shear rates than those of well-stabilized dispersions. Flocculated dispersions do have the advantage that any settling forms soft pigment-bearing sediments that are easily stirred back to uniformity. However, settling problems can usually be minimized by the addition of thixotropic additives such as treated clay or gels, without the adverse results of flocculation.

There are two mechanisms for stabilization: charge repulsion and entropic repulsion. (As discussed in Section 9.1.1, some authors prefer to use the terms *osmotic repulsion* or *steric repulsion* instead of *entropic repulsion*). In *charge repulsion*, particles with like electrostatic charges repel each other. Calcium and zinc soaps can sometimes be effective pigment dispersants; by absorbing on pigment surfaces they can place ionic charges on the surface that stabilize dispersions. However, in most cases, entropic repulsion is the primary stabilizing mechanism in non-aqueous media. Charge repulsion is more important in aqueous dispersions, as discussed in Section 21.3.

Entropic repulsion is a term used to describe the repelling effect of layers of adsorbed material on the surface of the particles of a dispersion, which prevents the particles from getting close enough together for flocculation to occur. In many dispersions of pigments in organic media, the adsorbed layer consists of polymer molecules swollen with solvent. The particles are in rapid random (Brownian) motion. As they approach each other, their adsorbed layers become crowded; there is a reduction in the number of possible conformations of molecules of polymer and associated solvent in the adsorbed layers. The resulting decrease in disorder constitutes a reduction of entropy, which corresponds to an increase in energy and requires force; hence, resistance to the reduction of entropy leads to repulsion, owing to the more favorable, lower energy state of the separated particles. Similarly, compression of the layers could lead to a more ordered system by squeezing out solvent. The accompanying reduction in entropy would again lead to repulsion. Only certain parts (*anchors*) of the polymer are adsorbed, with other parts sticking out into the solution (*loops* and *tails*).

Much of our understanding of entropic stabilization of pigment dispersions comes from the seminal work of Rehacek [2]. He devised an experimental technique to determine the thickness and composition of the adsorbed layer on the surface of a pigment dispersed in a polymeric resin solution. First, he made a series of solutions of the resin in a solvent with different concentrations, c_1. He then dispersed a known amount of pigment in each solution. Samples of the pigment dispersions were centrifuged until a pigment-free layer formed. The concentration of resin, c_2, in this supernatant layer was determined. He plotted $(c_1 - c_2)/P$, where P is grams of pigment, for each sample against c_2. [Unfortunately, he labeled $(c_1 - c_2)/P$ as "adsorption." It would have made it easier to understand his papers if he had labeled this axis "apparent adsorption."]

A schematic representation of typical data is presented in Figure 21.1; in all cases, the shape of the curve is the same. Rehacek extrapolated the straight line portion of the curve to intercepts with both axes. The intercept with the c_2 axis represents the concentration of resin in the adsorbed layer on the pigment surface. The intercept with the $(c_1 - c_2)/P$ axis represents milligrams of resin solids adsorbed per gram of pigment. It can be proven mathematically that these two values remain constant at all points on the linear portion of the curve. At the intercept with the c_2 axis, the apparent adsorption is zero; this does not mean that no resin is adsorbed. It means that the concentration of resin in the adsorbed layer is the same as the concentration in the initial resin solution, c_1, and in the resin solution after

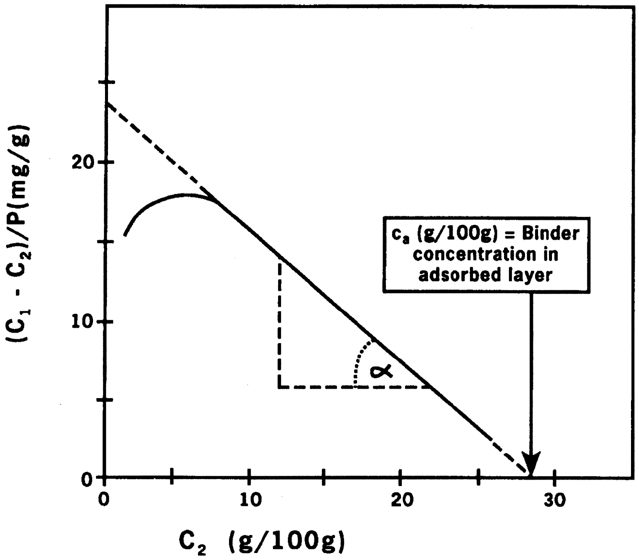

Figure 21.1. Plot of $(c_1 - c_2)/P$ versus c_2 in studies of adsorption of resin and solvent on pigment surfaces. (Adapted from Ref. [2], with permission.)

pigment was dispersed in the resin solution, c_2. Thus, the amount of resin and solvent in the adsorbed layer is established. The surface area of a gram of pigment can be determined by nitrogen adsorption. Using the densities of the pigment and the resin solution, one can calculate the thickness of the adsorbed layer of resin and solvent in the linear range of the plot.

In Rehacek's work, as well as that of others [3,4], it has been found that if the adsorbed layer thickness of resin plus solvent is less than 9 to 10 nm, the dispersion is not stable and flocculation occurs. This adsorbed layer thickness is an average layer thickness; some places are thinner and others are thicker. Similar studies in mixed solvent systems with no resin present show that the adsorbed layer thickness of a combination of solvents is 0.6 to 0.8 nm and not sufficient to stabilize against flocculation [4]. With monofunctional surfactants, the adsorbed layer can be thinner and still protect against flocculation. In one case, McKay [5] has shown that an adsorbed layer thickness of 4.5 nm of surfactant and associated solvent was adequate. In contrast to the adsorbed layer of resin, which is nonuniform in thickness, the surfactant layer is comparatively uniform, so it does not have to be as thick to provide stabilization. The advantages and disadvantages of resin–solvent versus surfactant–solvent stabilization are discussed later.

Referring back to Figure 21.1, it is of interest to understand why the plot deviates from linearity at lower values of c_2. The values of $(c_1 - c_2)/P$ are lower at low values of c_2. In other words, there is less apparent absorption of resin per unit area of pigment surface. This can be explained by competition between resin and solvent adsorption, which depends on both the relative affinity of resin and solvent molecules for the pigment surface and the concentration of resin. If the concentration of resin is high enough, the resin "wins" and there is a complete adsorbed resin layer swollen with solvent. However, at lower concentrations, both solvent and resin are adsorbed on the particle surface, so the average layer thickness is insufficient to prevent flocculation.

Rehacek observed three other differences in the behavior of dispersions with c_2 values above and below the start of the linear section of the curve. The low shear viscosities of the dispersions below the critical concentration were higher than those above it, separation of pigment during centrifugation was more rapid, and the bulk of the centrifugate formed was greater. This behavior indicates that the system is flocculated below the critical concentration. Viscosity at low shear rates increases and the system becomes shear thinning when flocculation occurs, as discussed in Section 3.5. Also, in a flocculated system under low shear conditions, particle sizes are larger than in a nonflocculated system; this causes more rapid settling in centrifugation. Furthermore, the floccules occupy more volume than that of a stable dispersion of the same amount of pigment, since continuous phase is trapped inside the floccules; this leads to the bulkier layer of sediment.

What controls the thickness of the adsorbed layer? In the case of a surfactant with its polar end adsorbed on the surface of a polar pigment, the length of its nonpolar aliphatic chain is the primary factor. In the case of resins with several adsorption sites, the largest single factor is probably molecular weight (MW). For example, Saarnak showed that the adsorbed layer thickness on TiO_2 dispersed in a series of BPA epoxy resins in MEK increased from 7 nm to 25 nm as the MW of the epoxy resin increased [3]. With the lowest MW resin, the layer thickness of 7 nm was insufficient to prevent flocculation. Dispersions in solutions of the higher MW epoxy resins were stable.

Adsorbed layer thickness is also affected by the pigment surface. Organic pigments are more likely to give significant differences in adsorbed layer thickness with different resin–solvent combinations than are more polar inorganic pigments. However, even with inorganic pigments, significant differences can be encountered. For example, a TiO_2 surface treated with alumina forms a more stable dispersion than that of a TiO_2 surface treated with silica in the same long oil alkyd solution [6]. The authors proposed that the adsorbed layer is more compact on the silica-treated TiO_2. Commonly, the interactions between pigment surfaces and adsorbed molecules are considered to be hydrogen-bond interactions, but some authors prefer to interpret the interactions as acid–base interactions [7,8].

The spacing and number of functional groups along a resin chain affect layer thickness. As an extreme example, a linear aliphatic chain resin with a polar group on every other carbon atom would be expected to adsorb strongly on the surface of a polar pigment such as TiO_2. At equilibrium, adsorption of single molecules with interaction of successive polar groups with the pigment surface would be favored, resulting in a thin adsorbed layer. However, if the resin has only occasional polar groups along the chains, at equilibrium, the longer segments between polar groups give loops and tails of resin swollen with solvent projecting out from the pigment surface: hence, a thicker adsorbed layer.

Layer thickness is also affected by solvent–resin interaction. If the loops and tails interact more strongly with the solvent, there are more solvent molecules in the layer, the average conformation of the resin is more extended, and the layer thickness is greater. Resin molecules that have multiple adsorbing groups have an advantage in competition with solvent molecules, but if the solvent interacts strongly with the pigment surface and the resin only interacts weakly, the more numerous solvent molecules will "win" the contest. For example, it has been found that toluene favors adsorption of macromolecules such as nitrocellulose, polyurethanes, and phenoxy resins on magnetic iron oxide pigment particles more than does tetrahydrofuran [8]. Addition of solvent to a stable pigment dispersion can, in some circumstances, lead to flocculation. If the ratio of resin to solvent is just sufficient to allow adequate adsorption of resin to stabilize the dispersion, addition of more of the same solvent can shift the equilibrium, displacing part of the resin and reducing the average adsorbed layer thickness below the critical level for stabilization, resulting in flocculation. The dispersion is said to have been subjected to *solvent shock*.

For most conventional solventborne coatings, the resin used as binder in the coating can stabilize the pigment dispersion. Most conventional alkyds, polyesters, and thermosetting acrylics stabilize dispersions of most pigments. In the past, most dispersions were made in the resin to be used in the paint. If there was a problem, the two most common changes to give adequate stability were to increase the MW or the number of hydroxyl, amide, carboxylic acid, or other polar groups on at least that part of the resin to be used in the mill base. It has been shown that the higher MW components of resins are selectively adsorbed [7].

It is frequently difficult to make stable pigment dispersions in the resins used in high-solids coatings. Increasing the solids of organic solution coatings requires decreasing the MW of the resins and reducing the number of functional groups per molecule. Reduced MW results in thinner adsorbed layers of resin and associated solvent molecules. The reduced number of functional groups per resin molecule decreases the probability of the adsorption of resin molecules; there is a greater probability of solvent adsorption being favored and hence a greater likelihood of flocculation.

21.1.3.1. Pigment Dispersion Stabilizers for Non-aqueous Coatings

The trend is modern paint formulation is to add pigment dispersion stabilizers during the dispersion process. They may be used in combination with a primary resin for the coating or, in some cases, by themselves. This practice often produces superior dispersions for conventional-solids coatings and is essential with many high-solids coatings. Conventional monofunctional surfactants can be used for this purpose. However, if the concentration of surfactant is low, the solvent is likely to outcompete most surfactant molecules, due to the larger number of solvent molecules, even though the surfactant may be more strongly adsorbed. This can be offset by increasing the concentration of surfactant molecules to shift the equilibrium favor of surfactant, but doing so leaves excess surfactant in the final film, which tends to reduce performance properties such as adhesion to metal. Thus, in organic media, monofunctional surfactants are not generally a desirable choice for stabilization. A commonly used additive is *lecithin*, a naturally occurring choline ester of phosphoglycerides. It is quite strongly adsorbed on many pigments.

Surfactants have been designed that are so strongly adsorbed on a pigment that they are preferentially adsorbed even in the presence of a large amount of solvent. For example, phthalocyanine blue modified by covalently attaching long aliphatic side chains has been used as a surfactant with phthalocyanine blue pigment; the phthalocyanine end of the molecules of surfactant in effect joins the crystal structure of the surface of the pigment particles so that little, if any, is in solution [5]. The average adsorbed layer thickness needed to protect against flocculation was shown to be about 4.5 nm. Specific proprietary surfactants have been designed for other pigments. Although effective, this approach finds only limited use because the special surfactants are expensive and are designed to work with specific pigments.

These difficulties have led to the design of special dispersing aids called *polymeric dispersants*, *A-B dispersants*, *hyperdispersants*, or *superdispersants* [9–11]. Jakubauskas describes the design parameters of such dispersants [9]. He concluded that the most effective class of dispersant has a polar end with several functional groups (anchoring groups) and a less polar tail that is soluble in the medium and has sufficient length to provide a surface layer that is at least 10 nm thick. Tails are more effective than loops. (See Ref. [11] for a further review of the use of hyperdispersants.) Examples of such dispersants include polycaprolactonepolyol–polyethyleneimine block copolymers [9], polycaprolactone capped with toluene diisocyanate postreacted with triethylenetetramine [9], low MW polyesters from polyhydroxystearic acid [10], and proprietary hyperdispersants [11].

Controlled free radical polymerization (CFRP) (Section 2.2.1.1) is used to synthesize dispersants, as detailed in Section 21.3.1. In some cases it is desirable to treat the surface of a pigment to provide sites on the surface to interact with the anchors of the dispersant [12,13].

A single dispersant that would anchor firmly to all pigments and be compatible with all types of coatings would be desirable. Then a single series of dispersions could be used in all products, substantially reducing production costs. This ideal is not attainable, but part of the potential savings can be realized by using broadly effective dispersants to reduce the number of series of dispersions.

Another approach to stabilization is to covalently bond long chains to the surface of pigments. For example, the surface of SiO_2 pigment particles has been reacted with trialkoxysilanes with long chain alkyl substituents [14]. Titanate orthoesters with three ethyl groups and one alkyl group with a long alkyl chain reduce the viscosities of dispersions of some inert pigments. It may be that the ethyl groups exchange with hydroxyl groups on the pigment surfaces. In many cases, pigment manufacturers offer pigments that have been surface treated to provide stable dispersions even when the pigment is dispersed in solvent. (See Refs. [13] and [15] for reviews of the surface treatment of pigments.)

21.1.3.2. Other Considerations In high-solids coatings there is a further problem of adsorbed layer thickness on pigment surfaces. In conventional coatings, the volume of pigment in the wet coating of even highly pigmented coatings is quite low, so differences in adsorbed layer thickness do not make a large difference in the viscosity of the wet coating (provided that the dispersion is stable against flocculation). However, in high-solids coatings, especially highly pigmented high-solids coatings, the adsorbed layer thickness can have a significant effect on the viscosity. This problem is especially limiting in the formulation of high-solids primers, where high pigment loadings near the critical pigment volume concentration (CPVC; Chapter 22) are often desirable. The effect of layer thickness can be seen by considering a modification of the Mooney equation (Section 3.5) which takes into account that the internal phase volume due to the adsorbed layer, V_a, in addition to that due to the pigment, V_p, is included in V_i: Using Eq. 21.1, model calculations were made to illustrate the effect of adsorbed layer thickness on viscosity [16].

$$\ln n = \ln n_c + \frac{2.5(V_p + V_a)}{1 - (V_p + V_a)/\phi} \tag{21.1}$$

Figure 21.2 shows the calculated dependence of the viscosity of coatings with 70 NVV as a function of the pigment volume concentration in dry films to be prepared from the coatings. The possible level of pigmentation is more limited with the thicker adsorbed layer than with the thinner one. The following principal assumptions were made in making the calculations: $V_i = 1.2V_p$ and $V_i = 2V_p$ (these values are equivalent to an 8-nm and a 25-nm adsorbed layer, respectively, on a 200-nm pigment); $\phi = 0.65$;

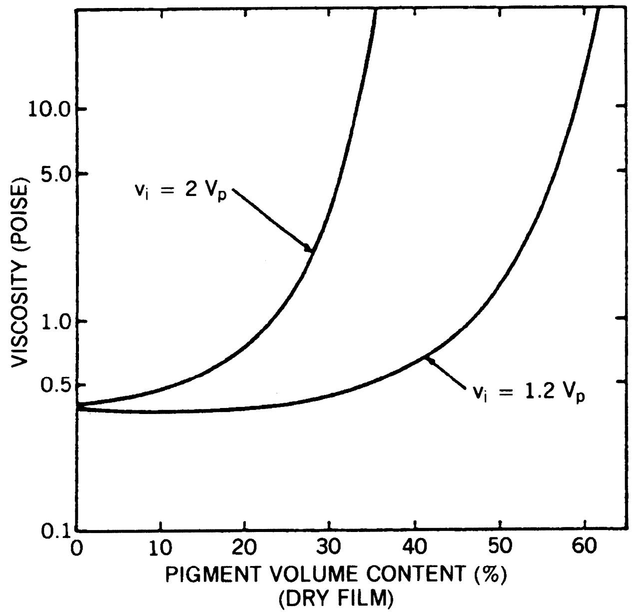

Figure 21.2. Calculations of the effect of PVC on the viscosity of two formulations, both at 70 *NVV but differing in thickness of the layer of adsorbed polymer solution. See the text for assumptions. (From Ref. [16], with permission.)*

solvent: $\rho = 0.8$ and $\eta = 0.4$ mPa•s; and oligomer: $\rho = 1.1$ and $\eta = 40$ mPa•s at 70 NVV, 4×10^5 mPa•s at 100 NVV. The viscosity dependence was assumed to follow Eq. 21.2, in which w_r is weight fraction of resin:

$$\ln n = \ln n_s + \frac{w_r}{0.963 + 0.763 w_r} \tag{21.2}$$

In retail outlets, paints are usually inventoried as white paints and white tinting bases. Colors are made to order by adding color pigment dispersions (*colorants*) to the white base paints. Since both waterborne and solventborne paints have to be tinted, it is desirable to have *universal colorants*, dispersions that can be used in both types of paint. Examples of vehicles for such dispersions are a proprietary dispersing agent, water, propylene glycol, modified alkylpolyglycol ether surfactant, biocide, and antifoam [17].

21.2. FORMULATION OF NON-AQUEOUS MILL BASES

The combination of resin (and/or dispersant), solvent, and pigment used to make a pigment dispersion is called a *mill base*. The formulator must design a mill base for dispersing a pigment in the most appropriate dispersion equipment at optimum efficiency. Pigment dispersion machinery is the most expensive machinery in a coatings factory from the standpoint of both capital and operating costs. It is therefore important to maximize the amount of pigment dispersed per unit time. Higher pigment loading means more efficient production; high loadings are possible when the viscosity of the vehicle (solvent plus resin) used in the mill base is low. Low viscosity also gives faster wetting. A properly stabilized pigment dispersion exhibits Newtonian flow, and its viscosity follows the Mooney equation:

$$\ln n = \ln n_c + \frac{K_E V_i}{1 - V_i/\phi} \tag{21.3}$$

Although mill bases usually contain a single pigment, there are circumstances in which it is advantageous to mill two or more pigments together. Such mill bases are called *composite grinds*.

The volume of pigment (internal phase) can be maximized by using a vehicle of the lowest possible viscosity (η_e). Solvent alone gives low viscosity, fast pigment wetting, and high pigment content, but solvent alone cannot stabilize a dispersion against flocculation. Therefore, it is necessary to include some resin (or hyperdispersant) in the mill base. For maximum pigment loading, it is desirable to use the minimum concentration of resin solution that provides stability. The Rehacek procedure could be used to determine the minimum concentration that still gives a point on the linear section of the curve. However, the procedure is time consuming. Many years ago, Fred Daniel devised a simpler and faster, although less accurate method [18].

21.2.1. Daniel Flow Point Method

The *Daniel flow point method* is a powerful tool for formulating mill bases efficiently, especially for dispersions to be made in ball and other media mills [18]. It provides an estimate of the most appropriate resin concentration to use with a particular pigment. One makes a series of solutions with different resin concentrations. Then one determines the amount of each solution that must be added to a weighed amount of pigment so that when it is dispersed by rubbing vigorously with a spatula on a flat glass plate, the resulting dispersion has a viscosity just low enough to flow readily off the spatula. The spatula is used as both a dispersion machine and a viscometer. Since the clearance between the spatula and the glass plate is small, the shear rate is high; a spatula is a fairly good dispersing machine. One plots the volume of each solution needed for flow against the concentration of that solution. This plot is an isoviscosity plot; that is, the viscosity of each of the dispersions is approximately the same. (The actual low shear rate viscosity is approximately 10 Pa•s.) An example is shown in Figure 21.3; in addition to the volume of resin solution, the volume of solvent in the resin solution is also plotted.

Any resin–solvent–pigment combination that can give a stable dispersion shows a minimum in the curve. Let us consider the significance of the minimum. To the right of the minimum, the viscosity of the external phase is increasing because the concentration of resin is increasing. As can be seen from Eq. 21.3, if η_e increases and the viscosity stays constant, V_i must decrease; that is, the amount of vehicle required per unit of pigment must increase. To the left of the minimum, the amount of vehicle per unit of pigment is also increasing, even though η_e is decreasing. The concentration of resin is insufficient to stabilize the dispersion. The pigment dispersion flocculates increasingly as the concentration of resin in the solutions decreases, and the viscosity increases more and more steeply, so additional resin solution must be added to reach the isoviscosity level. The minimum point corresponds to the minimum concentration of that resin in that solvent that permits preparation of a stable dispersion of that pigment. Since the determination

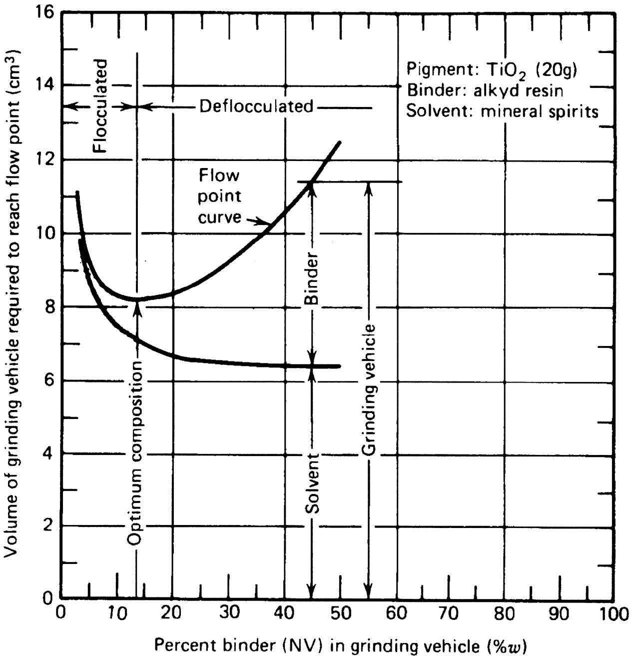

Figure 21.3. Daniel flow point plot: milliliters of solutions of an alkyd resin in mineral spirits per 20 g of TiO_2 as a function of NVW resin in solution. (From Ref. [18], with permission.)

is not highly accurate, it is usual to start experimental dispersions with a somewhat higher resin concentration. If one adds more solvent to a stable dispersion at nearly the minimum resin concentration, the dispersion will flocculate. In some cases, no minimum is found; the amount of resin solution required per unit of pigment keeps decreasing as the concentration increases. This behavior signifies that a stable dispersion of that pigment cannot be made with that combination of resin and solvent. Patton gives examples of data on the Daniel flow point method [18]. He also gives information expressed in volume units of pigment as well as the more conventional weight units.

21.2.2. Oil Absorption Values

In the early days of formulating coatings, it was observed that the weight of pigment that could be incorporated with linseed oil in a mill base varied greatly from pigment to pigment. To simplify formulating mill bases to approximately equal viscosity, *oil absorption values* were determined. Linseed oil was slowly added to a weighed amount of pigment while rubbing with a spatula. Initially, balls of pigment wet with oil formed. When just enough oil had been added and worked into the pigment so that one coherent mass formed, the end point was reached. The oil absorption value is calculated as the number of pounds (grams) of linseed oil required to reach the endpoint with 100 lb (100 g) of pigment. At the endpoint, there is just enough linseed oil to adsorb on the surface of all the pigment particles and to fill the interstices between close-packed particles.

Oil absorption values for different pigments vary over a wide range. The smaller the particle size, the higher the oil absorption. A small particle size pigment has more surface area; therefore, a larger amount of linseed oil is adsorbed on the surface. In some cases, such as some grades of carbon black, the pigment particles are porous. Some oil penetrates these pores, increasing the amount of oil required and hence the oil absorption value. Diatomaceous earth (Section 20.3) has a very high surface area and hence very high oil absorption values. Pigment density also has a major effect. High density pigments require less weight of oil to adsorb on the surface of a unit weight of pigment and to fill the interstices; hence, they have lower oil absorptions. Vehicles other than linseed oil give similar oil absorption values. Therefore, data obtained with linseed oil can be used in formulating mill bases with any vehicle that gives stable dispersions.

The precision of oil absorption determinations by the spatula method is not high. Operators working in different laboratories commonly report values that vary by $\pm 15\%$. It has been said that with experience, deviations by a single operator can be reduced to ± 2 to 3%. Despite these error ranges, it is common to see oil absorption values given with three supposedly significant figures. Improved accuracy and precision can be achieved by using a mixing rheometer (Section 3.3.2), such as a Brabender Plastometer, for carrying out the determination [19]. The mixer is loaded with a known amount of linseed oil; pigment is added slowly. The mixer imparts the necessary shear to separate pigment aggregates. The power required to turn the blades is recorded. As the amount of pigment is increased, the power requirement increases, and when the oil absorption end-point is passed, the dispersion mass breaks up into chunks, leading to erratic readings. The values obtained are more reproducible and are generally a few percent higher than those obtained by the spatula method. Formulators can also take advantage of oil absorption values provided by pigment vendors. These oil absorption values permit one to set a starting point for pigment content when formulating a mill base. Batch-to-batch variations can be expected. The relationship between oil absorption of pigments and the critical pigment volume concentration of films containing those pigments is discussed in Section 22.1.

21.3. DISPERSION IN AQUEOUS MEDIA

Dispersion of pigments in aqueous media involves the same factors as in organic media: wetting, separation, and stabilization. However, the unique properties of water add extra complications. First, the surface tension of water is high, so there is more likely to be a problem in wetting the surfaces of low-polarity pigment particles. Second, in some cases, water interacts strongly with the surface of pigments; therefore, the anchor groups on the stabilizers have to interact more strongly with the pigment surface to compete with water. Furthermore, many applications of aqueous dispersions are in latex paints, so the systems have to be designed such that stabilization of the latex dispersion and of the pigment dispersion do not affect each other adversely.

Inorganic pigments such as TiO_2, iron oxides, and most inert pigments have highly polar surfaces, so there is no problem with wetting them with water. The surfaces of inorganic pigments interact strongly with water, but the adsorbed layer of water does not by itself stabilize against flocculation. Most organic pigments, however, require the use of a surfactant to wet the surfaces. Some organic pigments are surface treated with adherent layers of inorganic oxides to provide a polar surface that is more easily wet by water [13].

21.3.1. Stabilization of Aqueous Dispersions

In contrast to dispersions in organic media, stabilization by charge repulsion can be a major mechanism in aqueous media (Section 9.1.1). The stability of the dispersions depends on pH, since pH affects surface charges. For any combination of pigment, dispersing agent, and water, there is a pH at which the surface charge is zero; this pH is called the *isoelectric point* (*iep*). At *iep*, there is no charge repulsion; above *iep*, the surface is negatively charged; and below *iep*, it is positively charged. The stability of dispersions is at a minimum at *iep* ± 1 pH unit [20]. The *iep* value for pigments varies: for example, 4.8 for kaolin clay and 9 for $CaCO_3$.

Since latex paints were introduced in the 1950s, continuous efforts have been made to improve colorants. Relatively recently, a need has developed for good solvent-free colorants for use in "zero-VOC" paints. By the 1990s, introduction of waterborne automotive base coats (Section 30.1.2) increased the need for high quality aqueous pigment dispersions. These needs motivated intensive research on pigment dispersants that continues today. An early goal was to find polymeric dispersants that were effective in aqueous media. A variety of acrylic copolymers made by conventional free radical polymerization proved to be useful. For example, copolymers of (1) (meth)acrylic acid, (2) monomers bearing one or more highly polar anchoring groups that can absorb on pigment surfaces, and (3) a mono-(meth)acrylic ester of polyethylene oxide are effective. Such copolymers are often used in combination with conventional surfactants.

Controlled free radical polymerization (CFRP) techniques have been studied to obtain polymeric dispersants that are more effective and more efficient than is possible from conventional polymerization. Intensive research on dispersants made by CFRP is summarized in a recent review [21]. These techniques can be adapted to produce AB and ABA block copolymers, and graft, star, and hyperbranched copolymers with controlled structures. When made with appropriate adsorbing and stabilizing groups and properly structures, all these types of polymers can function as pigment dispersion stabilizers. (See Section 2.2.1.1 for discussion of CFRP methods.)

One type of CFRP, atom transfer radical polymerization (ATRP), permits synthesis of polymers having predictable MWs, low MW distributions, and controllable block structures. For example, an AB block copolymer pigment dispersant is synthesized by (1) loading a reactor with toluene, then 1-naphthalene sulfonyl chloride, copper powder, 2,2′-bipyridyl, and glycidyl methacrylate and polymerizing at 80°C for 6 hours to form the A block; (2) adding the methacrylate of the monomethyl ether of polyethylene glycol in methyl 2-hydroxypropyl ether and polymerized for an additional 4 hours at 80°C to attach a hydrophilic B block; (3) reacting the glycidyl epoxy groups with undecanoic acid to make the A block highly hydrophobic; and (4) removing the copper complex by precipitation with magnesium silicate and filtration. The resulting AB block copolymer solution is reduced to 70 wt% solids, dispersed in water, and the pH is adjusted to 8 with DMAE [22].

Another type of CFRP, catalytic chain transfer polymerization (CCTP), differs from ATRP in that a conventional initiator is used in combination with a cobalt (or other metal) complex that mediates the reaction [23]. In one example, a graft copolymer dispersant is prepared using an azo initiator with a cobalt(II) complex as chain transfer agent.

First, CCTP is used to prepare an acrylic macromonomer with 20 wt% methacrylic acid. This macromonomer is then copolymerized with a hydrophilic nonionic macromonomer and hydrophobic monomers. The result is a graft copolymer with a hydrophobic backbone and both anionic and nonionic hydrophilic side chains. When neutralized with AMP, it becomes an effective dispersant. In aqueous media, the hydrophobic backbone presumably anchors the polymer to pigment surfaces, and the hydrophilic grafts act as tails, providing entropic and charge stabilization. Dispersions of TiO_2 in the dispersant gave base coats with higher gloss and higher gloss after being clear coated [23].

Another type of CFRP is nitroxide-mediated polymerization (NEM) using hindered nitroxide compounds as mediating agents to prepare narrow MW distribution block copolymers. For example, a block copolymer of butyl acrylate and dimethylaminoethyl acrylate useful as a pigment dispersion stabilizer is made by sequential bulk polymerization using piperidine nitroxyethers as mediators [24].

The possibilities are almost limitless, but the polymer structures must be designed correctly for good results. For example, an AB diblock copolymer of 2-(dimethyl amino)ethyl methacrylate and *t*-butyl methacrylate, made by living ionic polymerization is very effective; whereas a corresponding ABA triblock copolymer of the same components, having amine-functional blocks on both ends, leads to particle bridging and severe flocculation [25].

A broad study of stabilization of aqueous TiO_2 dispersions by anionic and nonionic surfactants concluded that a high MW nonionic copolymer provided the greatest resistance to flocculation both in the dispersion and during drying of a gloss latex paint film [26]. Since stabilization resulted primarily from entropic stabilization, not charge repulsion, it was not affected by changes in pH. On the other hand, a study of stabilization of TiO_2 dispersions with sodium polyacrylate showed that both charge and entropic repulsion affected stability. The surface layer thickness did not have to be as great as in solvent based dispersions. Even as little as an average 1-nm layer thickness combined with the charge repulsion sufficed for stabilization. Adsorption on the TiO_2 surface was flat but there were loops and tails extending into the water phase. Higher MW gave thicker films and adversely affected viscosity [27].

Surface treatments can have important effects on the stability of aqueous pigment dispersions. Special treated TiO_2 pigments have been developed for waterborne coatings. Substantial differences in dispersion stability can result from differences in the composition and completeness of the surface treatment [28]. In some cases, the amount of surface treatment is such that the TiO_2 content is as low as 75% of the pigment weight. Since hiding is related to the actual TiO_2 content, larger amounts of such highly treated pigments are needed to obtain equivalent hiding.

Slurries of up to 80 wt% TiO_2 in water are used on a large scale with substantial cost savings (Section 20.1.1). The dispersions are stabilized with carboxylic acid–functional polymeric dispersants; pH is controlled by adding amine. The formulations are established to permit minimal flocculation to retard settling. Bactericide is added to inhibit microbial growth.

Dispersion of fine particle size pigments such as transparent iron oxide in water to give coatings without haze can be difficult. It has been shown that good results can be obtained using dispersants prepared by copolymerizing vinyl ether–terminated polyethers with maleic anhydride. High color yield dispersions can be achieved that give films with much less haze than other dispersing agents. For special frosty appearance effects, dispersions of fine particle size "transparent" TiO_2 can be used [29].

Most latex paint formulations contain several pigments and several surfactants. The *iep* of the various pigments are different, which complicates the problem of charge stabilization. Commonly, mixtures of surfactants are used. Anionic surfactants are frequently used as one component. Polymeric anionic surfactants (such as salts of acrylic copolymers in which acrylic acid and hydroxyethyl acrylate are used as co-monomers) provide salt groups for strong adsorption on the polar surface of the pigment and hydroxyl groups for interaction with the aqueous phase; nonpolar intermediate sections add adsorbed layer thickness. Ammonia or amine salts are recommended since the base can escape from the film during drying giving films that are less vulnerable to water than when sodium or potassium salts are used. Polymeric surfactants are less likely than monomeric surfactants to lead to performance problems in the final films. Since polyacrylates are not good wetting agents, they are frequently used with nonionic surfactants and/or an anionic surfactant. It is also common to add potassium tripolyphosphate, the basicity of which may assure that the pH is above the *iep* of all pigments. Note that potassium tripolyphosphate is used in paints, not the sodium salt used in laundry detergents. The potassium salt is less likely to deposit on the surface of a film as scum after being leached out of a dry paint film by water. Large paint producers develop proprietary surfactants for their major product lines.

Additives can sometimes affect dispersion stability. For example, a hydrocarbon solvent used in a latex paint as a defoamer was shown to cause flocculation [30]. The paint formula had several surfactants. It was found that the order in which the surfactants were added controlled whether or not flocculation occurred.

Unless surface treated, organic pigments generally have surface free energies lower than the surface tension of water. Therefore, surfactants are needed to reduce the surface tension of the water to permit the wetting essential for pigment dispersion. Either anionic or nonionic surfactants can be used. In the case of anionic surfactants, the dominant mode of stabilization is probably charge repulsion. In the case of nonionic surfactants, the relatively long polyether alcohol end is oriented out into the water and associated with multiple water molecules; stabilization is probably predominantly by entropic repulsion.

It has been reported that organic pigments dispersed in aqueous polyurethane dispersions (PUDs) show greater color strength than when dispersed in solventborne media. Depending on the pigment, the increase is between 10 and 30%. The effect is attributed to water's ability to dissolve salts in the pigment agglomerates; these salts are not dissolved by organic solvents and increase adhesion within the agglomerates. However, it is also reported that some pigments, particularly some quinacridone and diketopyrrololpyrrole pigments that are non-bleeding in solventborne coatings bleed from some waterborne base coats into clear coats. This is attributed to the aggressive solvents that are present in some aqueous vehicles, especially *N*-methylpyrrolidinone and butoxyethanol [31].

In many cases, paint manufacturers make only white paints and supply separate color dispersions and formulations for the paint stores to mix with the white paints to make a large number of colored paints for their customers. Many latex paint manufacturers buy rather than manufacture their color pigment dispersions. The wetting and stabilization methods used are proprietary.

There is need for more research on the factors leading to stability of dispersions in latex paints. There is reasonable understanding of the stabilization of single pigment systems. However, paints often contain several pigments, commonly with both polar and nonpolar surfaces and one or more latexes (Chapter 32). Furthermore, the formulations may contain one or more water-soluble polymers and/or associative thickeners (Section 32.2) to adjust the rheological properties of the paint, and these can interact with dispersants. As a result, the selection of appropriate dispersing agent combinations is done at least partly on an empirical basis. As in any situation in which empirical knowledge is the key to success, it is desirable to build a database of combinations that work and do not work to facilitate formulating with a new pigment combination or latex.

21.4. DISPERSION EQUIPMENT AND PROCESSES

A variety of equipment is used to make pigment dispersions. An important difference between different machines is in the level of shear stress that they can exert on the pigment aggregates. Easily separated pigment aggregates can be dispersed in low shear stress equipment, whereas some pigment aggregates require very high shear stress for separation. Discussion of all types of such machinery and their operation is beyond the scope of this book. Patton provides more discussion of some types [18]. Detailed and up-to-date engineering information is often available from the machinery manufacturers. Reference [1] deals more fundamentally with engineering aspects of some dispersion methods. We discuss a few important types with emphasis on their advantages and disadvantages. A formulator must become familiar with dispersion equipment available in his or her company's factories to design formulations appropriate for production with that machinery.

From a processing point of view, there are three stages in making and using pigment dispersions: (1) premixing, that is, stirring the dry pigment into the vehicle and eliminating lumps; (2) imparting sufficient shear stress to separate the pigment aggregates in the presence of a dispersion stabilizer; and (3) *let down*, that is, combining the pigment dispersion with the balance of the ingredients to make a coating. Some machines can carry out only the second step, some can do two of the three, and others can do all three.

Some pigment dispersions are made for specific batches of a coating; after the pigment dispersion is made, it is let down with the other components to make the final coating. Other pigment dispersions are made for use in several related types of coatings or as *tinting pastes* for color matching a variety of coatings. To minimize the inventory of tinting pastes, one tries to select vehicle and stabilizer combinations that are compatible with a range of coatings made by that company.

21.4.1. High-Speed Disk Dispersers

High-speed disk (HSD) *dispersers* consist of a shaft with a disk that rotates at high speed in a vertical cylindrical tank. High-speed disk dispersers are also called *high-speed impellers*, *dissolvers*, and *high-intensity mixers*. The disks have flanges around the perimeter that are bent at a sharp angle from the plane of the disk. A schematic drawing of a typical disk is shown in Figure 21.4. Increasingly, the disks are made from engineering plastics that provide greater abrasion resistance than steel. The shearing action takes place by the differential laminar flow rates streaming out from the edge of the disk, which typically rotates with a peripheral speed of 20 to 26 m s^{-1}. Sometimes, the speed of an HSD disperser is expressed in revolutions per minute (rpm), but the important speed is the peripheral speed, which depends on the radius of the disk. The shear stress developed is relatively low, and therefore HSD machines are appropriate only for relatively easily separated

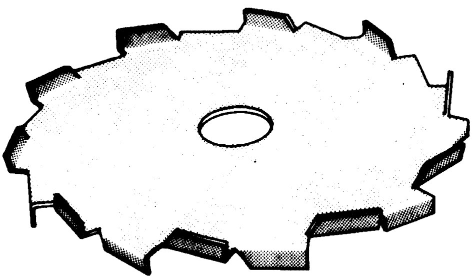

Figure 21.4. *High-speed impeller disk. (From Ref. [18], with permission.)*

pigments. Obtaining predominantly laminar flow requires some minimum viscosity, depending on the dimensions; it is usually somewhat over 3 Pa•s. The higher the viscosity, the greater the shear stress exerted on the aggregates and therefore the faster the process. The viscosity should be set such that the motor driving the shaft is run at peak power.

For maximum efficiency, pigment loading should be maximized. In solvent-based coatings, this can be done by using a vehicle solution with as low a resin concentration as provides stabilization against flocculation. The Daniel flow point method can be used to estimate the resin–solvent ratio. Then the ratio of this vehicle to the pigment is set to achieve a viscosity at a high shear rate such that the motor draws peak amperage. In making latex paints, water-soluble polymers are commonly included in the pigment dispersion stage to increase viscosity during dispersion.

A diagram of flow in using an HSD disperser is shown in Figure 21.5. Centrifugal force leads to flow up the sides of the tank. If the mill base is Newtonian and the dimensions and

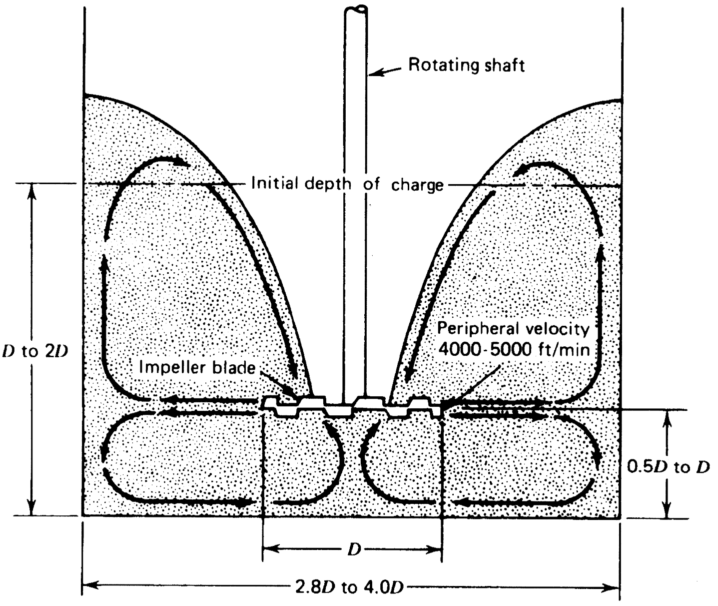

Figure 21.5. *High-speed impeller disperser showing the correct positioning of disk and optimum dimension ratios. (From Ref. [18], with permission.)*

operating conditions are appropriate, the entire charge becomes intimately mixed and all portions of the mill base pass repeatedly through the zone of highest shear, near the edges of the disk. However, if the mill base is shear thinning, the viscosity is high at the upper edge of the material on the sides of the tank where the shear rate is low, resulting in hang up and incomplete mixing. Some mill bases contain a pigment designed to make the final coating shear thinning. The resulting hang up problem can be minimized by dispersing all of the pigments except the one that gives the shear thinning effect. After the balance of the pigments has been separated, the pigment that causes shear thinning is added slowly. A desirable approach to minimizing the hang up problem is to design the dispersing tank with a slow-speed scraping blade that travels around the upper inside of the tank while the high-speed disk is spinning in the center of the tank.

HSD machines are commonly used for premix, dispersion, and let down operations. One initially loads the vehicle components, mixing at a low rpm, and then slowly loads the dry pigment near the shaft. After the pigment is loaded, the speed is turned up for the dispersion stage. In a properly formulated mill base, the dispersion stage requires about 15 minutes. The speed is reduced and the let down is carried out with the rest of the components in the formulation. When producing latex paints, the latex cannot be present during the dispersion stage, since most latexes coagulate when exposed to high shear. The latex is added in the let down stage at low speed.

Compared to other dispersion equipment, HSD machines generally have the lowest capital and operating costs. No separate premix is required, and the let down can be carried out in the same tank. Cleaning to change from one color to another is relatively easy. Solvent loss can be kept to a minimum by using a covered tank. The major limitation is that the shear stress imparted to pigment aggregates is relatively low, so the equipment can only be used for relatively easily separated pigments. Pigment manufacturers have made substantial progress in making pigments with easily separated aggregates. Laboratory HSDs are available, and results correlate well with production machines.

21.4.2. Rotor–Stator Mixers

Shear stress imparted to pigment aggregates can be increased by substituting rotor–stator mixers for HSD machines. These mixers are somewhat similar to HSD machines, but the rotating disk spins in close proximity to fixed elements. The mixers can be used for large batches or in-line. For a general review comparing these mixers with HSD machines, see [32]. It is claimed that, in some cases, rotor–stator mixers give superior dispersions in aqueous media, including critical dispersions for automotive basecoats.

21.4.3. Ball Mills

A *ball*, or *pebble*, *mill* is a cylindrical container, mounted horizontally and partially filled with balls or pebbles. The mill base components are added to the mill, and it is rotated at a rate such that the balls are lifted up one side and then roll in a cascade to the lower side, as shown schematically in Figure 21.6. Intensive shear is imparted to pigment aggregates when the balls roll over each other with a relatively thin layer of mill base between them.

Two classes of such mills are used. In steel ball mills, the balls and lining of the cylindrical mill are steel. In pebble mills, the balls are ceramic and the mill lining is porcelain. In early days, the balls were large smooth pebbles, hence the term *pebble mills*. The term used by some to mean either class of mill and by others to mean only steel ball mills.

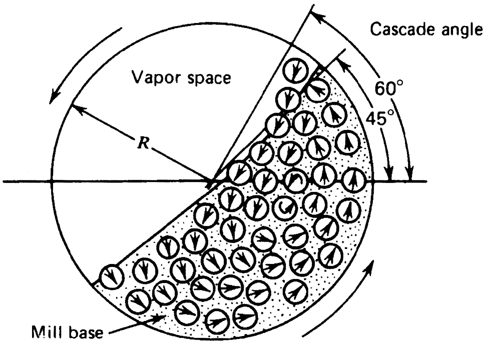

Figure 21.6. *Cascading pattern in a ball mill. (From Ref. [18], with permission.)*

We use *ball mill* in the general sense and *steel ball mill* and *pebble mill* to specify each particular class. Steel balls have the advantage of higher density, and therefore shearing is greater and milling times can be shorter. But their use is limited to dark colored pigments and pigments where color is not critical (primers) because the balls wear and discolor light colors. Pebble mills are used when discoloration is a disadvantage.

Ball mills operate most efficiently when their diameter is large, so that the length of the cascade is long. The efficiency of operation is dependent on the loading of the mill. A mill should be loaded about half full of balls; this gives the longest cascade. The mill base volume should be just over the volume needed to cover the balls when the mill is at rest. If excess mill base is used, the time required for satisfactory separation increases. In a properly loaded mill, the volume of balls is approximately 32% and the volume of mill base is only a little over 18%, assuming that the balls are spheres of equal diameter. If the balls or pebbles are not spheres and/or not uniform in size, there is even less space for mill base.

Operation of a ball mill requires care in setting the rpm of the mill. If the rpm is too low, the balls are not carried high enough. If it is too high, the balls are carried past the 60° angle shown in Figure 21.6, and some fall rather than cascade. This reduces shear, can lead to ball breakage, and is more likely to lead to breaking the ultimate crystals of the pigment rather than just shearing the aggregates. Experienced mill operators can judge whether the rpm setting is proper by the sound. Milling efficiency is also affected by the viscosity of the mill base. If the viscosity is too low, ball wear is high. If the viscosity is too high, the balls roll more slowly and efficiency is reduced. Optimum viscosity depends on the density of the balls and mill size. Viscosities in the neighborhood of 1 Pa•s are commonly used.

The Daniel flow point method (Section 21.2.1) was originally developed to help formulate mill bases for ball mills. It permits loading the maximum amount of pigment at the viscosity required. Proper mill base formulating and use of proper volumes of balls and mill bases can make large differences in the time required for satisfactory separation. The time required depends on how easily the pigment aggregates are separated. The minimum time is usually on the order of 6 to 8 hours. Even difficult pigments should require no more than 24 hours. Sometimes one hears of 72 or more hours being required for dispersion. This almost always indicates poor formulation or improper mill loading.

Ball mills can be used to disperse all but the most difficult to separate pigments. Although the capital cost of ball mills is relatively high, operating cost is low. No premixing is required, and the mills can run unattended. They are difficult to clean and therefore are most appropriate for making batch after batch of the same dispersion. Another difficulty is that batch sizes are limited because the mills contain only about 18% by volume of mill base.

There is no directly comparable laboratory mill available. This is because the efficiency of a ball mill is so dependent on its diameter. Production mills range from 1.25 to 2.5 m (4 to 8 ft) in diameter. Some laboratories use *jar mills*, which are usually less than 30 cm (1 ft) in diameter and rolled at a much less than ideal rpm rate. Correlation with production operations is usually poor.

In the laboratory, *quickee mills* are more appropriate and are much faster for making small batches of dispersions roughly similar to production dispersions in a ball mill. A steel container is filled a little over half full with 30 mm steel balls and enough mill base to somewhat more than cover the balls. The container is then shaken on a paint shaker of the type used in paint stores. Easily separated pigments require 5 to 10 minutes. Difficult to separate pigments may take up to an hour of shaking. Glass jars or vials partly filled with glass beads, sand, or ceramic media can also be used as quickee mills.

21.4.4. Media Mills

Media mills (also called *agitator mills*) were invented to get around batch size limitations of ball mills. In the earliest mills, the media was sand that had an average diameter of about 0.7 mm, and the mills were called *sand mills*. Sand is still used, but more commonly, small ceramic balls are used; sometimes the mill is then called a *bead mill*. Small steel balls are also used; then the mill is commonly called a *shot mill* because the steel balls look like the shot used in shotgun shells. Shot mills are generally used to disperse carbon black or other dark pigments.

A schematic drawing of a vertical media mill is shown in Figure 21.7. A high-speed rotor with disks is mounted in a cylinder. The space between the rotor and the cylinder is partially filled with sand or other media. A premixed mill base is pumped into the bottom of the mill. It flows up through the mill, being exposed to shear as it passes between the rapidly moving particles and out through a screen that keeps the media in the mill. A typical vertical media mill operates with a peripheral rotor speed of 10 m s^{-1}. This impels the particles at high speed, so that even though their size is small, the shear rate between them is high, and, of course, in passing through the mill, a pigment aggregate passes between many pairs of particles. Mill bases should be formulated using slightly higher resin concentrations than the minimum in the Daniel flow point curve. The higher the viscosity of the mill base, the longer the average residence time in the mill and hence the greater the degree of shear. For easily separated pigments, it is desirable to use lower viscosity to achieve a greater flow rate through the mill. Viscosities range from 0.3 to 1.5 Pa•s. For pigments that are two or three more difficult to separate, passes through a mill (or a battery of mills in series) may be required. Mills have been designed that automatically recycle part of the mill base.

The mill shown in Figure 21.7 has a vertical rotor, but use of horizontal media mills is increasing. A variety of designs are available. Some have simple disks on the rotor, whereas others have perforated, offset, or cam-shaped disks. Pin mills are also being used increasingly. Pins are placed in opposite walls of a rotating cylinder so that the pins on one side fit between pins on the other side. A pin mill with a motor of the some horse power runs at higher speed, which enhances separation of beads, resulting in higher grinding efficiency and higher energy efficiency.

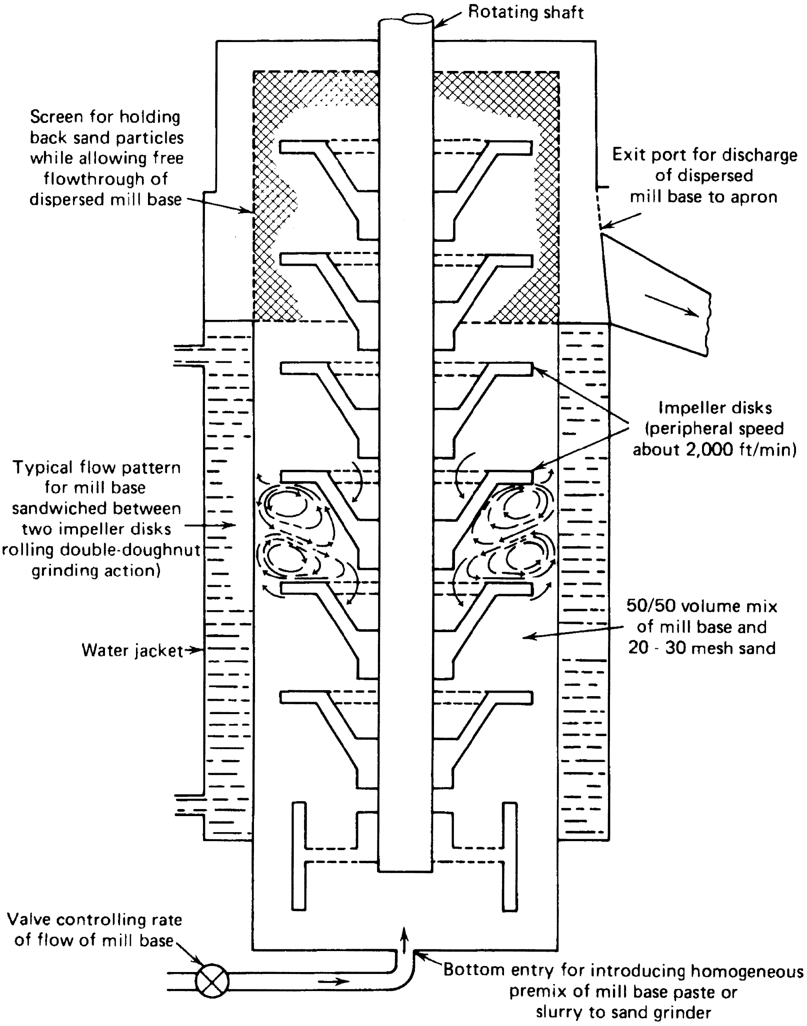

Figure 21.7. *Media mill. (From Ref. [18], with permission.)*

Nano-pigments are particularly difficult to disperse, and pin mills are recommended. Reference [33] provides a discussion of the factors involved as the size of the media is reduced. The ultimate size of the dispersed pigment decreases as the size of the media decreases, so that the smallest particle size media will provide the smallest particle size pigment dispersion in the shortest time. However, as the particle size of the media decreases, the difficulty of separating the media balls from the pigment dispersion increases. The factors that affect separation of the mill base from the media are:

- *Mill base viscosity.* High viscosity increases the power necessary to rotate the shaft and may surpass the design limit for rotating the shaft rapidly enough to disperse pigments. Also as the viscosity increases, the media beads are carried toward the screen, leading to screen blockage.

- *Flow rate.* If the flow velocity is higher than the separation velocity, the beads are carried to the screen.
- *Mill base density.* It becomes harder to separate the dispersion from the beads as density increases.
- *Bead size and density.* As bead size decreases, separation of the beads centrifugally becomes more difficult. As the density of the beads is increased, separation becomes easier: from glass balls (density = 2.6), to yttrium-stabilized zirconium oxide (density = 6), to steel balls (density = 7.8), to tungsten carbide (density = 14).
- *Agitator speed.* Higher speed gives better separation, but there are practical limits.
- *Design of the separation system.* The size of the screen is critical. There must be sufficient screen area in order that the velocity of the material passing through the screen is not so high that media balls will be carried there and clog the screen.
- *Machine design.* Horizontal pin mills are more efficient than the traditional horizontal disk mills discussed above with small media balls.

Capital investment and operating costs of media mills are relatively low. Premixing is required and let down must be done separately. Batch size is flexible. Cleaning is not easy; generally, certain mills are reserved for similar colors, to minimize cleaning. Media mills are effective for separating all but the most difficult pigment aggregates, provided that the aggregates are small compared to the particles. Laboratory media mills are available that correlate well with production mills. Instead of pumping the premix in from the bottom of the mill, it is poured into the top of the mill. Horizontal laboratory mills are also available. The use of media mills and related equipment is probably second only to that of HSD machines.

21.4.5. Three Roll and Two Roll Mills

Although formerly widely used to make dispersions for coatings, the use of *three roll mills* is much more limited today. Figure 21.8 shows a schematic drawing of a three roll mill. Aggregate separation results from the shear developed as the mill base passes through the nip between each pair of rolls. The viscosity of the mill bases is higher than for the other methods discussed thus far, 5 to 10 Pa•s or even higher. Since the mill base is exposed on the rolls, solvents must have low vapor pressures to minimize evaporation.

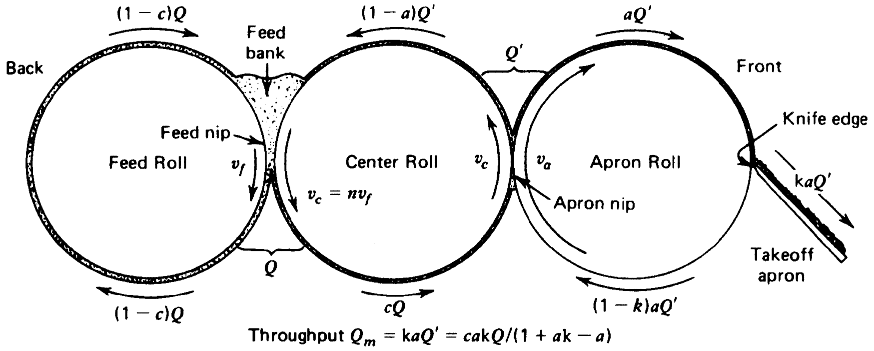

Figure 21.8. Three-roll mill. (From Ref. [18], with permission.)

Three roll mills have comparatively high capital and operating costs. Skilled operators are required. Premixes are required and let down is a separate operation. On the positive side, shear rates are high, so difficult to separate pigment aggregates can be processed, batch size is versatile, and cleanup is relatively simple. Production use today is limited almost entirely to small batches of dispersions with no solvent, or only low volatility solvent, to make high viscosity dispersions. Three roll mills are convenient for laboratory use.

Two roll mills exert even greater shear rates than three roll mills. They are generally used with solvent-free high MW polymer–pigment systems. They can separate even the most difficult aggregates. They are most commonly used for dispersing very expensive pigments. The high capital and operating costs are justified when the economic value of achieving the last 10 to 20% of potential color yield creates a substantial difference in product cost. Two roll mills are particularly appropriate when the dispersion is to be used in a transparent coating. This requires that essentially all of the pigment aggregates should be broken down to ultimate particle size to eliminate (or at least minimize) light scattering. Another use is for dispersing certain carbon black pigments when the desired jetness is attainable only with virtually complete separation.

Two roll mills have very high capital and operating costs. Volatile loss is complete. Premixes are required, and further processing of the dispersion is required to make a liquid dispersion that can be incorporated into a coating. Few coatings companies operate two-roll mills; most purchase pigment dispersions of the type for which two roll mills are appropriate from companies that specialize in making pigment dispersions.

21.4.6. Extruders

Extruders are used increasingly for pigment dispersion. Pigment dispersion for almost all powder coatings is done in extruders (Section 28.4.1); also, some high viscosity liquid dispersions are processed in extruders. Extruders have one or two screws feeding through a cylinder and forcing the material out the end through a die. The barrel of the extruder can be operated over a wide temperature range. Extruders can be configured so that the shear imparted by the screw(s) is very high, and almost any pigment aggregates can be broken down in an extruder. Difficult to disperse pigments require longer residence times. In the case of solids, the product is usually chopped into small pieces and then pulverized either for use as a powder or for ease of dissolving.

21.4.7. Ultrasound Dispersion

Ultrasound for pigment dispersion was evaluated experimentally about 60 years ago. Low-frequency ultrasound ($f \approx 20$ kHz) at intensities above the cavitation threshold generates alternately growing and imploding bubbles in the liquid. The mechanical effect breaks pigment aggregates into individual particles. In sonication times on the order of 15 seconds, tinting strength equals conventional pigment dispersions. It is reported that scaling up of the process to industrial volumes is being studied [34].

21.5. EVALUATION OF DISPERSION

Assessment of *degree of dispersion* is a critical need for establishing original formulations and optimizing processing methods as well as for quality control. Differences in degree of dispersion come from two factors: incompleteness of separation of the original aggregates into individual crystals and flocculation after separation. Frequently, the coatings industry does a poor job in this critical evaluation.

For white and colored pigments, the most effective evaluation method is by determination of *tinting strength* in comparison to a standard. For a white dispersion, one weighs out a small sample of the dispersion and mixes into it a small weighed amount of a standard color dispersion: for example, blue. One also weighs out a standard white sample with the same ratio of the blue standard. After thorough mixing, one puts a small amount of each tint mixture adjacent to the other on a piece of white paper and draws down both samples with a stiff flat-ended spatula so that the edges of the two samples touch each other. One can then compare the color of the two drawdowns. If the batch is a darker blue than the standard, the tinting strength of the batch of white is low, usually meaning that it is not equally dispersed. To test a color dispersion, say blue, one carries out the same procedure but uses the standard white in both samples and the standard blue and the batch of blue.

With dispersions of pigments that are to be used in applications such as automotive metallic coatings, transparency is a critical requirement. Transparency can be tested by drawing down a standard and a batch side by side on a glass plate. The degree of haze or difference from the standard can be evaluated visually or measured instrumentally.

One can check for flocculation by pouring onto a flat surface some of the tint mix made for the draw down. One then rubs the wet coating with a forefinger. If the color changes, the dispersion is flocculated. For example, if a mix of blue with white becomes bluer where it is rubbed, the blue pigment dispersion is flocculated. If the rubbed portion becomes a lighter blue, the white is flocculated. Flocculation can also be detected by examining the flow of the dispersion. Well-stabilized dispersions have Newtonian flow properties. If a dispersion is shear thinning (and does not contain a component designed to make it shear thinning), it is flocculated.

A further method of assessing pigment dispersion is by settling or centrifugation experiments. The rate of settling is governed by particle size and difference in density of the dispersed phase from the medium. A well-separated, well-stabilized dispersion settles or centrifuges slowly, but when settling is complete the amount of sediment is small. A well-separated but poorly stabilized dispersion settles quickly to a bulky sediment. The floccules settle more quickly because of their large size, and they form a bulky sediment because continuous phase is trapped within the floccules. Flocculated sediment is readily stirred, or shaken back to a uniform suspension, in contrast to the sediment formed from the nonflocculated dispersion. If the pigment settles or centrifuges relatively quickly to a compact layer, the separation step is incomplete. The larger aggregates settle more quickly, but the volume is not large, because less internal phase is trapped in the sediment than with a flocculated dispersion. Settling or centrifugation tests provide qualitative or semiquantitative information sufficient for development work and quality control purposes. For research purposes, one can determine more quantitative data; the degree of flocculation can be calculated from rates of centrifugation [5].

One can also examine the dispersion with a microscope. Brownian motion is observed in de-flocculated dispersions, but flocculation stops the motion. One must use caution in preparing the samples for examination. In general, it is necessary to dilute the sample. If the sample is diluted with solvent, there is a possibility of solvent-induced flocculation. In such a case, one may report that the dispersion is flocculated when the flocculation was actually a result of sample preparation. In assessing TiO_2 dispersions with an optical microscope, for example, only the largest particles are seen. Electron microscope studies of the surfaces of etched dry coating films can be useful for assessing variations in dispersion [35].

Laser light scattering is probably the most precise way of measuring pigment particle size and particle size distribution. Instruments are now available that make the measurements in liquid dispersions fast and reproducible [36]. Concentrated dispersions must be diluted to perform the measurements, and shear forces are applied as the measurement is in progress. These instruments are therefore better suited for measuring deagglomeration than for measuring flocculation.

Use of infrared backscattering was pioneered by Balfour and Hird to study TiO_2 dispersions [37]; they called it the *flocculation gradient technique*. Backscattering can be used to measure the degree of pigment dispersion in both liquid coatings and dry films. The extent of scattering of 2500-nm infrared radiation by a film as a function of film thickness was measured. (Particles generally scatter longer wavelength radiation more effectively than they do visible light.) There must be a significant difference between the pigment and the vehicle in the refractive index at 2500 nm. A plot of backscatter against film thickness gives a straight line whose gradient increases with increasing flocculation. Other examples of the use of infrared backscattering measurements are given in Refs. [8] and [38].

The most widely used method of testing for *fineness of grind* in the coatings industry is a drawdown gauge, commonly the *Hegman gauge*. Similar gauges are available, a sketch of one such gauge being shown in Figure 21.9. A sample of the dispersion is placed on the steel block before the zero reading and drawn down by a steel bar scraper. One then lifts the block up and quickly looks across the drawdown sample to see at which graduation one can start to see particles projecting or streaks caused by particles being dragged along. It is said that the higher the scale reading, the "better" the dispersion.

Unfortunately, the device is not capable of measuring degree of dispersion. First, we should remember that a major problem in making satisfactory dispersions is avoiding flocculation. However, the gauge cannot detect flocculation at all, since the drawing down step breaks up any floccules. Next, the particle sizes of properly dispersed pigments are small compared to the depth of the groove on the gauge. The depth on some gauges ranges from 0 to 10 mil (250 μm) in graduation units of 1.25 mil (approximately 30 μm). The gauge shown in Figure 21.9 ranges from 4 mils (100 μm) to 0 in steps of 0.5 mil (12.5 μm).

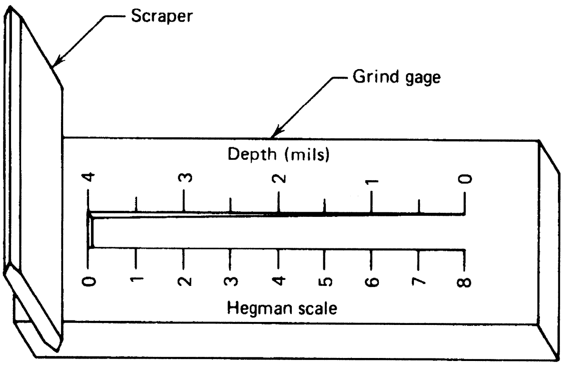

Figure 21.9. *Grind gauge and scraper for measuring the "fineness of grind" of pigment dispersions. (From Ref. [18], with permission.)*

TiO_2 pigment particles have an average size of about 0.23 μm, about two orders of magnitude smaller than the graduation steps of the gauge. Even aggregates of 10^4 to 10^5 particles could escape detection. Many color pigment particles are even smaller, and carbon black particles can be as small as 5 nm. Some inert pigment particles are as large as 2 or 3 μm, still an order of magnitude smaller than the groove depths. Obviously, the gauge cannot test whether or not all or most of the particles are less than the groove depths. Blakely showed that in TiO_2 dispersions only approximately 0.1% of the total pigmentation of a coating was responsible for an unacceptable fineness of grind rating [39].

Why are such devices used? They do give some idea of whether the big aggregates are getting broken up, and they do give some idea of the presence of dirt particles. The determinations are fast, taking about $\frac{1}{2}$ minute. A tinting strength determination by an experienced person requires 2 or 3 minutes, but after spending this time, one has an assessment of the dispersion instead of a close to meaningless number. In the nineteenth century, when very coarse, difficult to separate pigments were all that was available, the gauge might have had some value. There is no excuse for using it in the twenty-first century.

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22

Effect of Pigments on Coating Properties

Although color and hiding are major reasons for including pigments in coatings, there are many other effects that result from pigmentation. Pigmentation affects the viscosity of liquid coatings as discussed in Sections 3.5 and 25.1.2. In this chapter we address the effects of pigments on coating film properties. Most of these effects are related to the pigment volume concentration (PVC) and the critical pigment volume concentration (CPVC). Therefore, we discuss these concepts first. An extensive review of these effects is available [1].

22.1. PVC AND CPVC

Traditionally, coatings formulators have worked with weight relationships, but volume relationships are generally of more fundamental importance and practical significance. Although there had been a few previous isolated examples of recognition of the importance of volume considerations in the performance of coatings, credit for full realization of this importance belongs to Asbeck and Van Loo [2]. They looked at a series of performance variables as a function of PVC, that is, the volume percent of pigment in a *dry* film. The term PVC should never be used to specify the volume of pigment in a wet coating. This has been done occasionally in the literature and has been responsible for serious misinterpretations. Although PVC is usually expressed as a percentage, some authors express PVC as pigment volume fraction in equations without bothering to tell the reader.

Asbeck and Van Loo observed that many properties of films change abruptly at some PVC as PVC is increased in a series of formulations. They designated the PVC at which these changes occurred as CPVC. They also defined CPVC as that PVC where there is just sufficient binder to provide a complete adsorbed layer on the pigment surfaces and to fill

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Organic Coatings: Science and Technology, Third Edition, by Zeno W. Wicks, Jr., Frank N. Jones, S. Peter Pappas, and Douglas A. Wicks

all of the interstices between the particles in a close-packed system. Below CPVC, the pigment particles are not close-packed and binder occupies the “excess” volume in the film. Above CPVC, the pigment particles are close packed, and there is not enough binder to occupy all of the volume between the particles resulting in voids in the film. Slightly above CPVC, the voids are air bubbles in the film, and as PVC increases, the voids interconnect and film porosity increases sharply.

22.1.1. Factors Controlling CPVC

There are large variations in CPVC, depending on the pigment or pigment combination in a coating and the extent, if any, of pigment flocculation. With the same pigment composition, the smaller the particle size, the lower the CPVC. The surface area/volume ratio is greater for smaller particle size pigments; hence, a higher fraction of binder is adsorbed on the surface of the smaller pigment particles, and the volume of pigment in a close-packed dry film is smaller. One can consider this effect from the standpoint of a modification of the Mooney equation (Section 3.5): The volume fraction of internal phase is the sum of the volume of pigment V_p and the volume of the adsorbed layer, V_a. In a solvent-free system, V_p equals PVC and V_p is equal to CPVC when $V_p + V_a = \phi$. Thus, if V_a is larger, the V_p corresponding to CPVC is smaller. Note that at CPVC, the viscosity of the dry film approaches infinity.

$$\ln n = \ln n_c + \frac{K_E(V_p + V_a)}{1 - (V_c + V_a)/\phi} \tag{22.1}$$

CPVC depends on particle size distribution; the broader the distribution, the higher the CPVC. As discussed in Section 3.5, broader particle size distribution of spherical, dispersed-phase systems increases the packing factor. In low gloss coatings, the least expensive component of the dry film is inert pigment; to minimize cost, it is desirable to maximize the inert pigment content. Since properties should remain constant, one does not want to change the PVC/CPVC ratio; the lowest cost systems are therefore, those with the highest CPVC. Accordingly, cost is reduced by minimizing the amount of very fine particle size pigment, since CPVC decreases with decreasing particle size, and at the same time, by maximizing particle size distribution, which increases CPVC. Compromises are needed, but broad particle size distribution is advantageous.

Pigment dispersion affects CPVC; CPVC of dry coatings in which the pigment is flocculated is lower than CPVC from corresponding coatings with non-flocculated pigment. Coatings with flocculated pigment clusters have non-uniform distribution of pigment and hence are more likely to have portions where there are local high concentrations of pigment. Solvent containing resin can be trapped inside clusters of pigment particles. When the coating dries, the solvent diffuses out of the resin solution trapped in the floccules, leaving behind insufficient binder to fill the spaces. In one example, it is reported that CPVC decreased from 43 to 28 with increasing flocculation [3]. Asbeck suggests using the term *ultimate CPVC* (UCPVC) to designate CPVC with a non-flocculated pigment combination [3]. It seems to us better to recognize that flocculation is one of many variables that affect CPVC, especially since it may be difficult to determine UCPVC experimentally.

CPVC with different pigments varies over a wide range, at least from 18 to 68%. One might expect CPVC to be dependent on binder composition, since the composition affects the thickness of adsorbed layers; thicker adsorbed layers might be expected to lead to lower CPVC. Actually, CPVC with a given pigment or pigment combination seems to be essentially independent of the binder composition (except in latex paints, which are discussed in Section 22.2). It may be that the differences are too small to detect with the relatively imprecise methods used for determining CPVC. It may also be that the shrinkage forces encountered when films are formed press the particles against each other to the extent that only a minimal layer of binder is left between particles, regardless of the original adsorbed layer thickness. No basic studies of this phenomenon have been reported.

22.1.2. Determination of CPVC

Critical pigment volume concentration has been determined by many different procedures [4,5]. In many cases, the precision—that is, the reproducibility of the value—is relatively poor, and the accuracy—that is, nearness to the supposed true value—is also sometimes poor or indeterminate. A further complication is that there is no single true value because CPVC depends on the method of measurement. Bierwagen has emphasized that in the formation of films with PVC at or near CPVC, local fluctuations within a film of volume fractions of binder and pigment are possible [6,7]. Thus, there could be parts of a film with PVC > CPVC, whereas the average composition might be less than CPVC. In view of these uncertainties, one must be careful in assessing the importance of small differences in PVC and CPVC values.

Many changes in film properties have been used as a means of determining CPVC; tinting strength is one of the most widely used. A series of white paints with increasing PVC are prepared and tinted with the same ratio of color to white pigment. Above CPVC, the white tinting strength of the coating increases due to the "white" air bubbles above CPVC. It is suggested that the values of CPVC obtained by this and other optical methods are somewhat low, due to nonuniform distribution of pigment, resulting in parts of a film being above CPVC while others are below [6]. The technique is most easily applicable to white paints, but can also be applied to colored paints.

Another method is to measure film density as a function of PVC. Since the density of most pigments is higher than those of binders and the density of air is lower than those of binders, density is maximized at CPVC. Due to nonuniform distribution of pigment in the films, it is suggested that the density method tends to give high CPVC values [6]. The CPVC can be determined by filtering a coating and measuring the volume of the pigment filter cake. Asbeck recommends a specially designed filter that he calls a *CPVC cell* [3].

The CPVC for a pigment or pigment combination can be calculated from oil absorption (OA) (Section 21.2.2), as shown in Eq. 22.2, provided that the OA value is based on either a non-flocculated dispersion or determined at a sufficiently high shear rate that any floccules are separated. The definitions of both OA and CPVC are based on close-packed systems with just sufficient binder to adsorb on the pigment surfaces and fill the interstices between the pigment particles. Oil absorption is expressed as grams of linseed oil per 100 g of pigment, CPVC is expressed as milliliters of pigment per 100 mL of film, ρ is the density of the pigment(s), and 93.5 is 100 times the density of linseed oil. (Both OA and CPVC are expressed as percentages, not as fractions.)

$$\mathrm{CPVC} = \frac{1}{1 + (\mathrm{OA})(\rho)/93.5} \tag{22.2}$$

The significance of the interrelationship depends on the observation that oil absorption and CPVC are approximately independent of the binder, provided that the pigment particles are not flocculated. Since the accuracy of calculated CPVC depends on the accuracy of OA determinations, OA values determined by a mixing rheometer such as a Brabender Plastometer (Section 3.3.2) are preferable to values determined by the spatula rub up method [8]. Such an intensive mixer provides a greater shear rate for separation of pigment aggregates than spatula rubbing; and also the data points are taken while the dispersion is under high shear, so even if the binder does not stabilize the pigment against flocculation, the volume fractions still represent a non-flocculated system. The effects of variation in the procedure for determination of OA, including the use of liquids other than linseed oil, are reported in Ref. [9]. The discussion of OA determination in this paper is interesting and useful; however, the conclusions drawn by the author about CPVC are erroneous. The author failed to recognize that when the pigment dispersions were diluted with solvent, the pigment flocculated.

Since many OA values are not accurate, Asbeck recommends against using such calculations [3], but many workers have found the calculations useful. Although the CPVC for individual pigments and for specific combinations of pigments can be calculated from oil absorptions, CPVC values of pigment combinations cannot be calculated from these values alone, since differences in particle size distribution with pigment combinations affect the packing factor. The OA values for each combination of pigments can be determined experimentally. A variety of equations has been developed to calculate CPVC from data on individual pigments [5]. The most successful equations use OA values, densities, and average particle sizes of the individual pigments [10,11]. The equations assume that the particles are spheres, a fair assumption for many, but not all, pigments. Calculated values correspond reasonably well to CPVC values determined experimentally.

22.1.3. CPVC of Latex Coatings

There is considerable controversy about the applicability of CPVC to latex paints. Some maintain that one cannot apply the concept. Others maintain that there is no fundamental difference in the CPVC concept between solventborne and latex paints. Still others maintain that the concept is useful in latex paints but that CPVC must be thought of differently in latex paints than in solvent-based paints. Bierwagen emphasizes that experimental errors in determining CPVC of latex paints are even greater than with solventborne paints, so one must use caution in reaching conclusions [12]. Reference [13] includes a review of the literature.

In a study of the effect of PVC on hiding of latex paints, it was concluded that CPVC was lower in latex paint than in solvent-based paint made with the same pigment composition [14]. Patton recommended that the term *latex CPVC* (LCPVC) be used to distinguish this CPVC from CPVC of solventborne paints. Although CPVC is approximately independent of the binder in solventborne paints, LCPVC varies with the latex and some other components of latex paints. It has been found that LCPVC increases as the particle size of the latex decreases. Also, LCPVC increases as the T_g of the latex polymer decreases, and a coalescing agent increases LCPVC. Since LCPVC is smaller than CPVC, the ratio of volume percent of binder in the film of a solvent based paint, V_s, to that of a latex based paint, V_l, will always be less than 1 with the same pigment combination. This ratio has been called the *binder index e* [15]:

$$e = \frac{V_s}{V_l} \tag{22.3}$$

It has been proposed and demonstrated with a limited number of examples that this ratio is independent of the pigment combination. If this proposal is generally true, it follows that if one knows the binder index for a latex, one can calculate the LCPVC for paints made with that latex and other pigments from the CPVC values calculated from oil absorptions (or, for mixtures, by calculation from OA, density, and particle size).

The difference between CPVCs of latex- and solvent-based paints results from the difference in film formation. To illustrate, let us consider a highly idealized comparison. Let us assume that all the pigment particles in the solvent-based paint are spheres with the same diameter and that the CPVC is 50%. In the latex paint, we will use the same pigment together with spherical latex particles that have the same diameter as the pigment particles. In the solvent-based paint, there is a layer of resin swollen with solvent on the surface of all the pigment particles. Ideally, when a solventborne paint with PVC = CPVC is applied, the solvent evaporates and the "resin-coated" pigment particles arrange themselves in a random close-packed order, with binder filling in the spaces between the pigment particles. At the same ratio of pigment to binder as in the solvent-based paint, the idealized latex paint would contain the equal numbers of latex particles and pigment particles. When we apply a layer of the latex paint, the water evaporates and we get a closely packed system of particles. However, some of the particles are pigment and some are latex. There would not be a uniform arrangement of alternating latex and pigment particles in a three-dimensional lattice; rather, there would be a statistical distribution of particles. In some areas there would be clusters of pigment particles, and in other areas there would be clusters of latex particles. As the film forms, the latex particles coalesce, flowing around the pigment particles. However, the viscosity of the coalescing binder is high, and it is difficult for the polymer to penetrate into the center of clusters of pigment particles. As film formation proceeds, the water left inside the pigment clusters diffuses out of the film, leaving behind voids. Although the PVC of 50% in the solvent-based paint equaled CPVC, the same PVC of 50% in the latex paint results in a film with PVC > LCPVC.

The probability of having clusters of pigment particles can be decreased by increasing the number of latex particles until void-free films are obtained, but this necessarily reduces PVC. If the T_g of the polymer is lower, the viscosity of the polymer at the same temperature is lower, and the distance that the latex can penetrate into clusters of pigment particles increases. Thus, the LCPVC of paint made with lower T_g latex is higher, although still lower than the CPVC of a solvent-based paint. Analogously, the reduction of the viscosity of the polymer by a coalescing agent increases the LCPVC. It follows that the higher the temperature during film formation, the higher the LCPVC should be, although no experimental test of this hypothesis has been published. It also follows, although again untested, that LCPVC should depend on time. Although the viscosity of the polymer is high and inhibits flow between the particles, the viscosity is not infinite, and perhaps in time, voids would fill.

If a smaller particle size latex is used with the same ratio of pigment to binder volume, the number of latex particles in our idealized paint would be larger than the number of pigment particles. Now the probability of clusters of pigment particles forming would be reduced. As a result, one would expect, as is found experimentally, that the LCPVC increases with decreasing particle size of the latex. Particle size distribution of a latex affects its packing factor [16], which would presumably affect LCPVC. A quantitative study of the effect of latex particle size on LCPVC using a series of monodisperse vinyl acetate/butyl acrylate latexes with TiO_2 pigment showed that

LCPVC depended on the ratio of the number of latex and pigment particles and the ratio of their diameters [13].

Not only does larger particle size latex decrease LCPVC, but flocculation of the latex particles would also be expected to decrease LCPVC. If one formulates a latex paint so that the PVC is slightly less than LCPVC with an unflocculated latex but the latex flocculates, the PVC would be greater than LCPVC. No data have been published on the effect of latex flocculation on LCPVC. A simulation program using particle size distributions of latex and pigment and a measure of the deformability of latex particles has been developed to predict the CPVC of simple latex paints [17].

Floyd and Holsworth proposed a different point of view about LCPVC [18]. They suggest that a phase inversion occurs at LCPVC in which air becomes the external phase and the pigment–latex phase becomes the internal phase. The proposal is based on the information that latex films are somewhat porous at PVC values considerably below LCPVC. The porosity is caused by clustering of pigment particles and of latex particles as described above. When films dry, there will be air pockets in the film; and as the PVC increases, more and more of these air pockets join to make continuous passages of air through the film. As PVC reaches LCPVC, the rate of increase of pore formation increases rapidly with increased PVC. The result of this behavior is that there is not an abrupt change of all properties at LCPVC. For example, scrub resistance shows a broad transition retaining significant scrub resistance above LCPVC. On the other hand, opacity increases quite abruptly at LCPVC. Since porosity increases at PVC well below LCPVC (at PVCs of the order of 20 to 30 PVC), barrier related properties such as permeability and corrosion resistance begin to change at these relatively low PVCs.

22.2. RELATIONSHIPS BETWEEN FILM PROPERTIES AND PVC

22.2.1. Mechanical Properties

Changes in volume relationships almost always control the physical properties of pigmented films. Thus, there is a major advantage to formulating coatings on the basis of volume rather than weight relationships. For any particular application, there is a PVC/CPVC ratio most appropriate for the combination of properties needed for that application. Once this ratio has been established, changes in pigment combinations for that application should be made such that this PVC/CPVC ratio is maintained. This important concept is developed in detail by Bierwagen [4]. He also emphasizes that one must exercise particular care when formulating with PVC near CPVC, since relatively small changes in pigment ratios or in packing, flocculation, or film formation can substantially affect film properties [7].

Although it is desirable to have accurate determinations of CPVC available, even reasonable estimates can be useful, since they permit one to focus a series of experiments within a range approximating the desired PVC/CPVC ratio. The decision as to the proper pigment loading of a particular formulation should be based on actual experimental data, not on the theoretically best PVC value. Even without CPVC data, the concept is of value to the formulator. It is critical to recognize that performance properties vary with volume, not with weight relationships, and that CPVC increases with increasing particle size distribution. Qualitative use of oil absorption and density values for individual pigments, together with recognition that CPVC increases when mixtures of pigments with different particle size distributions are used, permit one to start formulating in a reasonable range of compositions. On the other hand, using weight relationships, one is working blindly.

In the majority of cases, T_g increases with PVC; however, there are examples in which T_g decreases or is unchanged. It is common for there to be two T_gs, one resulting from the continuous phase of binder and the other from the adsorbed layer of resin on the pigment surfaces.

Tan delta is generally lower, broader, and the peak is shifted to a higher temperature for heavily pigmented coatings than for unpigmented binder. The broadening and temperature shift increase with increasing PVC/CPVC ratio and are more pronounced with lamellar pigments than with spherical pigments. Figure 22.1 shows a schematic representation of tan delta as a function of temperature for a pigmented coating compared to an unpigmented binder.

An increase in pigmentation usually increases the elastic modulus, especially in the glass transition and rubbery regions, as shown in Figure 22.2. This results from the replacement of binder with rigid pigment. In Figure 22.2, CPVC is located between PVC 45 and 55%, as indicated by the lower E' in the glassy region of the coatings pigmented at PVC, of 55% and 60%.

The tensile strength of films generally increases with PVC to a maximum at CPVC but then decreases above CPVC. Below CPVC, the pigment particles serve as reinforcing particles and increase the strength. It can be considered that polymer molecules adsorb on the surface of multiple pigment particles, providing the equivalent of cross-links. Accordingly, more force is required to break this physical network as the pigment level increases. However, above CPVC, air voids weaken the film; abrasion and scrub resistances of films drop above CPVC.

The relative tensile strength of an acrylic binder with a series of pigments is shown in Figure 22.3. As expected, the tensile strength of films pigmented with TiO_2 and barytes rises to CPVC, then drops off. However, if the bonding between pigment particles and the resin is poor, as with $CaCO_3$, the tensile strength of the films drops steadily as PVC increases. With microtalc, the structure of the pigment gives especially high reinforcement at a low PVC.

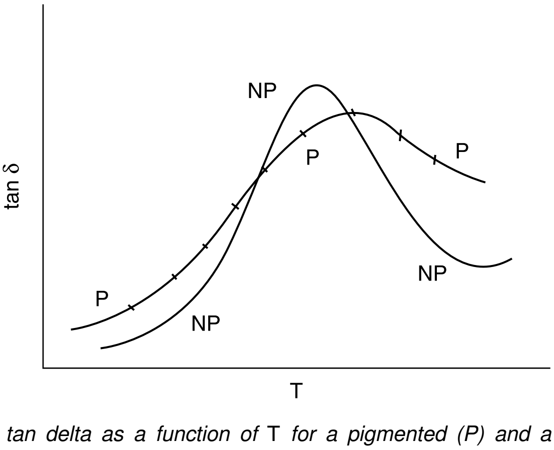

Figure 22.1. *Plot of tan delta as a function of* T *for a pigmented (P) and a non-pigmented (NP) coating. (From Ref. [1], with permission.)*

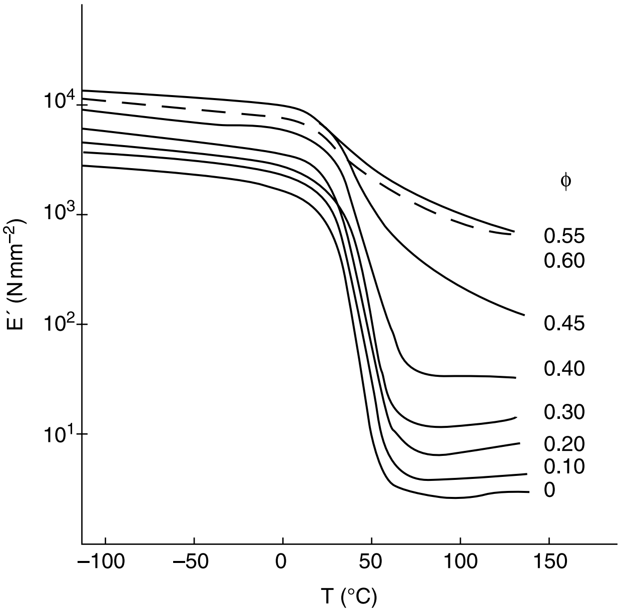

Figure 22.2. Storage elastic modulus (E′) *as a function of temperature* (T) *for a polyacrylate coating with a different PVC (ϕ) of TiO_2. (From Ref. [1] with permission.)*

The thermal expansion coefficient is affected by pigmentation. As shown in Figure 22.4, the thermal expansion coefficient of a TiO_2 pigmented epoxy coating decreases as the PVC increases.

Internal stress in dried films of coatings whose $T_g > T$ increases as PVC increases up to CPVC and then decreases. Accordingly, the probability of delamination or film cracking increases for such a system as a result of the stress.

22.2.1.1. Nano-pigment Effects Nano-pigments are those with small particle sizes; some authors include those with average particle sizes of less than 100 nm, but more commonly the particle size is below 25 nm. The term is new, but nano-pigments have been used in coatings for many years. For example, high strength channel blacks have particle sizes in the range 5 to 15 nm. A review paper on nano-material technology applications in coatings is available [19].

Compared to the effects of conventional pigments, the use of nano-pigments, especially nano-fillers, has the potential to improve important coating properties. Improvements in scratch, abrasion, heat, radiation, and swelling resistance, decrease in water permeability, and increases in hardness, weatherability, modulus, and strain to failure are all possible with nano-pigments. Of course, substantial improvements in one property may be accompanied by undesirable changes in other properties, so formulators must be judicious in the use of nano-particle pigments and fillers. The changes in properties reflect the high surface area of nano-particles, which results in an increase in adsorption of resin on the pigment surfaces and hence a larger fraction of immobilized resin. In some cases, the films have two T_gs. When the particle size of the largest pigment particles or clusters is

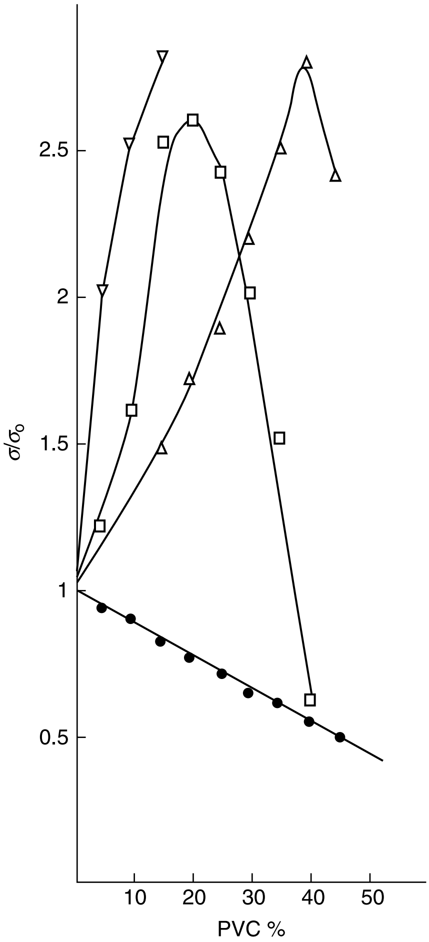

Figure 22.3. *Relative tensile strengths (ratio of pigmented film strengths to the strength of unpigmented film) dependence on PVC for an acrylic system containing $CaCO_3$ (•), microtalc (▽), TiO_2 (△), and barytes (□). (From Ref. [1], with permission.)*

smaller than the wavelength of light, coatings pigmented with nano-pigments are transparent [1]. Based on an adsorbed layer of 10 nm, the fraction of resin adsorbed on 300-nm pigment particles has been calculated to be 3%, and on 50-nm particles to be 22% [19].

It can be difficult to make stable dispersions of nano-pigments. Due to their high surface areas, nano-pigments have a strong tendency to agglomerate. If there is significant agglomeration, the advantages of nano-pigments will not be realized. Various approaches have been utilized, surface treatment of the pigments, in situ polymerization in the presence of the pigments, ultrasonic dispersion, and in some cases, conventional pigment dispersion [1]. Ball mills are used to disperse nano(aluminum silicate) in an acrylic resin with a commercial dispersing agent. The dispersion is used in making mar resistant clear coats [20].

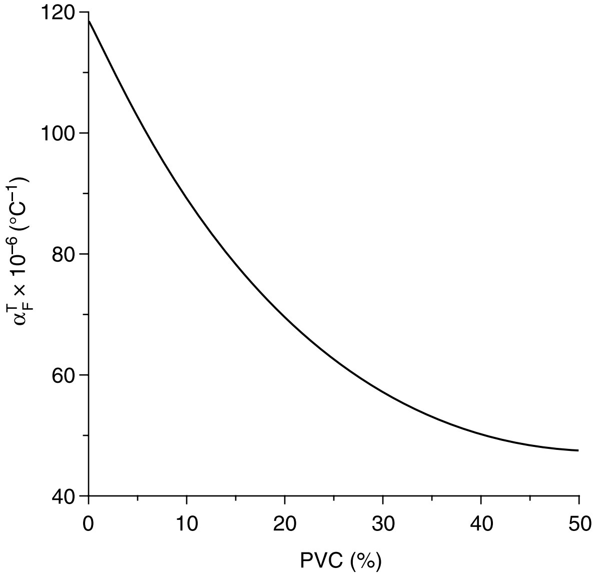

Figure 22.4. *Thermal coefficient dependence on PVC at 21°C and 0% RH for TiO_2 pigmented epoxy coatings. (From Ref. [1], with permission.)*

22.2.2. Effects of Porosity

Stain resistance decreases above CPVC, since staining liquids can penetrate pores, leaving color behind that is difficult to remove. Porosity also affects other properties. If one applies a single coat of a coating with PVC above CPVC to steel and exposes the panel to humidity, rapid rusting can occur, since the pores permit water and oxygen to get to the surface of the steel with little interference.

It is almost always desirable to make primers with a high PVC, since the rougher, low gloss surface gives better intercoat adhesion than does a smooth, glossy surface. In most cases, primers for metals should have a PVC that is high enough to roughen the surface and to minimize the permeability of water and oxygen but that is lower than CPVC, where the permeability increases. Minimum permeability often occurs at roughly $PVC/CPVC = 0.9$. In primers for non-metals it is sometimes desirable to formulate the primer with $PVC > CPVC$. Adhesion of a top coat to such a primer is enhanced by mechanical interlocking, resulting from penetration of vehicle from the top coat into pores of the primer. The primer PVC should be only enough higher than CPVC to assure good adhesion. If PVC is too high, many of the pores in the primer are filled with binder from the top coat, which decreases the PVC of the top coat, resulting in a loss of gloss. Such a primer is said to have poor *enamel hold out*.

In zinc-rich primers it is important that the PVC be greater than the CPVC. The porosity permits water to enter the film, establishing a conductive circuit with the steel surface. Primers using 2K urethane coatings that have $PVC > CPVC$ have the additional advantage that the porosity permits CO_2 to escape without blistering.

PVC (Section 19.3) also affects hiding; as the pigmentation increases, hiding generally increases. Initially, hiding increases rapidly but then tends to level off. In the case of rutile TiO_2, hiding goes through a maximum, gradually decreases with further increase in PVC, and then increases above CPVC. This increase in hiding above CPVC results from air voids left in the film when PVC is above CPVC. The refractive index of air (1.0) is less than that of the binder (approximately 1.5), so there is light scattering by the air interfaces in addition to the interfaces between pigment and binder. The effect becomes large as interfaces between air and pigment increase with increasing PVC. For example, if rutile TiO_2, with a refractive index of 2.73, is in the formulation, the difference between the refractive index of TiO_2 and air (1.73) is larger than that between TiO_2 and binder (1.23). For this reason, white ceiling paints are often formulated at PVC $>$ LCPVC. Tinting strengths of white coatings increase as the PVC of a series of coatings is increased beyond CPVC. The air voids present above CPVC increase light scattering so that a colored paint dries with a lighter color than one having the same amount of color pigment but with PVC below CPVC.

If one applies an alkyd-based coating with PVC above CPVC to a wood substrate, one is less likely to get blistering than with a similar coating having PVC below CPVC. When water gets into the wood behind the coating, it can escape through pores in an alkyd coating when PVC is above CPVC but not when PVC is below CPVC.

22.2.3. Effects on Curing and Film Formation

There are many examples of the effects of pigmentation on curing of thermosetting coatings. Titanium oxide coated with alumina inhibits the curing of coatings with MF resins as the cross-linker. The basic alumina neutralizes the acid catalyst. Silica coated TiO_2 is acidic and does not inhibit the cure. In powder coatings, carboxy-functional resins and alumina-coated TiO_2 can interact, leading to higher yield values and higher viscosity.

Diallyl phthalate prepolymers catalyzed by dicumyl peroxide pigmented with silica cure well. However, kaolinite virtually eliminates the curing because the acidic groups present on the clay surface decompose the initiator [1]. On the other hand, UV-cure coatings pigmented with natural iron oxide gel in a matter of hours because of salts on the surface of the pigment. Synthetic iron oxide pigmented coatings can be used without difficulty.

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23

Application Methods

Many factors affect the choice of method to be used for a particular application, including capital costs, operating costs, film thickness, appearance requirements, and the structure of the object to be coated. Reduction of VOC emissions and improved efficiency are driving forces for improvement of application methods and equipment. Formulation of coatings and development of application methods are strongly linked. Electrodeposition and application of powder coatings are discussed in Chapters 27 and 28, respectively. Further information and discussion of additional application methods can be found in the general references at the end of the chapter.

23.1. BRUSHES, PADS, AND HAND ROLLERS

Brushes, pads, and hand rollers are frequently used for the application of architectural paints. Although the same paints can usually be applied by spray gun, few do-it-yourselfers use spray guns; on the other hand, to save time, professional painters use spray guns whenever possible.

23.1.1. Brush and Pad Application

A variety of brushes is available: narrow and wide, long handled and short handled, nylon, polyester, and hog bristle [1]. Hog bristles are appropriate for solventborne paints but not for waterborne paints. Nylon bristles are appropriate for waterborne paints but are swollen by some solvents. Polyester bristle brushes can be used with either. Brushes have in common a large number of bristles that hold paint in the spaces between the bristles. When the paint is applied, pressure forces paint out from between the bristles. The forward

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Organic Coatings: Science and Technology, Third Edition, by Zeno W. Wicks, Jr., Frank N. Jones,
S. Peter Pappas, and Douglas A. Wicks

motion of the brush splits the layer of paint so that part is applied to the surface and part remains on the brush. Open-cell polyurethane foam “brushes” are also used.

The characteristics of paint viscosity are critical in using brushes. Pickup of paint on the brush is controlled by paint viscosity at a relatively low shear rate, around 15 to 30 s^{-1}, the shear rate of dipping and removing a brush from a paint can. If the viscosity is too high, too much paint is brought out of the container with the brush; if the viscosity is too low, too little paint is on the brush. Ease of brushing requires a low viscosity. The shear rate between the brush and the substrate is relatively high, in the range 5000 to 20,000 s^{-1} [2]. The viscosity at high shear rate controls the ease of brushing; high viscosity leads to high “brush drag.” Film thickness applied is affected by the viscosity at a high shear rate; applied film thickness increases with increasing viscosity. For most applications, a viscosity at a high shear rate of 0.1 to 0.3 Pa•s is appropriate. (See Chapter 32 for further discussion.) Solvents with relatively slow evaporation rates must be used to slow the increase in viscosity of the paint on the brush.

When paint is applied by brush, the surface of the wet film has furrows called *brush marks*. These furrows do not result from the individual bristles of the brush, as is evident from comparing the size and number of brush marks with the bristles of the brush. When polyurethane foam brushes are used, brush marks still result, even though the brush has no bristles. Brush marks result from splitting the wet film between the brush and the substrate as the paint is applied. Whenever layers of liquids are split, the surfaces are initially irregular. These irregularities are made into lines by the linear movement of the brush. It is desirable to formulate a coating such that the brush marks flow out before the film dries. Low viscosity promotes leveling but increases the probability of sagging (Sections 24.2 and 24.3). Thixotropic flow properties are generally desirable because they delay the increase in viscosity after brushing, permitting a compromise between leveling and sagging. Formulation problems are particularly challenging in the case of latex gloss paints (Section 32.3.2).

Pad applicators are also used in the do-it-yourself market [1]. The most common type of pad consists of a sheet of nylon pile fabric attached to a foam pad that is attached to a flat plastic plate with a handle. For low-viscosity coatings such as stains and varnishes, a lamb’s-wool pad is used. Pads have a number of advantages over brushes. Pads hold more paint than a brush of similar width and can apply paint up to twice as fast. In general, pad application leaves a smoother layer than brush application. Extension handles can be used with pads, reducing the need for moving ladders. Pads, especially refills, are less expensive than brushes. On the other hand, pads require the use of trays, which results in some paint loss and solvent evaporation. Cleanup of pads is more difficult than cleanup of brushes.

23.1.2. Hand Roller Application

Hand rollers are the fastest method of hand application and are widely used in applying architectural paints to walls and ceilings. A variety of rollers and roll coverings is available [1]. There are rollers with built-in wells to minimize the need for dipping in the tray; there are also power-filled rollers.

Viscosity requirements are similar to those for brush application. When paint is applied by roller, there is also film splitting. As the roller moves, the film is stretched; flow is in an extensional mode (Section 3.6.3) within the film. Due to imbalances of pressures, the film breaks at different times, leaving a ribbed surface. Some of the film extends into fibers still farther from the nip. As the roller moves, fibers are drawn longer and longer and eventually break. After breaking, the ends of the fibers are pulled by surface tension to minimize the surface area of the applied coating, but if there is not sufficient time at low viscosity for leveling to occur, track marks are left in the coating. A further complication arises with longer fibers that may break in two places; as a result, droplets of loose paint fly off to land on the painter or on the floor. This is called *spattering*. If spattering could be eliminated, painting speed could be increased, and time spent on masking and laying drop cloths could be reduced. However, all current formulations spatter, some much more than others. The phenomenon is not completely understood. Glass [3–5] has pointed out that as the fibers are drawn out, extensional (elongational) flow rather than shear flow is involved (Section 3.6.3). It follows that extensional viscosity rather than shear viscosity affects the development of fibers from roller application and, in turn, the roughness of the film and the degree of spattering. Spattering can occur with any kind of paint, but is particularly difficult to minimize in latex paints (Section 32.2).

23.2. SPRAY APPLICATION

Spraying is a common method for applying paints and coatings in architectural and especially in industrial applications. Spraying is much faster than application by brush or hand roller. Spraying is used on flat surfaces, but is particularly applicable to coating irregularly shaped articles. Many different types of equipment are used for spraying; all atomize the liquid coating into droplets. Droplet size depends on the type of spray gun and coating; variables include air and fluid pressure, fluid flow, surface tension, viscosity, and in the case of electrostatic application, voltage. The choice of spray system is affected by capital cost considerations, efficiency of paint utilization, labor costs, and the size and shape of objects to be coated, among other variables. Coating formulations must be adjusted for the particular spray equipment and conditions.

The principal disadvantage is the inefficiency of application, since only a fraction of the spray particles are deposited on the object being sprayed. One must mask work areas where coating is not desired, and there is a likelihood of contaminating the area with spray dust. Some of the droplets approach the surface and *bounce back*, carried by eddy currents of air. The higher the pressure, the higher the forward velocity of the air and as a result, the greater the percentage of bounce back. Some droplets miss the object being coated, resulting in *overspray*. Some droplets may fall out of the spray pattern under the force of gravity. *Fallout* is higher with large spray patterns and longer distances between the spray gun and the surface being sprayed. The sum of all this waste determines *transfer efficiency*; transfer efficiency is defined as the percentage of coating solids leaving the gun that is actually deposited on the coated product.

Spray dust can cause many problems. If spray dust lands on the surface of a wet coating, dirt contamination results. If the surface tension of the spray droplets is different than that of the wet-surface, cratering will result (Section 24.4). Minimizing spray dust by choice of application equipment, ventilation, and careful maintenance and cleaning of equipment is vital.

Transfer efficiency is an important cost factor, since high transfer efficiency means that less coating is used for the same surface area; VOC emissions are also reduced. Transfer efficiency is affected by many variables. The size and shape of the product being coated is a major variable. Transfer efficiency is low when spraying a chain link fence and high

TABLE 23.1. Typical Baseline Transfer Efficiencies

Type of Spray Gun	Transfer Efficiency (%)
Air	25
Airless	40
Air-assisted airless	50
High volume low pressure air	65
Electrostatic air	60–85
Electrostatic rotary	65–94

Source: Ref. [6].

when spraying a large wall. Less obvious variables are conveyor line speed, localized air flows, and the way that objects being coated are hung on a conveyor line. The spray method has a major effect on transfer efficiency, whether the application is manual or automated; whether air, airless, or rotary spray guns are used; and whether an electrostatic system is used. For manual systems, the skill of the sprayers is very important. For automated systems, system design is critical. Some factors involved are distance between the gun and the surface, angle of the spray gun, stroke speed uniformity, extent and uniformity of overlapping, and precision of triggering.

To compare transfer efficiency of different spray methods, the EPA, together with spray gun and coatings manufacturers, has developed a standard procedure for comparing *baseline transfer efficiency*, adopted by the ASTM as Method D-5009-96. Measurement of transfer efficiency is difficult because small changes in air flow can affect the results. Typical percentages are given in Table 23.1; actual efficiencies are affected by many variables besides the spray method. For example, transfer efficiency in coating a chain link fence is low at best, and transfer efficiency in coating large wall expanses is high in any case.

Very reactive coatings with short pot lives, such as some two-package polyurethane coatings, require dual feed spray guns. Most commonly, the two components are metered into a small, efficient mixing chamber just before the spray gun orifice. The average dwell time in the mixing chamber is a fraction of a second, and the average residence time in the gun is not much longer. The equipment is designed to flush the mixing chamber and the gun with solvent automatically, to prevent clogging when spraying is interrupted. Frequent checking and maintenance are required to assure that the proper ratio of components is being applied. In other types of equipment, the components are sprayed from two orifices; mixing occurs after atomization so that the coating cannot gel in the equipment.

23.2.1. Air Spray Guns

Air spray guns (Figure 23.1) cause atomization of a coating by fine streams of compressed air. It is the oldest spray method and is still used. A stream of coating is driven through the nozzle orifice at relatively low pressure, 10 to 50 kPa (1.5 to 7 psi), or by the suction caused by rapid air flow past the outside of the orifice. The stream of coating coming out of the orifice is atomized into small droplets by fine streams of compressed air at pressures of 250 to 500 kPa (35 to 70 psi). The degree of atomization is controlled by (1) the viscosity of the coating (the higher the viscosity at the high shear rate encountered going through the orifice, the larger the particle size), (2) air pressure (higher air pressure,

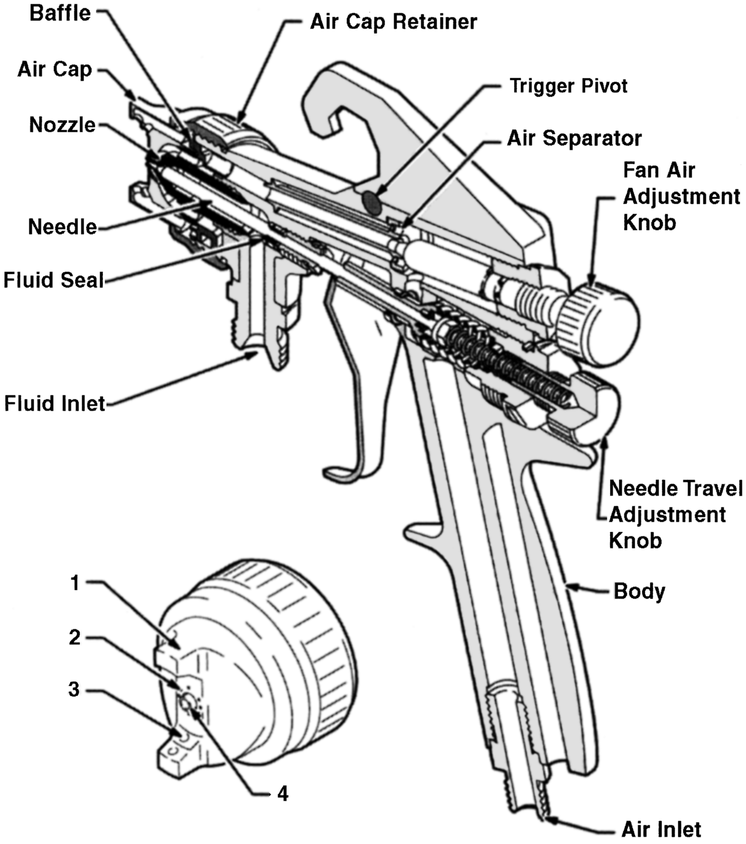


Figure 23.1. *Cross section of an air spray gun and of spray gun nozzle (Delta Spray, Graco, Inc.). 1, Wings or horns; 2, angular converging holes; 3, side-port holes; 4, annular ring around the fluid tip. (Courtesy of Graco, Inc., Minneapolis, MN.)*

smaller particle size), (3) the diameter of the orifice (smaller orifice, smaller particle size), (4) pressure forcing or pulling the coating through the orifice (higher pressure, smaller particle size), and (5) surface tension (lower surface tension, smaller particle size). The outer jets of compressed air shown in the figure adjust the shape of the stream of atomized particles coming from the gun. If these jets were not present, a cross section of the stream would be roughly circular. Generally, an elliptical cross-sectional pattern permits more efficient application; the pattern is a flattened cone, often called a *fan*. Guns can be hand held or attached to robots.

Air spray guns are less expensive than other types of guns. Atomization can be finer than with other spray guns. The system is versatile, and any sprayable object can be sprayed with air spray. The level of control can be high if the operators are skilled. However, transfer efficiency is the lowest of all the spray methods (Table 23.1).

A substantial improvement in transfer efficiency of air spraying has been made by use of *high volume low pressure* (HVLP) air guns. These guns are designed to operate at lower air pressures, 20 to 70 kPa (3 to 10 psi), but with higher air volumes and large, unrestricted air passages to handle a large volume of air. Because of the low pressures, bounce back is reduced and transfer efficiencies of 65% or even higher can be achieved. HVLP guns are used increasingly in automotive repair shops. California South Coast VOC regulations require 65% transfer efficiency and air pressures of 70 kPa or less. An alternative approach to HVLP guns is low volume low pressure (LVLP) guns. In LVLP guns, the air pressure is also less than 70 kPa, but the air volume is reduced by mixing the air and coating inside the gun.

23.2.2. Airless Spray Guns

With airless spray guns, coating is forced out of an orifice at high pressure, 5 to 35 MPa. The coating comes out of the orifice as a "sheet." As the sheet extends in moving away from the orifice, flow instabilities cause the formation of ligaments, followed by further disintegration into droplets [7]. Atomization is controlled by the relative velocity between the sheet and the contiguous air (higher relative velocity, smaller droplets), viscosity (higher viscosity, larger particle size), pressure (higher pressure, smaller particle size), and surface tension (lower surface tension, smaller particle size). The shape of the fan or pattern of the spray is controlled by the orifice size and shape. Air-assisted airless spray guns are also available; the atomization is airless but there are external jets to help shape the fan pattern, confining the smaller droplets within the spray pattern [8]. Both hand held and robot airless guns are available.

The size of droplets from airless spray guns is larger than those from air spray guns, 70 to 150 μm as compared with 20 to 50 μm [9]. Airless guns give a *fishtail spray*; that is, there is a relatively sharp edge to the spray droplet fan, with quite uniform droplet distribution within the fan. In contrast, the fan from air guns is *feathered* at the edge; that is, the number of droplets decreases at the edge of the fan, with some being quite widely spaced. As a result of these differences, one can generally achieve more uniform film thickness with air spray than with airless spray; air-assisted airless application gives intermediate results.

Coatings can be applied more rapidly by airless than by air guns, permitting more rapid production. However, as the application rate increases, the likelihood of applying excessive coating thickness also increases, particularly when coating objects with complex shapes. Excess coating thickness is not only wasteful, but may also lead to sagging. Since there is not a stream of compressed air accompanying the particles and because the droplet size is generally larger, there is less solvent evaporation from the atomized particles from airless guns than from air guns. Solvents with higher relative evaporation rates are generally required in formulating coatings for airless spray application.

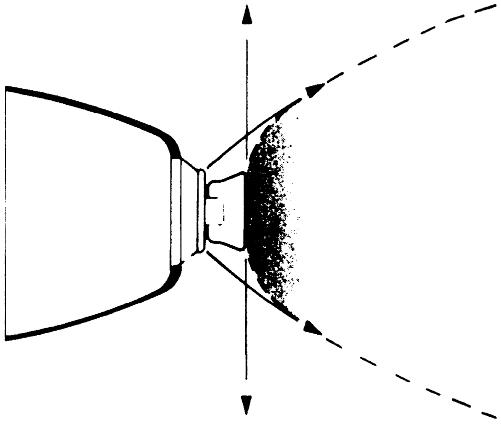
The absence of the air stream in airless guns reduces the problem of spraying into closed recesses of irregularly shaped objects. On the other hand, spraying down a recessed section that is open on the opposite end is easier with an air gun, since the air stream helps to carry the particles along. Airless spray equipment can cause problems with some waterborne coatings. More air is dissolved in the water under the high pressure; it comes out in bubbles when the pressure is released as the particles leave the gun. Entrapment of bubbles in the film can result in pinholing (Section 24.7). Also, with some latex coatings, particle size of particles leaving the gun are larger than would be expected from the shear viscosity of the coating. It has been shown that the extensional viscosity is relatively high in such coatings [5].

2K coatings can be applied with dual feed airless spray equipment, which permits combining the advantages of airless spray and dual spray [10]. Such equipment has been developed to the point where it is possible to spray coatings that cure within a few seconds, enabling use of 2K polyurea coatings (Section 12.4.1). An aerosol coating container is a type of airless spray unit. A liquefied gas, commonly propane, supplies the pressure to force the coating out of the orifice. Since the pressure is relatively low, the viscosity of the coating must be low to achieve proper atomization.

23.2.3. Electrostatic Spraying

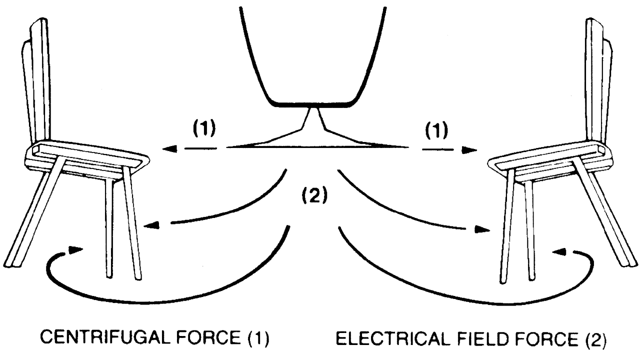
Transfer efficiency can be substantially higher with electrostatic spray units (Table 23.1). In the simplest case, a wire is built into the orifice of the spray gun. An electric charge on the order of 50 to 125 kV is impressed on the wire. At the fine end of the wire, an electric discharge leads to ionization of the air. As atomized coating particles pass through this zone of ionized air, they pick up a negative charge. The object to be coated is electrically grounded. When the coating particles approach the grounded surface of the object, the differential in charge attracts the particles to the surface. Taking the example of a chain link fence, an increased fraction of coating deposits on the metal fence even to the extent that particles that had passed through the holes are attracted back to the back side of the fence. This *wrap around* effect permits coating both sides of the fence by spraying from only one side; there is a lower but still fairly high overspray loss even with electrostatic spraying. In large-scale production, most of the paint is applied precisely by computer-controlled robots. With objects such as automobile bodies, overspray losses can be reduced by over 50%, resulting in transfer efficiencies above 80%.

Different types of devices can be used for electrostatic spraying. Figures 23.2 and 23.3 show bell- and disk-type spray units called *rotary atomizers*. In both cases, coating is pumped through a tube leading to the middle of the disk or bell; the unit is rotated at a speed of about 900 rpm or higher, depending on the diameter, and the coating flows out to the edge of the unit. As the coating is thrown off the edge of the unit, it is atomized



The Bell: The geometry of the spray pattern is varied according to the object to be painted by adjusting an annular compressed air shroud

Figure 23.2. Bell electrostatic spray equipment. (From Ref. [1], with permission.)



The Disc: The combined centrifugal and electrostatic forces of the ultra-high speed disc provide an extremely uniform finish and excellent penetration. Transfer efficiencies are high

Figure 23.3. *Disk electrostatic spray equipment. (From Ref. [1], with permission.)*

and then passes through an electrostatic field that charges the droplets. Droplet size is controlled by viscosity and the peripheral speed of the unit. Small (2 to 6 cm in diameter) bells that spin at speeds up to 60,000 rpm permit the application of coatings with viscosities as high as 1.5 to 2 Pa•s, compared to 0.05 to 0.15 Pa•s used with conventional speed disks and bells as well as spray guns. The spray pattern is adjusted with *shaping air*. This ability to handle higher viscosity coatings permits use of less solvent. However, it has been reported that application of pigmented coatings by high speed electrostatic bells tends to give films with lower gloss [11]. It is suggested that the centrifuging effect leads to differences in pigment content among atomized particles, leading to formation of uneven films. The uniformity of application and transfer efficiency can often be improved by compressed air shaping of the cloud of atomized coating, analogously to the effect of the shaping air in conventional air guns.

Low overspray losses and good wrap around with electrostatic spray depend on the charge pickup by the atomized particles, which is controlled by the coating conductivity. If it is too low, the particles do not pick up sufficient charge from the ionized air. This is most likely to be a problem with coatings that have only hydrocarbon solvents, especially aliphatic hydrocarbons. Nitroparaffin or alcohol solvents can be substituted for a portion of the hydrocarbon solvents with good results. For coatings with free carboxylic acid groups on the resin, addition of a small amount of a tertiary amine such as triethylamine increases conductivity sufficiently to provide good charging. If the conductivity is too high, there is increased danger of electrical shorting. Generally, conductivity is measured, but the results are expressed as resistivity; optimum resistivity varies with equipment and the coating operation, ranging from 0.05 to 20 MΩ. Newer gun designs permit operation with a wide range of conductivities.

The conductivity of waterborne coatings is higher than that of solventborne coatings; resistivities on the order of 0.01 MΩ have been reported [12]. The addition of slow evaporating water-miscible solvents with nonpolar ends, such as 2-butoxyethanol, reduces surface conductivity somewhat. However, spray equipment must be specially designed so that the coating line is isolated electrically; otherwise, the charges will be dissipated and the atomized droplets will not be charged. Furthermore, the hazard of shocks would be high. Although the entire application line could be isolated electrically, this is expensive and there is still a hazard of electric shocks. Alternatively, just the atomizer and a short hose connected to a voltage blocking device can be charged [13]. Another alternative to electrical isolation is to fit the gun with an external probe that charges the atomized paint. These expedients permit effective charging of the atomized droplets and reduce the hazard of shocks at substantially lower cost than that to isolate the entire application line.

Electrostatic spray application is not without limitations. The substrate must be electrically conductive so that the necessary charge differential can be set up by grounding the object to be sprayed. It can also be difficult to get coating into recessed areas even with airless electrostatic spray application, due to the *Faraday cage effect*. A Faraday cage results from the pattern of field lines between the electrode on the gun and the grounded object. The strong electrical field induced by the difference in voltage establishes field lines that the atomized particles follow between the gun and the object. However, areas surrounded by grounded metal, such as inside corners of a steel case, are shielded from the electric fields by the metal; a Faraday cage is established and few particles enter such a shielded area.

Electrostatic spray is the most important method for applying powder coatings (Section 28.5.1).

23.2.4. Hot Spray

Since the viscosity of coatings must be relatively low, generally, 0.05 to 0.15 Pa•s, for proper atomization, the solids must be quite low, especially for lacquers made with relatively high molecular weight (MW) resins. An approach for increasing solids is use of *hot spray*, also called *temperature conditioned spray*. A hot spraying unit is designed with a heat exchanger to heat the coating to temperatures from 38 to 65°C. The unit is designed so that the coating is recirculated when the gun is turned off, even temporarily. At the elevated temperature, the viscosity is reduced sufficiently to permit a significant increase in solids. Although these systems were originally designed for use with quite low solids coatings such as lacquers, they are useful for high-solids coatings. For example, it is reported that the solids of a top coat for appliances can be increased from 55% to 65% using a heater before a disk electrostatic spray gun [2]. The viscosity of high-solids coatings generally decreases more sharply with increasing temperature than that of conventional coatings, which is a desirable characteristic for hot spray application. A further advantage is that the temperature drops between leaving the spray gun orifice and arrival on the work, leading to a correspondingly large viscosity increase. This characteristic is desirable for reducing sagging, which can be serious with high-solids coatings (Section 24.3). Another advantage is that temperature control eliminates the effects of variation in ambient temperature on viscosity of the coating.

23.2.5. Supercritical Fluid Spray

Some industrial coatings are applied by *supercritical fluid spray* [14,15]. The supercritical fluid of choice is carbon dioxide, which has a critical temperature of 31.3°C and a critical pressure of 7.4 MPa. In the supercritical state, carbon dioxide exhibits solvency characteristics similar to that of hydrocarbons, but it is not counted as VOC. A dual feed gun is used with a low solvent content coating as one feed and supercritical CO_2 as the other. The temperature must be controlled and the pressure must be above 7.4 MPa. The process has been used with a variety of solventborne coatings for many applications [14]. VOC is reduced by 30 to 90% without changing the MW of the resins. Waterborne coatings can also be applied using the process [14].

The high pressure means that expensive equipment and airless guns must be used. The supercritical fluid spray system minimizes some of the problems of utilizing airless spray with conventional coatings [15]. When the coating leaves the orifice of the spray gun, the very rapid vaporization of the CO_2 breaks up the atomized droplets, reducing the particle size and resulting in a narrower particle size distribution. The droplet size is comparable to that obtained with air spray guns and significantly smaller than that obtained with airless guns. Furthermore, the fan pattern is more similar to the feathered pattern obtained with air guns rather than the usual pattern for airless guns (Section 23.2.2). Loss of the CO_2 is essentially complete before the droplets reach the surface, so the viscosity of the applied film is relatively high, minimizing sagging. Transfer efficiency is also improved, reducing overspray and waste disposal problems.

23.2.6. Formulation Considerations for Spray-Applied Coatings

The formulation of solvent mixtures for spray-applied coatings and show effective use of spray guns requires taking into consideration the large surface area/volume ratio of the atomized coating droplets and the flow of air over the surface of those droplets. As discussed in Section 18.3, these factors affect the rate of solvent evaporation. When lacquers are applied by spray, over half the solvent in the coating may evaporate between the orifice of the spray gun and the surface of the object. If the solvent mixture is balanced properly and the spray gun is used properly, a relatively smooth, sag-free film can be obtained. Otherwise, sagging may occur when not enough solvent is evaporated or rough surfaces may result from dry spray. Low viscosity of the coating after it arrives on the surface generally facilitates leveling, but it also increases sagging (Sections 24.2 and 24.3).

Proper control requires a careful balance of solvent evaporation rate with the particular spray equipment and procedure. The greater the distance from the spray gun orifice to the work, the greater the fraction of solvent lost. Coatings are formulated to work best at a specific distance between the gun and the surface. This distance should be kept as constant as possible throughout the spraying operation. The problem can be illustrated by the result of a person spraying lacquer on a flat vertical surface by holding one's arm in a constant position and bending one's wrist to spray a wider area of the surface. When the gun is aimed perpendicular to the substrate surface, the distance is at a minimum. When the wrist is bent to the furthest degree, the distance is at a maximum. If the solvent mixture is properly balanced for an intermediate distance, the lacquer sprayed perpendicularly would be likely to sag; the lacquer film at the extreme distance would tend to show poor leveling. In extreme cases of poor spraying, both sagging and rough surfaces can occur on the same object.

The rate of solvent loss is affected by the degree of atomization. If the average particle size is smaller, the surface/volume ratio is higher and the extent of solvent loss is greater. The rate of solvent evaporation is also affected by air flow over the surface of the droplets. More solvent evaporates with air guns than with airless guns or spinning bells. The rate of air flow through the spray booth can affect the degree of solvent loss. Temperature in the spray booth can be an important factor; during hot weather, it is common to change the solvent mixture to slow the rate of evaporation. When formulating and testing a solvent mixture for a coating in the laboratory, the same type of spray gun at approximately the same distance from the work that will be encountered in the customer's factory should be used. A final adjustment must be made in the customer's plant under regular production conditions. If those conditions change, the solvent mixture has to be changed. This is one reason why industrial coatings are almost always shipped at higher concentrations than the customer will actually use. This permits modifications of both solvent levels and solvent composition (by changing the reducing solvent) to accommodate temperature changes in the spray booth and other variables.

The viscosity of the coating must be adjusted to obtain appropriate atomization for the spray gun being used. The critical viscosity for atomization is that at the high shear rates (10^3 to 10^6 s^{-1} [2]) encountered as the coating passes through the orifice of the gun. Coatings with high low-shear viscosity can be sprayed successfully if they are shear thinning. The upper limitation on viscosity at a low shear rate is the need to have a satisfactory flow rate of coating through the tubing to the spray gun, which varies from gun to gun. Architectural and maintenance paints, which must not sag significantly when thick films are applied to large wall expanses, are shear thinning. Generally, the same coating used for brush application can be used for spray; in the case of latex paints with some spray equipment, the viscosity at a low shear rate may have to be reduced by diluting with a small amount of water.

Many conventional industrial coatings exhibit Newtonian flow; however, most high-solids coatings and waterborne coatings are shear thinning. Viscosity for application is generally checked with an efflux cup (Section 3.3.5). However, efflux cups can be misleading because they do not detect shear thinning or thixotropic flow properties. They should only be used for control purposes. The proper way to establish viscosity for production spraying is by using the production spray gun under the conditions of use. Then, having found the optimum formulation, one can establish an efflux cup time as the standard for that coating for use in that gun under those circumstances.

Many water-reducible and high-solids coatings are shear thinning after reduction to spray viscosity, which means that to give proper atomization, the efflux cup time of the reduced waterborne coating will be longer than with most solventborne coatings. Atomization is controlled by the viscosity at high shear rate, and efflux cup time is controlled by the viscosity at a lower shear rate. Sagging of some spray-applied high-solids coatings cannot be controlled by adjustment of solvent evaporation rates. In such cases, the coating has to be formulated so that it is thixotropic (Section 24.3).

In spray application of waterborne coatings, air bubbles can be entrapped in the coating film. If they persist until the viscosity of the film surface becomes too high for the bubbles to escape, pinholing or popping will occur. The troublesome air voids are tiny ($\sim$10 μm). The problem can be particularly severe in airless spray application, since more air dissolves in the coating due to the high pressure. When the pressure is released as the coating leaves the spray gun, bubbles of air form in the droplets. Whereas larger air bubbles can escape by rising to the surface and breaking before the viscosity at the surface increases, microform bubbles dissipate only by dissolution of the air in the coating followed by diffusion through the film [16]. In air spray, HVLP spray, and air-assisted airless spray, the problem can be minimized by using CO_2 as the driving gas instead of air. The improvement results from the higher solubility of CO_2 than of air in a waterborne coating.

23.2.7. Overspray Disposal

In industrial production, the advantage of decreased overspray is not just savings in the cost of the lost coating and lower VOC emissions. Any overspray has to be trapped so that it does not contaminate the surrounding area. Water-washed spray booths (a spray booth in which the wall behind the work being sprayed is a continuous waterfall that is recirculated) are widely used. The overspray is collected as a sludge. Although it is sometimes possible to rework the sludge into low-grade coatings, generally the sludge must be disposed of in approved hazardous solid waste disposal landfills. Such disposal is expensive; increased transfer efficiency can reduce waste disposal cost.

Although water-washed spray booths work efficiently with solventborne coatings, the separation of sludge is less efficient when some waterborne coatings are sprayed. The overspray does not coagulate completely when it strikes the water as it does with solventborne coatings. This makes separation more difficult and can limit recirculation of the water. Froth flotation methods adapted from ore recovery processes permit relatively rapid separation of sludge [17]. Separation of sludge from waterborne coatings can be improved by adding to the water tank an emulsion of a melamine–formaldehyde resin together with water-soluble cationic and/or nonionic acrylamide polymers, which promote detackification and coating flocculation, respectively [18].

23.3. DIP AND FLOW COATING

Dip coating can be an efficient procedure for applying coatings; it offers both relatively low capital cost equipment and low labor requirements. The principle is simple: The object is dipped into a tank of coating and pulled out; excess coating drains back into the dip tank. In practice, satisfactory coating application by dipping is more complex. While excess coating is draining off the object, a gradation of film thickness develops; the coating thickness at the top of the object is thinner than at the bottom. During draining, solvent is evaporating. The differences in film thickness can be minimized by controlling the rate of withdrawal of the object from the dip tank and the rate of evaporation of the solvent. If the object is withdrawn slowly enough and the solvent evaporates rapidly enough, film thickness approaching uniformity on vertical flat panels can be achieved. In actual production, the rate of withdrawal is usually faster than optimum, so there is some thickness differential between the top and bottom of the object.

Care must be exercised in selecting or changing solvents for dip coating, owing to flammability hazards and changes in viscosity of the dip tank that result from evaporation of solvent. Changes in viscosity result in changes in film thickness, which increases with increasing viscosity. Achieving consistent results requires keeping the viscosity of the coating constant, which becomes more difficult as the volatility of the solvent is increased. Solvent is added to replace solvent lost from the tank.

Successful use of dipping in production lines requires that the coating be very stable. Viscosity can increase not only by loss of solvent, but also by chemical reactions of coating components. Only a small fraction of the coating in the tank is removed each time an object is dipped. Fresh coating is added to make up for these removals, but the coating in the tank is a mixture of old and newly added coating. Some of the original charge of coating is present for a long time. If cross-linking reactions occur in the bath, viscosity increases. The extent of such reactions must be minimal. While the viscosity can be reduced by adding more solvent, this reduces the solids, so dry film thickness is reduced. When oxidizing alkyds are the vehicle for a dip coating, an antioxidant must be added to avoid oxidative cross-linking. But the antioxidant must be sufficiently volatile that it escapes during the early stages of the baking cycle; otherwise, it inhibits cross-linking of the dry film. On the other hand, too high volatility would result in evaporation from the dip tank. Isoeugenol is an example of a suitable antioxidant for alkyds in dip coatings.

An advantage of dip coating is that all surfaces are coated, not just the outer surfaces accessible to spray. However, there are difficulties in dipping irregularly shaped objects. Coating may be held in pockets or depressions, giving pools of coating that do not drain. To minimize this problem, the point(s) at which the objects hang on the hooks of the conveyor line that carries it into and out of the tank must be designed and selected carefully. Objects to be dip coated must be designed with drain holes that minimize pooling but do not interfere with the performance or appearance of the product. Lower edges, especially lower corners, build up high film thickness. Buildup can be reduced by electrostatic *de-tearing*, that is, by passing the object over a highly charged electrode that causes a charge concentration at such points, causing drops to be pulled off. Waterborne coatings are supplanting solventborne dip coatings in many applications. They reduce flammability hazards and VOC emissions. Electrodeposition of coatings (Chapter 27) is a dipping process.

Flow coating and dip coating are related methods. Objects to be flow coated are carried hung on a conveyor through an enclosure in which streams of coating are squirted on the object from all sides. The excess coating runs off and is recirculated through the system. The volume of coating required to fill the lines of a flow coater is less than that required for a dip tank for objects of the same size. This reduces inventory cost and increases coating turnover, hence reducing somewhat the problem of bath stability. Flow coaters are designed so that the atmosphere in the enclosed area is maintained in a solvent saturated condition. In this way, evaporation of solvents is minimized until flow and leveling have been obtained. There is still a gradation of film thickness from the top to the bottom of the object, but usually less than that from dip coating. Highly automated flow coating lines have been used for applying coatings to major appliances. The design permits more rapid line speeds than with conventional dip tanks.

23.4. ROLL COATING

Roll coating is widely used and is efficient, but is applicable only to uniform flat or cylindrical surfaces. Relatively slow evaporating solvents must be used to avoid viscosity buildup on the rolls of the coater. The pot life of the coating must be relatively long, since the rate of turnover of coating through the system is relatively low. There are many types of roll coating procedures; the two most common are *direct roll coating* and *reverse roll coating*.

In direct roll coating, the stock passes between two rollers, an applicator roller and a backup roller, which are rotated in opposite directions. The rollers pull the material being coated between them as shown in Figure 23.4. Direct roll coating is used for coating sheet stock and sometimes for coil stock. In direct roll coating, the applicator rollers are generally covered with a relatively hard polyurethane elastomer. Coating is fed to the applicator roll by a smaller feed, or doctor, roll that is, in turn, fed by a

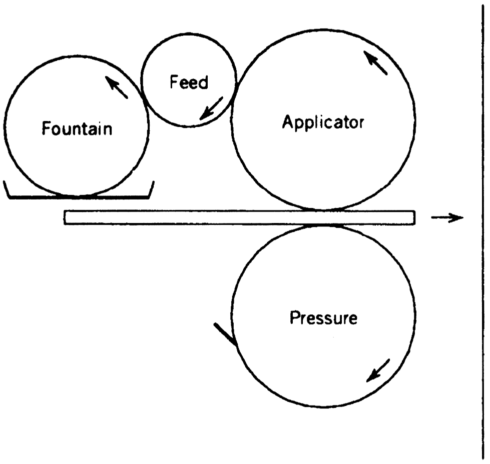


Figure 23.4. Direct roll coater. (From Ref. [1], with permission.)

pickup roll. The pickup roll runs partially immersed in a tray, called a *fountain*, containing the coating. Film thickness is controlled by the clearance between the feed and applicator rolls and by the viscosity.

Several variations on direct roll coating use different types of applicator rolls. The applicator rolls can have sections cut out so that they do not coat the entire substrate surface. The applicator roller can be engraved with small recessed cells over its entire surface. The cells are filled with coating, the surface is scraped clean with a doctor blade, and the coating remaining in the cells is transferred to the substrate being coated. Such *precision coaters* apply a controlled amount of coating only to the areas of the substrate that contact the roller. In another variation, the applicator roller is a brush roller for applying thick coatings to relatively rough surfaces.

In direct roll coating, as the coated material comes out of the nip between the rollers, the wet layer of coating is split between the roller and the substrate. As the coated stock comes out of the nip, the release of pressure results in cavitation. As the coated stock moves away from the nip, the walls between the cavities become filaments. Further along, filaments may break and fall back on the fresh coating, resulting in a ribbed surface called *roll tracking*. The coating must be designed to level so that this tracked appearance becomes less obvious, before the coating stops flowing. To minimize solvent loss on the rolls and to keep the viscosity low to promote leveling, slow evaporating solvents are used, and when possible, coatings are formulated so they exhibit Newtonian flow. The rate of shear on the coating as it passes through the nip depends on speed and gap distance but is on the order of 10^4 to $10^5\ s^{-1}$. If the coating exhibits thixotropy, it is desirable to have the rate of recovery of the low shear viscosity be as slow as possible.

As the coating comes out of a nip, the filaments may grow quite long. When they finally break, at least some split in more than one place, leading to drops being released, called *misting* (Figure 23.5). Extended filaments result when extensional viscosity is high [5].

In reverse roll coating, the two rollers rotate in the same direction, to the material being coated must be pulled through the nip between the two rolls, as shown in Figure 23.6. It is generally not feasible to coat sheets by reverse roll coating, but the process is widely used for coating coil stock. Reverse roll coating has the advantage that the coating is applied by

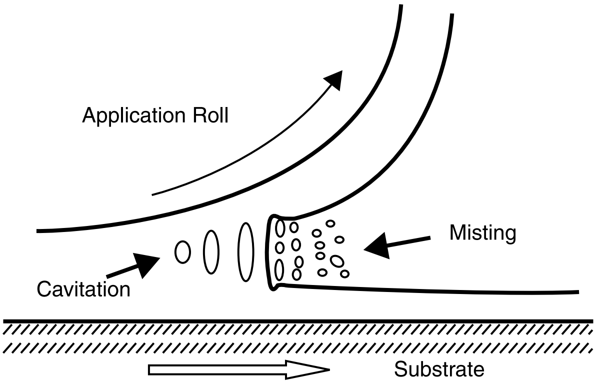


Figure 23.5. Cavitation and misting in roll application. (From Ref. [5], with permission.)

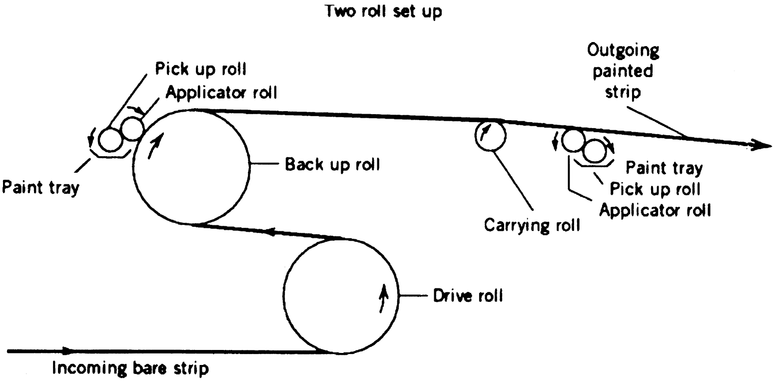


Figure 23.6. Reverse roll coater for coating both sides of coil stock. (From Ref. [1], with permission.)

wiping rather than by film splitting. A smoother film is formed, and the problems of leveling are minimized.

23.5. CURTAIN COATING

Curtain coating is widely used for coating flat sheets of substrate material such as wall panels and metal doors. Coating is pumped through a slot in the coating head so that it flows out as a continuous curtain. The sheet to be coated is carried through the curtain on a conveyor. The curtain must be wider than the substrate being coated, to avoid edge effects on the film thickness. A recirculating system returns to the coating reservoir the overflow from the sides and from between sheets. A schematic diagram is shown in Figure 23.7.

The width of the slot, the pumping pressure, the viscosity of the coating, and the rate of passage of the substrate being coated control film thickness. The faster the line runs, the thinner the coating. Where applicable, curtain coating is an excellent method. No film splitting is involved, so the film that is laid down is essentially smooth. Film thickness can be very uniform. The coating must be very stable; solvent is added to make up for

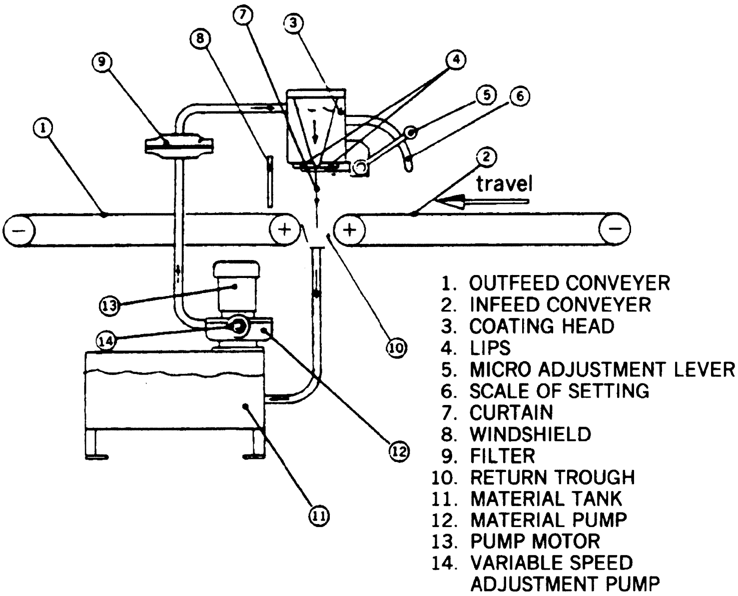


Figure 23.7. *Curtain coater. (From Ref. [1], with permission.)*

loss by evaporation. If a particle of low surface tension lands on a flowing curtain, surface tension differential driven flow can lead to a hole in the curtain that in turn leads to a gap in the coating being applied to the substrate (Section 24.4). As the surface tension of the coating is increased, particles in the air are more likely to have lower surface tensions than that of the coating, and the probability of holes is increased.

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24

Film Defects

Obvious defects can result from incomplete coverage during application of a coating, resulting in thin spots or holes, often called *skips* or *holidays*. Many other types of defects and imperfections can develop in a film during or after application. In this chapter we deal with the most important defects and to the extent possible, discuss the causes of the defects and approaches for eliminating or minimizing their occurrence. Unfortunately, the nomenclature for many defects is not uniform. Reference [1] provides definitions for coating terms, including those for film defects.

24.1. SURFACE TENSION

Many defects are related to *surface tension* phenomena. Surface tension occurs because the forces at an interface of a liquid differ from those within the liquid, due to the unsymmetrical force distributions on the surface molecules. The surface molecules possess higher free energy, equivalent to the energy per unit area required to remove the surface layer of molecules. The dimensions of surface tension are force exerted in the surface perpendicular to a line; SI units are newtons per meter or millinewtons per meter (mN m^{-1}). [Older units, still commonly used, are dynes per centimeter ($1\ \text{mN m}^{-1} = 1\ \text{dyne cm}^{-1}$).] Similar surface orientation effects are present in solids, which have surface free energies expressed in units of free energy per unit area, millijoules per square meter (mJ m^{-2}) that are numerically and dimensionally equal to mN m^{-1}. Frequently, people speak of the surface tension of the solids; although not formally correct, errors do not result, because the values are identical. Reference [2] is an excellent discussion of surface and interfacial properties, including data on many polymers.

Organic Coatings: Science and Technology, Third Edition, by Zeno W. Wicks, Jr., Frank N. Jones,
S. Peter Pappas, and Douglas A. Wicks

Surface forces work to decrease the surface free energy of liquids and solids. Surface tension works to draw liquids into spheres, since a sphere encloses a minimum ratio of surface area to volume. In a spaceship, liquid droplets assume a spherical shape; on Earth, the force of gravity distorts the spheres. For the same reason, surface tension drives flow of an uneven liquid surface toward becoming a smooth surface. The smooth surface has less interfacial area with air than the rough surface has; hence, there is a reduction in surface free energy as a surface becomes smoother.

Segments of molecules that minimize surface tension tend to orient at the surface. The lowest surface tension results from perfluoroalkyl groups at the surface. The next lowest is methyl groups. Poly(dimethylsiloxane) has a low surface tension; the very flexible easily rotatable backbone of siloxane bonds permits orientation of a large population of methyl groups at the surface. The surface tension of linear aliphatic hydrocarbons increases as the chain length increases, reflecting the larger ratio of methylene to methyl groups, Progressively higher surface tensions result from aliphatic chains, aromatic rings, esters and ketones, and alcohols. Dipolar groups such as ketones, and hydrogen-bonding groups such as alcohols, impart higher surface tension because the stabilizing intermolecular dipolar and hydrogen-bonding interactions are absent at the surface, resulting in higher surface energy. As the chain length of aliphatic esters, ketones, and alcohols increases, the surface tension increases because methylene groups give higher surface tensions than do methyl groups. Water has the highest surface tension of the volatile components used in coatings.

Addition of small amounts of surfactants to water reduces surface tension because the hydrocarbon chains go to the surface. Addition of poly(dimethylsiloxane) to an organic solvent solution reduces surface tension due to orientation of the methyl groups at the surface. When a liquid is agitated, the molecules at the surface are mixed in with the rest of the liquid. When the agitation is stopped, reorientation to give the lowest surface tension occurs, but the equilibrium surface composition is not reestablished immediately. When coating films are applied, they are subjected to considerable agitation. As Bierwagen has pointed out, the surface tension of importance in governing some aspects of coating behavior may not be the *equilibrium surface tension*, but rather, a *dynamic surface tension* [3,4]. The time to regain equilibrium after agitation has ceased varies widely, depending on the composition, viscosity, temperature, and probably other factors [5]. There has not been adequate quantitative study of the rates with different systems of importance in the coatings field. Qualitatively, one can say that equilibrium is established most rapidly when the coating contains small, flexible molecules and when there are large differences in the polarity of components in the system as in waterborne coatings. Reaching equilibrium takes longer when the molecules with the lowest potential surface tension groups are polymers. But if the polymers have moderate molecular weight and flexible backbones, they can apparently reach the surface relatively rapidly. Poly(dimethylsiloxane) is an example. Low molecular weight octyl acrylate copolymers are used as additives to reduce surface tension of coating films as they are forming. In waterborne coatings, it has been shown that surfactants differ in their rates of reaching equilibrium surface tension [5]. Surface tension increases with decreasing temperature, and solvents generally have lower surface tensions than those of resins. Therefore, surface tension increases as solvent evaporates from a film of resin solution, owing to the change in both concentration and temperature.

If two liquids with different surface tensions are in contact with each other, the liquid of low surface tension flows to cover the liquid with higher surface tension, since this results in a lower overall surface free energy. Such a flow is a *surface tension differential–driven* *flow*; some authors prefer the term *surface tension gradient–driven flow*. This type of flow has been observed for millennia, but Carlo Marangoni, a nineteenth-century Italian physicist, is credited with providing a scientific understanding of the phenomenon [6]. An example of the *Marangoni effect* is the flow that occurs when a clean glass containing wine is tipped, wetting the side of the glass with the liquid, and then returned to an upright position. Liquid then flows up the side of the glass, forming a bead of greater film thickness along the upper edge of the wetted area. When the amount of liquid collecting in the bead becomes large, droplets flow back down the side of the glass. These "tears of wine" have been known since biblical times, but why does the phenomenon occur? Ethyl alcohol has a higher relative evaporation rate and lower surface tension than water, evaporation occurs most rapidly along the edge of the layer of wine on the side of the glass. This leads to reduction in alcohol concentration and hence higher surface tension along the edge than in the bulk of the liquid. To minimize surface free energy, the low surface tension (higher alcohol concentration) liquid in the bottom of the glass flows up to cover the higher surface tension liquid at the edge. Evaporation continues at the edge, reducing the alcohol concentration and leading to a continuation of flow of lower surface tension liquid up the glass. The surface tension differential is also affected by the temperature change; as alcohol evaporates, temperature decreases, further increasing the differential in surface tension.

In summary, two types of flow result from surface tension effects. Surface tension driven flows occur to minimize the surface area of a liquid. Surface tension differential driven flows occur to cover a liquid or other surface of higher surface tension with a liquid of lower surface tension.

24.2. LEVELING

Most methods of application of coatings initially lead to formation of a rough, wet film. It is usually desirable for appearance and performance to have the irregularities level out. The most widely studied leveling problem has been leveling of brush marks. A person unacquainted with the field might first think that leveling results from gravitational effects. If gravity were a significant factor, paints applied to ceilings should level more poorly than paints applied to floors, but they do not. Based on studies of flow of mineral oil, Orchard proposed that the driving force for leveling is surface tension and established mathematical models for the variables that he proposed would control the rate of leveling [7]. Orchard's treatment has been widely applied to flow of coatings. Patton illustrated the model for an idealized cross section of a wet film exhibiting brush marks that follow a sine wave profile, as shown in Figure 24.1. He gives several forms

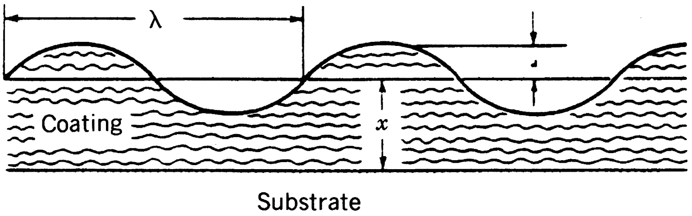

Figure 24.1. Cross section of brush marks. (From Ref. [8], with permission.)

of the Orchard equation and shows their derivations. A convenient form relating the change in amplitude of the sine wave to time is

$$\ln \frac{a_0}{a_\mathrm{t}} = \frac{5.3\gamma x^3}{\lambda^4} \frac{dt}{\eta} \tag{24.1}$$

where a_0 is the initial amplitude (cm), a_t is the amplitude at time t (cm), x is the average coating thickness (cm), λ is the wavelength (cm), γ is the surface tension (mN m^{-1}), η is the viscosity (Pa•s), and t is the time (s).

Leveling is fastest when the wavelength is small, the viscosity is low, the surface tension is high, and the film is thick. The formulator has little or no control over most of the variables. Wavelength is determined by application conditions; in brushing, it increases as pressure on the brush increases and as the thickness of the coating increases. High surface tension increases the rate of leveling; however, the formulator is limited in optimizing this factor, since high surface tension can lead to other defects. Thicker films promote leveling, however; increasing the film thickness increases the cost of coating and increases the probability of sagging (Section 24.3) on vertical surfaces. The principal means of control left is viscosity.

The Orchard model provides a satisfactory correlation between experimental data and predictions when the liquid film has Newtonian flow properties and sufficiently low volatility such that viscosity does not change during the experimental observations. With coatings, however, viscosity is usually changing during the time in which leveling occurs. As solvent evaporates, viscosity increases. Furthermore, if the system is thixotropic, the viscosity is reduced by the high shear rate exerted during application and subsequently increases with time at the low shear rate involved in leveling. Another potential shortcoming in the Orchard treatment is the assumption of constant surface tension.

Overdiep devised methods of observation that permitted following the location of the ridges and valleys [9,10]. He found for two alkyd coatings that brush marks leveled to an essentially smooth film, but then ridges grew where there had been valleys, and valleys formed where there had been ridges. Although surface tension can and does cause a ridged film to level, it cannot cause a level film to become ridged because that creates more surface area. Overdiep proposed that the surface tension differential is the major driving force for emergence of the new ridges. As shown in Figure 24.1, the wet film thickness in the valleys of the brush marks is less than in the ridges. When the same amount of solvent evaporates per unit area of surface, the fraction of solvent that evaporates in the valleys is larger than that in the ridges. As a result, concentration of resin solution in the valleys becomes higher than that in the ridges and the surface tension in the valleys is higher than that on the ridges. Following the Marangoni effect, coating flows from the ridges into the valleys. In other words, Overdiep proposed, and was able to demonstrate experimentally, that with volatile solvents, the primary driving force for leveling is not surface tension but surface tension differential. In some cases, these differentials lead to overshooting of the smoothest stage and cause the growth of ridges. The extent of the flow driven by surface tension differential depends on the rate of evaporation of the solvent.

Kojima and Moriga studied solvent evaporation and leveling of water-reducible coatings and showed that the forces driving leveling depend on the solvent in the formulation [11]. With a fast evaporating solvent, such as isobutyl alcohol, surface tension increased during drying, promoting leveling by surface tension differential forces, but with a slow evaporating solvent such as ethylene glycol monohexyl ether, surface tension decreased causing an adverse effect on leveling. Equations have been developed that model the drying process through the changes in surface tension differentials and changes in viscosity during solvent evaporation [12].

Overdiep was particularly interested in what happens with uneven coating films over a rough substrate [9]. He reasoned that surface tension–driven flow might give the smoothest film. However, as illustrated in Figure 24.2(*a*), this may be undesirable because protection in thin areas might be limited. On the other hand, as shown in Figure 24.2(*b*), surface tension differential–driven flow would tend to yield equal film thickness, with the surface of the film following the roughness of the substrate rather than being level. Overdiep suggests that it might be best to adjust a coating so that both types of flow are significant to achieve a compromise with reasonable film smoothness without places where film thickness is very thin, as shown diagrammatically in Figure 24.2(*c*). The balance could be controlled by the volatility of the solvent; with very low volatility, leveling would be surface tension driven; with relatively high volatility, the major effect would be surface tension differential; with intermediate volatility, both phenomena could be important.

Neither the Orchard equation nor Overdiep's work takes into account the effect of thixotropy. Cohu and Magnin developed equations that predict the effect of thixotropy on leveling of nonevaporative coatings [13]. Another result of poor leveling is reduction in gloss. A study of the effect of leveling on gloss showed that three factors are important: extent of roughness of the substrate, film thickness, and viscosity [14]. The addition of fluorocarbon surfactant did not significantly change leveling in these experiments; presumably, surface tension differentials did not develop in the drying of the films.

In spray application, surface roughness consists of bumps surrounded by valleys rather than ridges and valleys. Since the effect is somewhat reminiscent of the appearance of orange skins, it is called *orange peel*. Figure 24.3 shows an orange peel surface. The bumps are generally much larger than spray droplets. Most commonly, orange peel is

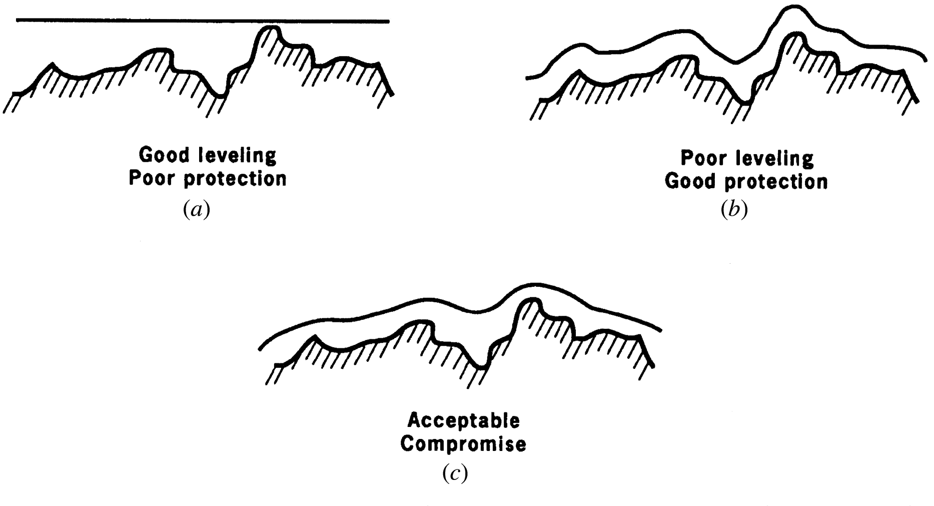

Figure 24.2. Alternate leveling (a–c) results after applying a coating to a rough surface. (Adapted from Ref. [9], with permission.)

Figure 24.3. *Typical orange peel pattern (15×). (From Ref. [16], with permission.)*

encountered when spraying coatings that have solvents with high evaporation rates. It is common for people to conclude that due to the fast evaporation, the viscosity of the coating on the substrate builds up so rapidly that the leveling is poor; in some situations, that is probably the case. However, in the late 1940s it was found that leveling of sprayed lacquer films could frequently be improved by addition of very small amounts of silicone fluid. Contrary to the common wisdom that all leveling is surface tension driven, that is, promoted by high surface tension, here was a case in which adding a material known to reduce surface tension improved leveling substantially.

Hahn provided an explanation for the phenomenon [15]. When one sprays a lacquer, initially the surface is fairly smooth, and if you watch, orange peel grows (Figure 24.3). Hahn proposed that the growth of orange peel results from a surface tension differential–driven flow. The last atomized spray particles to arrive on the wet lacquer surface have traveled a longer distance between the spray gun and the surface, hence have lost more solvent, a higher resin concentration and therefore a higher surface tension than the main bulk of the wet film. The lower surface tension wet lacquer flows up the sides of these last particles to minimize overall surface free energy; that is, surface tension differential–driven flow grows the orange peel. If one adds a surface tension depressant, such as a silicone fluid that orients very rapidly to the surface; the surface tension of the wet lacquer surface and the surface tension of the last atomized particles to arrive are uniformly low, so there is no differential to promote growth of orange peel. Octyl acrylate copolymer additives can also give an overall low surface tension and minimize orange peel growth.

It would be of interest to see what effect silicone fluid or octyl acrylate copolymers would have on leveling of brush applied coatings. To the extent that the leveling is surface tension differential driven, as found by Overdiep, the leveling should be made poorer, not improved. The results of such an experiment are not given in the literature, but such additives are not used to promote leveling in brush applied coatings, only in spray applied coatings.

Electrostatically sprayed coatings are likely to show surface roughness greater than nonelectrostatically sprayed coatings. It has been speculated that the greater surface roughness obtained with electrostatic spray results from arrival of the last charged particles on a coated surface that is electrically insulated quite well from ground. These later arrivals may retain their charges sufficiently long to repel each other and thereby reduce the opportunity for leveling. It has also been suggested that when coatings are applied by high-speed bell electrostatic spray guns, differentials in the pigment concentration within the spray droplets may result from the centrifugal forces [17]. These pigment concentration differentials can lead to rougher surfaces, reduction in gloss, and aluminum flake striping due to differential flake concentrations.

Leveling problems are particularly severe with latex paints. Latex paints, in general, exhibit a greater degree of shear thinning and more rapid recovery of viscosity after exposure to high shear rates than paints made with solutions of resins in organic solvents. Due to their higher dispersed phase content, the viscosity of latex paints changes more rapidly with loss of volatile materials than the viscosity of solventborne paints. No experimental work has been reported on the relative importance of surface tension and surface tension differentials in leveling of latex paints; however, it seems probable that the leveling is primarily surface tension driven. The surface tension of water is high, but the presence of surfactants imparts low surface tension to latex paints. Furthermore, it is probable that this low surface tension is established rapidly after the agitation of application stops. Perhaps more important, the surface tension is uniformly low, since it is almost unchanged as water evaporates. Thus, the generally poor leveling of latex paints may result in part from the absence of surface tension differentials to promote leveling. The low surface tension may not provide adequate driving force for leveling in a film whose viscosity increases rapidly with time. The problems of leveling of latex paints are discussed further in Section 32.3.2. The leveling of powder coatings is discussed in Section 28.3.

24.3. SAGGING AND DRIP MARKS

When a wet coating is applied to a vertical surface, the force of gravity causes it to flow downward (*sagging*). Differences in film thickness at various places lead to differing degrees of sagging, sometimes resulting in curtains, or drapes, of coating. The variables that affect the volume of coating that has sagged (V_s) after time (t) are given by Patton:

$$V_s = \frac{x^3 \rho g t}{300\eta} \tag{24.2}$$

where x is initial film thickness (cm), ρ is density (g cm^{-1}), g is gravitational constant (s cm^{-2}), t is time (s), and η is viscosity (Pa•s) [18].

Gravity is the driving force for sagging, which increases with coating density and thickness. Some latitude is available to the formulator in minimizing density and thickness, but the major variable available for controlling sagging is viscosity. The tendency to sag can be evaluated by observing the behavior of films applied under conditions simulating field use, and various tests have been developed. The most common test is a *sag-index blade*, a straight edge applicator blade with a series of $\frac{1}{4}$-in. gaps of different depths at $\frac{1}{16}$-in. intervals across the blade [19,20]. A drawdown, which is a series of stripes of coating of various thickness, is made on a chart, and immediately, the chart paper is placed in a vertical position. Sag resistance is rated by observing the thickest stripe that does not sag down to the next stripe. For research purposes, Overdiep developed the *sag balance*, a more sophisticated method, which provides a numerical basis for evaluating the extent of sagging [10]. Overdiep also developed equations for sagging that take into consideration the changes in viscosity after application.

In sprayapplied solvent solution coatings, sagging can generally be minimized while achieving adequate leveling by a combination of proper use of the spray gun (to avoid excessively thick areas) and control of the rate of evaporation of solvents. The goal is to manipulate viscosity so that it is initially low for leveling but builds up before noticeable sagging occurs. In brush and hand rollerapplied coatings where slow evaporating solvents are used, thixotropic systems permit leveling to occur before the viscosity recovers. Latex paints, which are almost always thixotropic, are less likely to exhibit sagging than are solvent solution paints.

Sagging can be a serious problem with high-solids coatings, especially when spray applied. Although other factors may be involved, a major cause of sagging of high-solids coatings is that substantially less solvent is lost during spraying (i.e., after the droplets leave the gun and before they arrive at the substrate surface) [20,21]. This low loss of solvent leads to less increase in viscosity of a high-solids coating than of a conventional coating, resulting in a greater likelihood of sagging. The reasons for lower solvent loss have not been clearly established, but are probably related to the following considerations. First, perhaps because of their higher surface tension, high-solids coatings atomize to give larger particle size droplets than those of conventional coatings. The lower ratio of surface area to volume would lead to lower solvent loss. However, one should be able to adjust spray equipment and conditions to obtain equivalent atomization. A second possibility is a colligative effect on solvent evaporation. Resins in high-solids coatings are lower in molecular weight, and their concentrations are higher. For both these reasons, the ratio of the number of solvent molecules to resin molecules is lower in the case of high-solids coatings than for conventional coatings. This undoubtedly leads to a decrease in rate of solvent loss (see Section 18.3.5 for a model calculation). However, it seems doubtful that this difference could account entirely for the large differences in solvent loss such as those reported by Wu [20]. A third theory is that the stage of diffusion control of the rate of solvent loss is reached after less loss of solvent from high-solids than from conventional coatings; thus, the solvent evaporation from spray droplets of high-solids coatings is markedly reduced [22,23]. At later stages of solvent evaporation from a film, the rate of diffusion of solvent molecules to the surface becomes the factor limiting the rate of evaporation of solvent. Solvents with linear rather than branched backbones are desirable since they can diffuse faster (Section 18.3.4).

Hot spraying can help control sagging (Section 23.2.4). When the coating cools on striking the object, the viscosity increase reduces sagging. The use of carbon dioxide under supercritical conditions is particularly helpful in controlling sagging, since the CO_2 flashes off almost instantaneously when the coating leaves the orifice of the spray gun, thereby increasing viscosity (Section 23.2.5). High-speed electrostatic bell application permits application of coatings at higher viscosity, which also helps control sagging (Section 23.2.3).

When sagging of high-solids coatings cannot be adequately controlled by adjustment of solvent composition of the coating and application variables, which is not uncommon, a useful approach is to employ additives to make the systems thixotropic. For example, dispersions of fine particle size silicon dioxide, precipitated silicon dioxide, bentonite clay treated with a quaternary ammonium compound, or polyamide gels can be added to impart thixotropy. One tries to formulate so that recovery to high viscosity is slow enough to permit reasonable leveling and rapid enough to control sagging. However, such agents increase the high shear viscosity somewhat and require higher solvent levels. They also tend to lower gloss and their effectiveness decreases as temperature rises.

The problem of sagging in high-solids automotive metallic coatings can be particularly severe (Section 30.1.2). Even a small degree of sagging, which might not be noticeable in a white coating, is very evident in a metallic coating, since it affects the orientation of the metal flakes. Use of SiO_2 to impart thixotropy is undesirable, since even the low scattering efficiency of SiO_2 is enough to reduce color flop in the coatings. Acrylic microgels have been developed that impart thixotropic flow by flocculation of the swollen gel particles [24]. In the final film, the index of refraction of the polymer from the microgel is nearly identical with that of the cross-linked acrylic binder polymer, so that light scattering does not interfere with color flop. The effect of the gel particles depends on interaction with the low molecular weight acrylic resin; Ref. [25] discusses the rheological properties of the systems. There can also be an improvement in the strength of the final film when microgels are incorporated [26].

Another problem that can be encountered with high-solids coatings is *oven sagging*, also called *hot sag* [22]. The coating appears to be fine until it is put into the oven; then sagging occurs. Oven sagging results from the strong temperature dependence of the viscosity of high-solids coatings. Compared to conventional coatings, there is a much steeper drop in viscosity as the coated product enters the hot oven, which promotes sagging; and the coating continues to flow even after the solvent is gone. Initial stages of cure are chain extension of the low MW resin. The viscosity does not jump until substantial cross-linking has occurred. Oven sagging can be controlled somewhat by zoning the oven. A lower temperature in the initial zone allows more time for solvent loss, and perhaps some cross-linking, so viscosity increases as a result of the higher solids or higher molecular weight before the film is subjected to high temperature.

Water-reducible coatings are less likely than high-solids coatings to give sagging problems, but there are circumstances in which they exhibit delayed sagging. The viscosity of these coatings is very dependent on the ratio of water to solvent as well as on the solids content (Section 8.3). As water and solvent evaporate, the residual water/solvent ratio can sometimes decrease, leading to lower viscosity despite the higher solids content; and sagging can result. Such behavior can depend on the relative humidity during the flash off period after spraying. It has been found for a water-reducible acrylic enamel that sagging occurred above, but not below, a critical relative humidity [27]. (See Sections 18.3.3 and 18.3.6 for the definition and discussion of critical relative humidity.)

A problem related to sagging is drip marks. For example, when one applies a coating to a vertical surface in which nail heads have been counter sunk, the coating may sag, but in addition, coating will flow out of the nail head depression where the film thickness is greater, so that an additional flow occurs. Similar effects can occur at other places on the paint surface, such as dripping from sharp corners, bolt holes, or cut outs, where film thickness tends to be greater.

An investigation of sagging and drip marks in latex paints is described in Ref. [28]. A computer model was developed that was correlated with the actual performance of the paints. The model takes into account not only the effect of gravity, thixotropy, and film thickness but also the change in flow properties of the thixotropic system with time. It is pointed out that during the flow of films, viscosity varies with shear stress rather than shear rate, as commonly thought. The model also accounts for nonuniform film thickness. As an example, the model was designed to predict the effect of a counter sunk nail head, which resulted in a locally thicker film. The thicker film is exposed to higher gravitational force for a longer time than the rest of the surface, resulting in greater flow out of the depression, resulting in a dip in the surface over the nail hole and formation of a drip mark below the depression.

24.4. CRAWLING, CRATERING, AND RELATED DEFECTS

If a coating that has a relatively high surface tension is applied to a substrate having a comparatively low surface free energy, the coating will not wet the substrate. The mechanical forces involved during application may spread the coating on the substrate surface, but since the surface is not wetted, surface tension forces tend to draw the liquid coating toward a spherical shape. Meanwhile, solvent is evaporating, and therefore viscosity is increasing, so that before the coating can pull up into spheres, the viscosity is high enough that flow essentially stops. The result is an uneven film thickness with areas having little, if any, coating adjoining areas of excessive film thickness. This behavior is commonly called *crawling* or *retraction* (Figure 24.4). For waterborne coatings, crawling can depend on the rate of establishment of equilibrium surface tension with different surfactants [5].

Crawling can result from applying a coating to steel with oil contamination on the surface. It is especially common in coating plastics. In some cases, crawling results from failure to completely remove a mold release agent from a plastic molded part. Application of a high surface tension top coat to a low surface tension primer can also lead to crawling. If a coating contains silicone fluids or fluorocarbon surfactants, there is likely to be crawling when a subsequent coat is applied. If one handles a primer surface with bare hands and then applies a relatively high surface tension top coat, it is likely that the top coat will draw away from the oils left behind in fingerprints. This type of crawling, which copies a pattern of low surface tension areas on the substrate, has been called *telegraphing*. Care is needed with this term, as this circumstance is only one of several phenomena called telegraphing.

Crawling can also result from the presence in the coating of surfactant-type molecules that can orient rapidly on a polar substrate surface. The polar group of the surfactant associates with the substrate, and the long nonpolar end becomes the surface. If one adds excess silicone fluid to a coating to correct a problem such as orange peel, small droplets of insoluble fractions of the poly(dimethylsiloxane) can migrate to the substrate

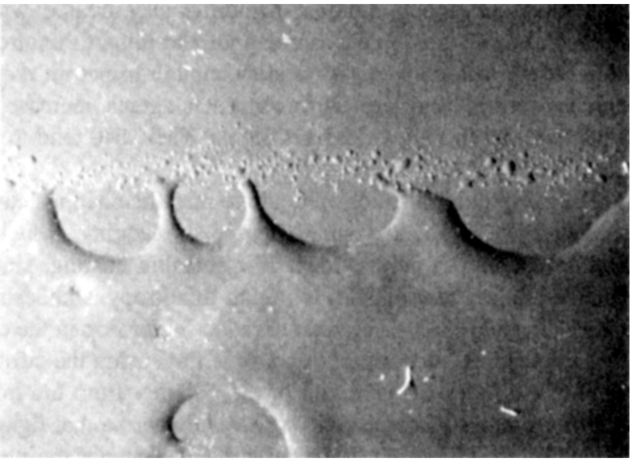

Figure 24.4. *Crawling of a top coat applied over a low surface energy primer (7×). (From Ref. [16], with permission.)*

surface and spread on it, leaving a new substrate surface that the coating cannot wet, resulting in crawling and/or cratering. A little silicone fluid can solve some defect problems, but even a small excess can cause what might be a worse problem. Higher molecular weight fractions of poly(dimethylsiloxane) are reported to be insoluble in many coating formulations [29]. Modified silicone fluids, such as polysiloxane–polyether block copolymers, have been developed that are compatible with a wider variety of coatings and are less likely to cause undesirable side effects. The effect of a series of additives on crawling and other film defects has been reported [30].

High-solids coatings often have higher surface tensions than those of conventional coatings. To achieve high-solids, lower molecular weight resins with lower equivalent weights must be used, which requires that the concentration of polar functional groups such as hydroxyl groups is higher, and hence surface tension is generally higher. Also, solvents that give the lowest viscosity coatings are likely to have relatively high surface tension. Accordingly, there is a greater likelihood of crawling problems with high-solids coatings.

Cratering is the appearance of small round depressions in a coating's surface, generally with a slightly raised crest. They often look somewhat like volcanic craters—hence the name. They are also called *fish eyes*. Schoff calls cratering "the nastiest, most frustrating defect of all" [31]. A schematic drawing and a photograph are shown in Figures 24.5 and 24.6, respectively. Cratering is sometimes mistaken for popping and vice versa; ways to differentiate them are described in Section 24.7.

Cratering results from a small particle or droplet of low surface tension contaminant, which is on the substrate, in the coating, or which lands on the wet surface of a freshly applied film [15]. The particles or droplets can be very small. Some of the low surface tension material dissolves in the adjacent film, creating a localized surface tension differential. As a result of the Marangoni effect, this low surface tension part of the film flows away from the particle to try to cover the surrounding higher surface tension liquid coating. Since, as the flow occurs, solvent evaporates, the differential in surface tension increases, and flow continues. However, loss of solvent causes an increase in viscosity, which impedes flow, leading to formation of a characteristic crest around the pit of the crater.

Craters must be avoided in applying coatings. The user applying the coating should try to minimize the probability of low surface tension contaminants arriving on the wet coating surface. For example, the spraying of lubricating oils or silicone fluids on or near the conveyor carrying freshly coated parts is an almost sure way to cause craters. Paint booth air must be filtered multiple times. However, in most factories, the presence

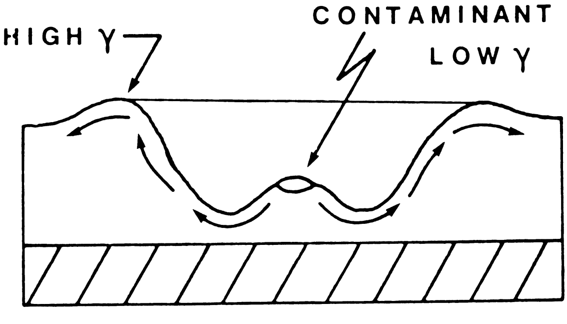

Figure 24.5. *Crater. (From Ref. [16], with permission.)*

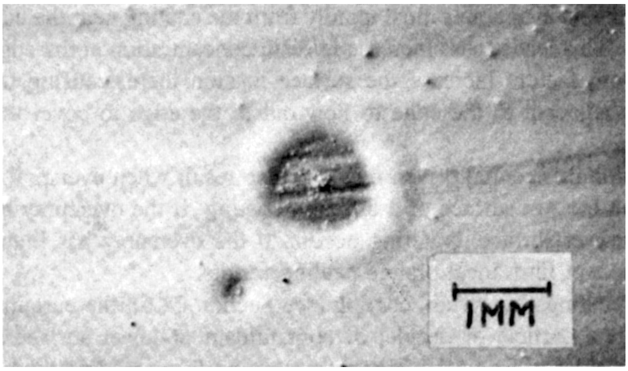

Figure 24.6. *Typical crater. (From Ref. [16], with permission.)*

of some contaminating particles cannot be avoided; therefore, the formulator must design coatings that minimize the probability of cratering. Lower surface tension coatings are less likely to form craters, since fewer contaminating particles will have even lower surface tensions. Alkyd coatings have low surface tensions and seldom give cratering problems (or crawling problems either). In general, polyester coatings are more likely to give cratering problems than acrylic coatings, which tend to have lower surface tensions. High-solids coatings, because of their generally higher surface tensions and low viscosities even after solvent loss, are more likely than conventional coatings to give cratering problems. Some waterborne coatings are also vulnerable to cratering. In a number of cases, particles from cosmetics worn by production workers have caused cratering of automotive coatings. Powder coatings are quite vulnerable to cratering, as discussed in Chapter 27.

It is possible in some cases to determine the nature and source of the contaminating particle, causing craters. Schoff and Hare advocate use of low power (2×–60× or 10× − 80×) optical microscopes for preliminary investigation of craters [31,32]. If necessary, more powerful optical microscopes and scanning electron microscopy (SEM) can be applied to the problem. SEMs with an x-ray attachment (EDX) are especially valuable. Two other powerful tools for such analyses are laser microprobe mass analysis (LAMMA) and time of flight secondary ion mass spectroscopy (ToF-SIMS). LAMMA is useful primarily in identifying inorganic materials, and ToF-SIMS is useful primarily in identifying organic contaminants; even between different silicone oils. In the case of a crater through a clear coat down to a base coat, ToF-SIMS showed that the contaminant was a poly(dimethylsiloxane). The source of the siloxane was traced to a resin supplied by a new supplier. In another case, craters in a primer coat on a car body were shown by LAMMA to be from a skin cream used by an employee in the paint shop. In another case, a contaminating particle in an *E*-coat primer was shown by LAMMA to be a welding pearl from a copper coated steel welding wire [33]. Even with these powerful tools, the cause cannot always be found, perhaps because the cratering agent has evaporated or dissolved in the film.

Additives can be used to minimize cratering. Small amounts of silicone fluid eliminate cratering, but as noted before, caution is required in selecting the amount and type of silicone fluid used to avoid crawling or recoat adhesion problems. Poly(2-ethyl hexyl acrylate) additives such as Modaflow usually reduce cratering. These additives operate by giving a uniform surface tension. Any low surface tension contaminant would spread itself widely across the surface. If the entire surface has a uniform surface tension, there will be no surface tension differential–driven flow and no cratering. A comparison of the effects of a range of additives on the control of defects such as cratering has been reported [34,35]. Side effects such as reduction of gloss and loss of adhesion of coatings applied over the coatings are discussed. Siloxanes with a polyether terminal group or side chain are reported to prevent film defects in waterborne coatings and to have little effect on recoatability. They are prepared by reacting allyl-terminated polyethers with poly(dimethylsiloxanes) with Si—H bonds [36].

There are many other examples of film defects that result from surface tension differential–driven flows. In coating tin plate sheets, the coating is applied by roller and the coated sheets are passed on to warm wickets that carry the sheets approximately vertically through an oven. In some cases, one can see a pattern of the wicket as a thin area on the final coated sheet. Heat transfer to the sheet is fastest where it is leaning against the metal wicket. The surface tension of the liquid coating on the opposite side drops locally because of the higher temperature. This lower surface tension material flows toward the higher surface tension surrounding coating, leaving an area of thin coating. This defect has also been called *telegraphing*. Similarly, on large plastic parts with thicker reinforced areas on the back of the part, telegraphing through to the top coat(s) can be encountered.

With the adoption of high-solids clear coats to paint plastic auto body components, there has been an increasing problem with *bond line readout*. Typically, this occurs over the areas of SMC plastic where, on the other side, there are adhesive joints to the car structure. A series of model system studies showed that the bond line defects resulted from differential surface tension–driven flow. The areas over the bond line heat more slowly than the adjacent areas, setting up differentials in surface tension and flow away from this bond line [37].

In spraying flat sheets, one can get an effect called *picture framing*, or *fat edge*. The coating is thickest at the edges and thinner than average just in from the edge. The contrast in hiding of the substrate can make the differences in film thickness very evident. Solvent evaporates most rapidly from the coating near the edge, where the air flow is greatest. This leads to a lower temperature and to an increase in resin concentration at the edge. Both factors increase the surface tension there, causing the lower surface tension coating adjacent to the edge to flow out to the edge to cover the higher surface tension coating.

Surface tension differential–driven flow can also result when overspray from spraying a coating lands on the wet surface of a different coating. If the overspray has lower surface tension than the wet surface, cratering occurs. If the overspray has high surface tension compared to the wet film, local orange peeling results.

In applying coatings by curtain coating (Section 23.5), the curtain of coating must remain intact. If a particle or droplet of contaminant of lower surface tension than the coating lands on the surface of the flowing curtain, surface tension differential–driven flow will cause a thin area in the curtain, which can cause a hole in the curtain. When this part of the curtain is deposited on the panel being coated, an uncoated area results. The problem is minimized by using coatings of the lowest possible surface tension. Since the curtain is flowing, dynamic surface tension is the important quantity. Bierwagen has discussed this phenomenon [4].

24.5. FLOATING AND FLOODING; HAMMER FINISHES

Two related defects result from uneven distribution of pigment in a film as it is drying: floating and flooding. Some people call both phenomena floating. We follow the more common terminology by which *floating* describes a mottled effect and *flooding* is used when the surface color is uniform but is darker or lighter in color than should result from the pigment combination used. Floating results from horizontal separation of different pigments within the film, whereas flooding results from vertical separation.

Floating is most evident in coatings pigmented with at least two pigments. For example, a light blue gloss enamel panel can show a mottled pattern of darker blue lines on a lighter blue background. The pattern tends to be hexagonal, but seldom perfectly so. Alternatively, with a different light blue coating, the color pattern might be reversed: The lines could be light blue with the background a darker blue. These effects result from pigment segregations that occur as a result of convection current flows driven by surface tension differentials while a film is drying. Rapid loss of solvent from a film during drying leads to considerable turbulence. Convection patterns are established whereby coating material flows up from lower layers of the film and circulates back down into the film. As the fresh material flows across the surface before it turns back down, solvent evaporates, concentration increases, temperature drops, and surface tension increases. The resulting surface tension differential sustains the convection current. The flow patterns are roughly circular, but as they expand, they encounter other flow patterns and the convection currents are compressed. If the system is quite regular, a pattern of hexagonal *Bénard cells* is established. The cells are named after a seventeenth-century French scientist who pointed out the commonness of hexagonal flow patterns in nature. As solvent evaporation continues, viscosity increases and it becomes more difficult for the pigment particles to move. The smallest particle size, lowest density particles continue moving longest and the largest particle size, highest density particles stop moving sooner. The segregated pattern of floating results.

Floating is particularly likely to occur if one pigment is flocculated and the other is a nonflocculated dispersion of fine particle size. The fine particle size pigment keeps moving longest and is trapped where the convection current turns back into the film at the border between adjacent cells. The border between the cells has a higher concentration of the finer particle size material, whereas the center of the cells is more concentrated in the coarser pigment. If in the example of the light blue coating, the white pigment is flocculated and the blue is not, one will find darker blue lines on a lighter blue background. If on the other hand, the blue is flocculated and not the white, there will be lighter blue lines on a darker blue background. Figure 24.7 shows convection patterns in Bénard cell

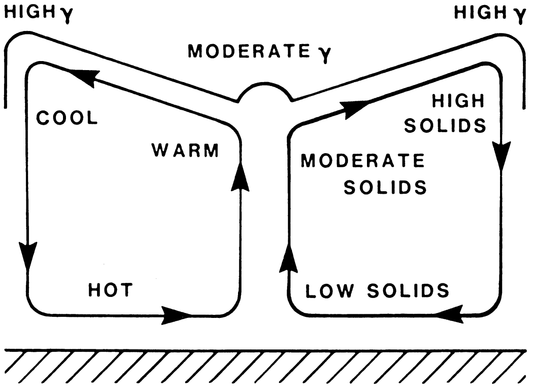

Figure 24.7. *Bénard cell formation. (From Ref. [16], with permission.)*

formation. Floating can also occur in single pigment coatings, resulting in uneven pigmentation of the surface, which reduces gloss.

Floating can be reduced by properly stabilizing pigment dispersions, so that neither pigment is flocculated. However, one can get floating even without flocculation. This can result from the use of pigments with very different particle sizes and densities. An example is use of fine particle size high-color carbon black with titanium dioxide to make a gray coating. Not only is the particle size of the TiO_2 several times that of the carbon black, but the TiO_2 also has about fourfold higher density. A much larger particle size, weaker black, such as lamp black, can be used to make a gray with a lower probability of floating.

Floating is reduced if slower evaporating solvents are used. Surface tension differentials are then less likely to be established, and Marangoni flow and floating do not occur. If a coating exhibits floating, the formulator should first reformulate to eliminate the problem; most commonly, selective pigment flocculation is the cause and should be corrected. Sometimes the flocculation is caused by the solvents used to reduce the coating to application viscosity, in which case solvent change eliminates the problem. In other cases, a change in the resin or dispersing agent used to stabilize the pigment dispersion is required (Section 21.1.3). The second choice is to use an additive. As with other flow phenomena driven by surface tension differentials, floating can be prevented by adding a minimum amount of a silicone fluid. To avoid crawling, the minimum amount of silicone must be used, which can be facilitated by using a very dilute solution of the silicone fluid in solvent. Since slow evaporating solvents also help reduce floating, slow evaporating solvents are commonly used to make additive solutions.

The term *flooding* is applied when the color of the surface is uniform but is different than should have been obtained from the pigment combination involved. For example, one might have a uniform gray coating, but a darker gray than that expected from the ratio of black to white pigments. The most troubling part of flooding is that the extent of flooding can vary with the conditions encountered during application, leading to different colors on articles coated with the same coating. Flooding results from surface enrichment by one or more of the pigments in the coating [16,38]. The stratification is thought to occur as a result of different rates of pigment settling within the film, which are caused by differences in pigment density and size or flocculation of one of the pigments. Flooding is accentuated by thick films, low vehicle viscosity, and low evaporation rate solvents—any factor that tends to keep the film at low viscosity longer and to allow more pigment settling. Flooding is easily detected by rubbing a section of a wet film: If the rubbed area has a higher color strength, the coating is flooding. The remedies are to avoid flocculation and low density fine particle size pigments, and if possible, to use faster evaporating solvents and higher viscosity vehicles. Floating, flooding, and related color defects are discussed in Ref. [38].

Floating and flooding can also occur in latex paints. The factors leading to floating and flooding in latex paints have been reported [39]. Latex paints include one or more surfactants in the latex, inorganic pigment dispersions, and organic pigment dispersions. In some cases, the combinations are unstable and lead to flocculation. In other cases, there can be incompatibility that affects only one of the pigments, which leads to floating or flooding. When a latex paint is diluted with water, floating can result. This is attributed to a shift in the equilibrium between the dispersed particles and water, resulting in less stabilizing dispersant on pigment surfaces. Also, the viscosity decreases, facilitating movement of particles; and increased surface tension may promote formation of Bénard cells. Decreasing the particle size of the inert pigments (kaolin and talc) reduces floating. Using a mixture of higher and lower molecular weight acrylic carboxylate dispersants gives the best compromise of dispersing efficiency and stabilization against floating. Compatibility between the thickener and the dispersants in the paint can be critical. TiO_2 content was found to affect floating in paints tinted with carbon black and monoazo red; the higher the TiO_2 content, the more pronounced the floating.

Although floating is usually undesirable, ingenious coatings formulators have taken advantage of the problem by purposely inducing floating to make attractive coatings. The coatings are called *hammer finishes* because they look a bit like the pattern one would get by striking a piece of metal with a ballpeen hammer. Hammer finishes were once used on a large scale, especially for coating cast iron components, for which it was desirable to hide the surface roughness. Such coatings contain large particle size nonleafing aluminum pigment and dispersions of transparent fine particle size pigments, commonly phthalocyanine blue. One way of getting a hammer effect is to spray a metallic blue coating and then spray a small amount of solvent on the wet film. Surface tension is lowest where drops of solvent land, and surface tension differential–driven convection flow patterns are set up, leading to floating where the lines have more blue and the centers of the patterns have more aluminum with less blue. There are *self-hammer coatings*, formulated to give a hammer finish pattern without need for a spatter spray of solvent. Fast evaporating solvents are used with a resin, such as a styrenated alkyd resin, which gives fast drying. Use of hammer finishes has decreased as smooth plastic molded parts replaced rough metal castings in many end uses.

24.6. WRINKLING AND WRINKLE FINISHES

The term *wrinkling* refers to the surface of a coating that looks shriveled or wrinkled into many small hills and valleys. In some cases, a wrinkle pattern is so fine that to the unaided eye, the film appears to have low gloss rather than to look wrinkled. However, under magnification, the surface can be seen to be glossy but wrinkled. In other cases the wrinkle patterns are broad or bold and are readily visible to the naked eye. Wrinkling results when the surface of a film becomes high in viscosity while the bottom of the film is still relatively fluid. It can result from rapid solvent loss from the surface, followed by later solvent loss from the lower layers. It can also result from more rapid cross-linking at the surface of the film than in the lower layers of the film. Subsequent solvent loss or cure in the lower layers results in shrinkage, which pulls the surface layer into a wrinkled pattern. Wrinkling is more apt to occur with thick films than with thin films because the possibility of different reaction rates and differential solvent loss within the film increases with thickness.

The earliest examples of wrinkling were with drying oil films, especially if all or part of the oil was tung oil, and cobalt salts were used as the only drier. Tung oil cross-links relatively rapidly when exposed to oxygen from air, and cobalt salts are active catalysts for the autoxidation reaction but are poor through driers (Section 14.2.2). These factors favor differential surface cure, which results in wrinkling of the surface layer. The wrinkle pattern can be fine or bold, depending on the ratio of tung oil to other drying oils, or in the case of alkyd systems, the oil length of the alkyd, and the ratio of cobalt to driers such as lead (or zirconium) salts that promote through dry. Although in many cases, wrinkling is undesirable, ingenious coating formulators turned the disadvantage into an advantage. For many years, *wrinkle finishes* were sold on a large scale for applications such as office equipment. Like hammer finishes, wrinkle finishes covered uneven cast metal parts. Their use has dropped since plastic molded parts have supplanted many metal castings.

Today, wrinkling is usually an undesired defect. It is most often encountered in improperly formulated or applied MF cross-linked coatings in which amines are used to neutralize acidity in the coating formulation and/or amine blocked sulfonic acid catalysts are used for package stability. The probability of wrinkling in such coatings increases as the volatility of the amine increases. For example, triethylamine leads to wrinkling under conditions in which dimethylaminoethanol does not. Increasing catalyst concentration tends to increase wrinkling, as does greater film thickness [40].

Another situation in which wrinkling can occur is in UV curing of pigmented acrylate coatings by free radical polymerization (Section 29.4). High concentrations of photoinitiator are required to compete with absorption by the pigment. Penetration of UV through the film is reduced by absorption by the pigment as well as by the photoinitiator. There is rapid cross-linking at the surface and slower cross-linking in the lower layers of the film, resulting in wrinkling. Wrinkling is likely to be more severe if the curing is done in an inert atmosphere rather than in air. In the latter case, the cure differential is reduced by oxygen inhibition of surface cure. UV curing by cationic polymerization, which is not air inhibited, is even more prone to surface wrinkling.

24.7. BUBBLING AND POPPING

Bubbles can occur near the surface of a film; *popping* is the formation of broken bubbles at the surface of a film that do not flow out. Both effects can occur when the surface viscosity increases to a high level while volatile material remains in the lower parts of the film. If the viscosity is very high at the surface, some of the bubbles of solvent rise to the surface but do not break. Popping occurs when the viscosity at the surface of a film increases sufficiently that solvent bubbles break but the coating does not flow out before further viscosity increase prevents leveling. If the pops are very small, the effect is sometimes called *pinholing*. There often is a mixture of open pops, bubbles, and pinholes in a surface.

Popping and bubbling result from rapid loss of solvent at the surface of a film during initial flash off. The surface develops a high viscosity relative to that of the solvent rich lower layers of the film. When the coated object is put into an oven, solvent volatilizes in the lower layers of the film, creating bubbles that do not readily pass through the high-viscosity surface. As the temperature increases further, the bubbles expand, finally bursting through the top layer, resulting in popping. Meanwhile, the viscosity of the film has increased enough so that the coating cannot flow together to heal the eruption. Popping can also result from, or at least be made worse by, entrapment of air bubbles in a coating. If the surface of the film has a high viscosity, the bubbles may remain in the film until the coating goes into the oven. The air expands with higher temperature, and the bubbles may burst through the surface. Air bubbles are especially likely to be entrapped during spray and hand roller application of waterborne coatings. Bubbling and popping can result from solvent that remains in primer coats or base coats when the top coat is applied.

Waterborne urethane coatings that have free isocyanate groups such as moisture-curable urethanes (Section 12.6) and 2K waterborne urethane (Section 12.7.3) coatings can show bubbling as a result of formation of CO_2 from the reaction of isocyanate groups and water.

In coating plastics, solvents can dissolve in the plastic, causing bubbling or popping during bake. More commonly, air or moisture in voids in the plastic blow out into the coating, causing pops. This is usually called *gassing* but often is indistinguishable from solvent popping. Similarly, hydrogen and methane trapped in or under the zinc layer in electrogalvanized steel can blow out and give pops (galvanized gassing). Electrical discharge and hydrogen evolution during cationic electrodeposition at high voltage can produce pop-like pinholes and craters. Another potential cause of popping is evolution of volatile by-products of cross-linking after the surface viscosity has increased to the extent that the bubbles of volatile material cannot readily escape through the surface. Automotive waterborne base coat and solventborne clear coat combinations can experience popping if the base coat dehydration bake does not remove enough water. The clear coat may also pop if the dehydration bake is so hot that a porous base coat results. If solvent from the clear is imbibed by the base coat, it may later blow out through the partially cured clear.

The probability of popping increases with film thickness, since there is a greater chance of developing a differential in solvent content as film thickness increases. A means of evaluating the relative likelihood that a series of coatings will show popping is to determine the maximum film thickness of each coating that can be applied without popping when the films are prepared, flashed off, and baked under standardized conditions [41]. This thickness is called the *critical film thickness for popping*. Popping can be minimized by spraying more slowly in more passes, by longer flash-off times before the object is put into the oven, and by zoning the oven so that the first stages are relatively low in temperature. The probability of popping can also be reduced by having a slow evaporating, good solvent in the solvent mixture. This tends to keep the surface viscosity low enough for bubbles to pass through and heal before the viscosity at the surface becomes too high.

Popping can be particularly severe with water-reducible baking enamels, as shown in Table 24.1. The pairs of enamels were identical except that in one set, they were reduced for application with solvent, and in the other set, with water [41]. As can be seen, the critical film thickness for popping was consistently lower for the water-reduced coatings. The data in Table 24.1 also illustrate another variable that affects the probability of popping. Critical film thickness for popping in these coatings decreases as the T_g of the acrylic resin in the coating increases. This is true in both solvent- and water-reduced coatings, but the effect is particularly large in the water-reduced compositions.

There are probably many reasons for the greater difficulty of controlling popping in water-reducible coatings. A variety of solvents with different evaporation rates is available for adjusting formulations of solventborne coatings, but water has only one vapor pressure–temperature curve, and its curve is steeper than for any organic solvent. Water can be retained by forming relatively strong hydrogen bonds with polar groups

TABLE 24.1. Critical Film Thickness for Popping

	Critical Dry Film Thickness (μm)	
Copolymer T_g (°C)	Water	Solvent
−28	50	120
−13	30	>70, <95
−8	20	>70, <95
14	10	55
32	5	25

on resin molecules at room temperature; these hydrogen bonds break at higher temperature, releasing the water. The heat of vaporization of water, 2260 J g^{-1}, is higher than that of organic solvents, 373 J g^{-1} for 2-butoxyethanol as an example. This higher heat of vaporization slows the rate of temperature increase of films of water-reduced coatings in an oven, further increasing the probability of popping [38] (Section 18.3.6).

In contrast to increased probability of popping with higher T_g water-reducible coatings, popping is more likely to occur with lower T_g latex polymers. Coalescence of the surface before the water has evaporated completely is more likely with a lower T_g latex.

Popping and cratering often appear similar. It is important to tell the difference because the remedies are different. One clue is that popping tends to be worst where the film is thickest, while cratering is more or less independent of thickness. Another is that pops are often accompanied by unbroken bubbles.

24.8. FOAMING

During manufacture and application, a coating is subjected to agitation and mixing with air, creating the opportunity for foam formation. Incorporation of foam in a coating can lead to pinholing or popping. The problem can be particularly severe with waterborne coatings applied by spray, especially airless spray, or by hand rollers. Formation of a foam involves the generation of a large amount of surface area; it follows therefore that the lower the surface tension, the less the energy required to generate a given amount of foam. However, foam bubbles in pure low viscosity liquids are not stable and break almost instantaneously; there must be something present to stabilize the foam. Although water has a high surface tension and therefore might not be expected to generate foam bubbles easily, bubbles in water are more readily stabilized, since a wider variety of components in water can rapidly migrate to the surface of a bubble to stabilize it. For example, a surfactant not only reduces the surface tension of water, facilitating foam formation, but also migrates to the surface of the droplets to give an oriented surface layer with a high viscosity, stabilizing the foam bubbles. In formulating a latex paint, an important criterion in selecting surfactants or water-soluble polymers as thickeners is their effect on foam stabilization [3,42]. Acetylene glycol surfactants such as 2,4,7,9-tetramethyl-5-decyne-4,7-diol alkoxylates are reported to be effective surfactants that do not increase the viscosity of the surface of bubbles as much as surfactants such as alkylphenol ethoxylates [43].

A variety of additives can be used to break foam bubbles. Most depend on creating surface tension differential–driven flow on the surface of bubbles. If the surface tension of a spot on the surface can be lowered, liquid from that area will flow away to try to cover neighboring higher surface tension areas, weakening and eventually breaking the thin wall of the bubble. For example, poly(dimethylsiloxane) fluids are effective in breaking a variety of foams, since their surface tension is low compared to almost any foam surface. Of course, as in other uses of silicone fluids, a little may be fine, but a little extra can cause problems. Other low surface tension additives, such as poly(octyl acrylates), act as defoamers. Small particle size hydrophobic SiO_2 can also act as a defoamer and/or a carrier for active defoaming agents [43]. Also, a small amount of immiscible hydrocarbon solvent will often reduce foaming of an aqueous coating. However, a hydrocarbon solvent used in a latex paint as a defoamer was shown to cause flocculation [44]. In this study the paint formula had several surfactants, and the order in which the surfactants were added controlled whether or not flocculation occurred.

Siloxanes with a polyether terminal group have been reported to prevent foaming in waterborne coatings as well as to minimize entrapment of air bubbles [36]. Several companies sell lines of antifoam additives and offer test kits with small samples of their products. The formulator evaluates the products in a coating to find one that overcomes, or at least minimizes, the foaming problem. Although it is possible to predict which additive will break a foam in a relatively simple system, such predictions are difficult for latex paints because of the variety of components that could potentially be at the foam interface. The combination of surfactants, wetting agents, water-soluble polymers, and antifoam can be critical. A variety of test methods has been used to compare foaminess of coatings [42,43,45].

24.9. DIRT

Dirt has been called the most common defect of all [46]. A wide variety of solid particles can land on the wet surface of a freshly applied film. If the particles contain low surface tension materials, they can cause cratering. If not, they become defects if they are large enough to be visible. Sanding dust, floor dirt, dust blown or tracked in from outdoors, fibers from wiping cloths or clothing worn by operators, and oven dirt are examples of such particles. Low power optical microscopy is invaluable for identifying the type of dirt. Prevention of dirt problems requires clean raw materials, clean paint, and a clean paint shop, preferably isolated from the rest of the factory. The air supply to spray booths and spray guns must be clean. Sanding should be minimized and sanding dust cleaned up before painting. Ovens should be cleaned carefully and frequently. Lint-free protective clothing and wiping cloths reduce lint contamination. In some applications, such as auto repair shops, such precautions cannot or probably will not be taken; then fast drying becomes a desirable characteristic of coatings.

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25

Solventborne and High-Solids Coatings

Chapters 25 through 29 present the principal classes of coatings: solventborne, waterborne, electrodeposition, powder, and radiation cure coatings. Our intent is to discuss the principles involved in these classes and to compare the various types of resins applicable to each group. In Chapters 30 through 33, end use applications for these various types of coatings are discussed.

Historically, almost all coatings were solventborne. The original motivation to reduce solvent was to lessen fire hazards and odor and to permit cleanup with water. Since the 1960s, a major driving force has been to reduce VOC emissions. There have been significant reductions in solvent use by shifting to other classes of coatings. Some expect that in the long run, solventborne coatings will disappear, but there are advantages to solventborne coatings over the alternatives. Capital cost for application is generally lower, especially as compared to waterborne coatings, for which stainless steel equipment is needed. Electrostatic spray installations for solventborne coatings are less expensive than those for waterborne coatings. Solvent evaporation is not dependent on humidity. There are fewer problems of air entrapment and popping. Significant reductions in VOC emissions have been made by shifting to high-solids coatings and by refining application methods to minimize solvent requirements. Current research and development is aimed at still higher-solids coatings and, ultimately, at *solventless* (solvent-free) liquid coatings.

For some end uses, especially when cost is particularly important, a single coating is adequate; however, for many other end uses, performance requirements can only be met by applying at least two coats. Almost always when more than one coat is to be applied, it is preferable to have a *primer* specifically designed to be the first coat, with a different coating for the *top coat*. The primer is designed to adhere strongly to the substrate and to provide a surface to which the top coat adheres well. It is not necessary

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for the primer to meet such other requirements as exterior durability that are critical for top coat performance. Commonly, primers are less expensive than top coats.

25.1. PRIMERS

The first consideration in formulating a primer is to achieve adequate adhesion to the substrate (Chapter 6). The substrate should be clean and preferably have a uniformly rough surface. The surface tension of the primer must be lower than that of the substrate. The viscosity of the continuous phase of the primer should be as low as possible to promote penetration of the vehicle into pores and crevices in the surface of the substrate. Penetration is also promoted by use of slow evaporating solvents, use of slow cross-linking systems, and whenever feasible, use of baking primers. The primer binder should have polar groups scattered along the backbone of the resin that can interact with the substrate surface. The presence of salts within the film should be minimal. Interaction between the binder and the substrate should be such that the coating will resist displacement by water when water molecules permeate through the coating to the interface (Section 7.2.3). For primers over metal substrates, as well as over alkaline surfaces such as masonry, saponification resistance of the primer is an important criterion in binder selection.

25.1.1. Binders for Primers

The binders in many primers for metal substrates are bisphenol A (BPA) epoxy resins and their derivatives (Sections 13.1 to 13.3 and 15.8). Although a full explanation is not available, experience has shown that in general, BPA epoxy resin–based coatings exhibit superior adhesion to clean metal. Addition of a small amount of an epoxy phosphate ester (Section 13.5) can further enhance adhesion, especially wet adhesion. For baked coatings, epoxy–phenolic coatings are particularly appropriate. For air dry coatings, epoxy–amine coatings are commonly selected. Both types have excellent wet adhesion and saponification resistance, critical for long-term corrosion protection. In general, baked epoxy–phenolics excel in these properties. Primers based on alkyd (Chapter 15) and epoxy ester (Section 15.8) resins are widely used. Material and application costs are less than with epoxy coatings, but wet adhesion is usually not as good, except possibly to metal contaminated with oily residues. Saponification resistance of alkyd resins is limited. The saponification resistance of epoxy esters is intermediate between those of alkyds and epoxy–amines.

The lowest cost binders used in metal primers are styrenated alkyds (Section 15.6). They are generally used in air dry primers. The higher T_g resulting from the large fraction of aromatic rings leads to primers that give dry-to-touch films, or even dry-to-handle films, rapidly. Styrenation reduces the fraction of ester groups by dilution and hence may increase saponification resistance. However, styrenated alkyds cross-link more slowly than do their nonstyrenated counterparts. As a result, the films develop solvent resistance slowly and have a wider time window within which they should not be top coated, owing to insufficient cross-linking. If the primer is top coated within this time interval, *lifting* is likely to occur, resulting in puckered areas in the top coat surface, due to nonuniform degrees of swelling by the top coat solvent and to uneven film shrinkage when the film finally dries.

The surface of galvanized steel is a layer of zinc hydroxide, zinc oxide, and zinc carbonate; all are strong, somewhat water-soluble bases. Especially if the metal is not phosphate treated shortly before coating, the binder in the primer must be resistant to saponification. Alkyd primers lack the necessary saponification resistance and are likely to perform poorly, especially if the galvanized surface has been exposed to moisture. For air dry coatings, acrylic latex vehicles are more appropriate than alkyds.

Primers are also required for surfaces other than metal substrates. Adhesion to polyolefin plastics can be difficult to achieve and can be enhanced by use of a primer based on a chlorinated polymer (Sections 6.5 and 31.2.2). Concrete and other masonry surfaces are alkaline and often require special surface treatments, most commonly washing with hydrochloric or phosphoric acid. The acid wash not only neutralizes the surface alkalinity but also etches the surface. Saponification resistant primers such as epoxy–amine or latex primers, provide longest life. Concrete blocks have very porous surfaces, and penetration of solventborne paints into the surface requires a relatively large volume of coating for coverage. Substantially better coverage can be achieved by using latex paints (Section 32.1).

25.1.2. Pigmentation of Primers

Selection of pigments and their amount is critical in primer formulation (Chapter 22). Pigmentation level affects adhesion of top coats to the primer film. Formulations with a high PVC/CPVC ratio are low-gloss coatings; the roughness and increased surface area of low-gloss films give improved intercoat adhesion. In some cases it is desirable to formulate primers with PVC > CPVC. The resulting primer film is somewhat porous, permitting penetration of top coat vehicle into the pores, thereby promoting intercoat adhesion. The PVC should be only slightly higher than CPVC or the loss of vehicle from the top coat may be enough to raise the PVC of the top coat film sufficiently to reduce its gloss. Primers with PVC > CPVC can be sanded more easily and are less likely to clog sand paper than primers with PVC < CPVC. Since inert pigments are generally the least expensive components of the dry film, high PVC minimizes cost.

Since primers almost always are low gloss coatings, inexperienced formulators may not think it is necessary to have good pigment dispersions for primers. This is not so! Since CPVC is affected by the degree of dispersion and particularly by the extent of flocculation, and since primers are usually formulated to be either slightly above or slightly below CPVC, pigment dispersion can be critical. If the pigment dispersion is not stabilized properly, CPVC decreases; so its PVC could become greater than CPVC.

If only one color top coat is to be applied over the primer, it is usually desirable for the primer to have a similar color, since this minimizes the effect of the primer color on the final top coat color. In many cases, top coats of several different colors are applied over the same primer; then, it is usually desirable to use a light gray primer. Gray primers have better hiding than white primers, when a pigment that strongly absorbs light, such as lamp black, is present. Light gray primers have relatively little effect on top coat color. Primers pigmented with red iron oxide provide good hiding at low cost but are harder to hide.

In addition to adhesion, water and oxygen permeabilities are important factors in corrosion protection of metals by barrier coatings (Section 7.2.3). The pigments can strongly affect oxygen and water permeability. Up to a PVC/CPVC ratio of about 0.9, the higher the PVC of the film, the lower the gas and vapor permeability. To occupy the largest possible volume of the dry film with impermeable pigment, a combination of pigments giving a high CPVC should be used with PVC close to CPVC. Platelet-shaped pigment particles tend to provide better barriers to oxygen and water permeability. Mica and micaceous iron oxide are widely used in primers for metals because of their platelet form. One must also use resin–pigment combinations in which the resin is strongly adsorbed on the pigment surface. If the pigment has a polar surface with a weakly adsorbed resin, water permeating through the film may displace the resin from the pigment surface, leading to an increase in water permeability.

Pigments for barrier primers should be completely insoluble in water. If, for example, zinc oxide were used as a pigment in a primer formulation, some of the zinc oxide would dissolve in water permeating through the film, resulting in establishment of an osmotic cell that can cause blistering. Passivating pigments can be useful for protecting steel against corrosion when the coatings on the steel substrate have been ruptured (Section 7.4.2). However, passivating pigments must be somewhat soluble in water in order to passivate the steel. Furthermore, dissolving the pigments requires that the binder is able to swell with water to a degree. These characteristics mean that blistering is more likely with a primer that contains a passivating pigment. In most baking primers for OEM products, it is preferable not to use passivating pigments but to rely on barrier properties to provide corrosion protection. However, coatings for bridges, storage tanks, ships, and offshore drilling platforms cannot be baked, and in such cases, film rupture must be anticipated. Passivating pigments or zinc-rich primers are commonly used for such applications (Sections 33.1.2 and 33.1.3).

25.1.3. High-Solids Primers

In conventional low solids primers, the effect of pigmentation on the viscosity of the coating is relatively small if the pigment is not flocculated. However, as solids are

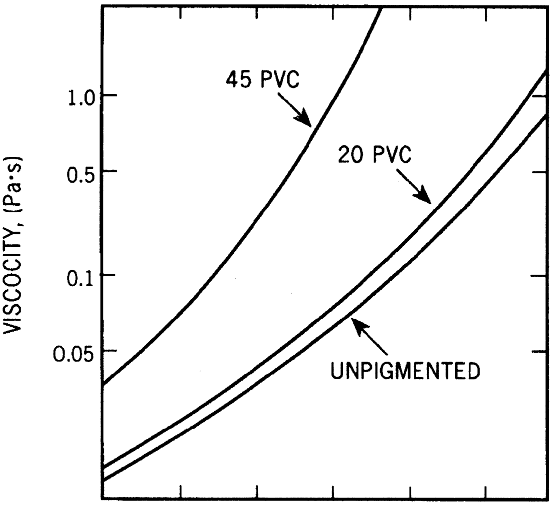

Figure 25.1. *Effect of pigmentation on viscosity as a function of volume solids for an unpigmented coating and for two pigmented coatings based on the same binder with pigment loadings sufficient to give 20% PVC and 45% PVC in the dry films. See Ref. [1] for the assumptions made in the calculations. (From Ref. [1], with permission.)*

increased, the volume of the dispersed phase (including the volume of both the pigment and of the adsorbed layer on the surfaces of the pigment particles) increases and becomes an important factor controlling the viscosity of the coating, limiting the solids at which a coating can be applied.

Pigmentation levels such as those encountered in low gloss coatings with PVC of 45 or higher substantially increase the viscosity of the wet coating, requiring reduction of solids for application. Figure 25.1, based on model calculations, shows plots of viscosity as a function of volume solids for three sets of calculations: one for an unpigmented coating, one for a 20 PVC (i.e., a gloss) coating, and one for a 45 PVC (i.e., low gloss) coating. The assumptions made in carrying out the calculations are provided in Ref. [1].

With the present status of our knowledge, somewhere in the neighborhood of 60 NVV is probably an upper limit for a primer with a PVC close to or above the CPVC. As a result, some high-solids primers are formulated with PVC that is much lower than optimum. A challenge to increasing solids content above 60 NVV at the optimum PVC is a means of stabilizing the pigment dispersion in a primer with thinner adsorbed layers at reasonable cost. However, even assuming stabilization with an adsorbed layer thickness of 5 nm, the upper limit of volume solids is at most 75 NVV. As a result of such limitations, the major thrust of development of reduced VOC primers is on waterborne primers.

25.2. TOP COATS

Top coats include coatings applied over primers and directly on a substrate. In the former case, the primer provides adhesion to the substrate and a major part of the corrosion protection for coatings on metal. The top coat must adhere well to the primer and provide the desired appearance and other properties. A single coating layer must combine both functions. In general, it is preferable to use a primer/top coat system; however, one coat application can be functional for many applications and is less expensive than multiple-coat systems. Single coats are used on products that need little corrosion protection and for which the need to maintain adhesion in the presence of water is not critical. When appearance and exterior durability requirements are minimal, a primer with excellent corrosion protection properties may be used without a top coat: for example, inside the ballast tanks of ships and for the interior of structural components of aircraft.

25.2.1. Binders for Top Coats

To an important degree, the properties of a top coat are controlled by the class of resin used as the principal binder in the top coat. The chemistry of these various binders is discussed in Chapters 8 through 17; in this chapter, the advantages and disadvantages of some classes of resins used in top coats, especially for OEM product coatings on metal, are compared.

25.2.1.1. Alkyds From the mid-1930s through the mid-1950s, alkyds (Chapter 15) were major binders for coatings. Although being replaced increasingly by other binders, alkyds are still used on a large scale. A major advantage of alkyds in many applications is lower cost. A second major advantage is that application of alkyd coatings is, in general, the most foolproof. Solventborne alkyd coatings are least subject to film defects of all the classes of coatings. This advantage results from the low surface tension of most alkyd coatings. Therefore, there are seldom problems with crawling, cratering, and other defects that result from surface tension–driven flows or surface tension differential–driven flows (Section 24.4). It is relatively easy to make pigment dispersions that do not flocculate. A further major advantage is their ability to cross-link by autoxidation. This makes air dry or low temperature baking possible and avoids the need for cross-linking agents with potential toxic hazards. In essence, air is the cross-linker.

The major limitations of alkyds are comparatively poor color retention on baking and limited exterior durability and saponification resistance. It is also difficult to achieve very high solids in alkyd solventborne coatings (Section 15.2). A further problem can be generation of smoke in baking ovens that causes visual air pollution problems.

Oxidizing alkyd binders are used for low cost coatings such as for steel shelving, machinery, coat hangers, and exterior coatings for drums. Individual applications may be relatively small, but there are a host of products for which the performance of these coatings is adequate. Oxidizing alkyds are also used for a significant fraction of architectural gloss enamels (Section 32.3.1). With metal salt driers, oxidizing alkyd coating films air dry in a few hours, force dry at 60 to 80°C in an hour, or bake at 120 to 130°C in half an hour. Baking time is shortest with highly unsaturated drying oil–derived alkyds having an oil length of about 60. Tung oil–modified alkyds give the fastest cross-linking, followed in turn by mixed tung–linseed oil alkyds and then linseed oil–modified alkyds. Cured films from these alkyds are quite yellow and turn yellow brown on overbaking. Generally, they are used only for dark color coatings. Since the cured films still contain substantial amounts of unsaturation and metal driers, the films embrittle with age. Better color and color retention can be obtained by using alkyds made with fatty acids or oils such as soy or tall oil fatty acids that are less unsaturated. These alkyds are also less expensive, but they cure more slowly than do more highly unsaturated alkyds.

Medium oil alkyds have a substantial number of hydroxyl groups on each molecule; these functional groups can be cross-linked with a variety of cross-linkers. Since melamine–formaldehyde (MF) cross-linkers are generally lowest cost, they are the most widely used. To achieve compatibility, butylated, isobutylated, or octylated MF resins are used, not methylated ones. Generally, the more reactive Class II MF resins with a high NH content are used (Section 11.2). The solvent system should contain some butyl alcohol to promote package stability and reduce viscosity compared to straight hydrocarbon solvents. Usually, no added catalyst is needed, since the residual unreacted carboxylic acid groups on the alkyd are sufficient catalyst for the Class II MF resin. If needed, relatively weak acid catalysts such as an alkylphosphoric can be used. Color and speed of cure are affected by the type of fatty acid used in the alkyd. Highly unsaturated alkyds are seldom used in top coats because of their dark color, soy, tall oil, and dehydrated castor alkyds are preferred. Some of the cross-linking results from the unsaturation and the balance from the reactions of the MF resin. The color, color retention, and resistance to embrittlement are better than those obtained using the oxidizing alkyd without the MF resin, since the MF cross-linking minimizes or eliminates the need for metal driers to catalyze the oxidation reactions.

The best color, color retention, and exterior durability are obtained using nonoxidizing saturated fatty acid–based alkyds. To minimize degradation due to hydrolysis under acidic conditions, alkyds made with isophthalic acid (or hexahydrophthalic anhydride) are used rather than those from phthalic anhydride. For example, solid color exterior top coats (monocoats) based on coconut oil alkyds and MF resins were used by many automobile manufacturers at one time. The exterior durability is good but not as good as the best acrylic coatings. Alkyd coatings are said to exhibit a greater appearance of depth than is obtained with acrylic–MF coatings. The cost of these coatings is similar to polyester–melamine coatings, and film defects during application are less likely.

The hydroxyl groups on alkyds can also be cross-linked at room temperature or under force dry conditions with polyisocyanates. IPDI isocyanurate prepolymers are often used for this purpose, since their color stability and exterior durability are superior to TDI derivatives (Section 12.3.2). In many cases, use of a polyisocyanate with an oxidizing alkyd permits sufficiently rapid development of tack free coatings so that metal driers are not needed; this further improves exterior durability.

25.2.1.2. Polyesters Polyester resins (Chapter 10) are one of the major classes of resins replacing alkyd resins in MF cross-linked baking enamels. Polyesters are also widely used in urethane coatings. Their cost is generally somewhat higher than that for oxidizing alkyds, but in some cases is less than that of nonoxidizing alkyds. Color, color retention, exterior durability, and resistance to embrittlement are better than those obtained with most alkyds, but exterior durability and resistance to saponification are generally not as good as with acrylics. The adhesion and impact resistance of polyester-based coatings without primers over clean, treated steel and aluminum substrates are comparable to those of alkyds and generally superior to those of acrylics. Polyester coatings generally have higher surface tensions than those of alkyd coatings and hence are more subject to crawling and surface tension differential–driven flow defects such as cratering. Most polyesters are hydroxy-terminated and are cross-linked with MF resins or with isocyanates. The MF resins are less expensive; methylated or mixed methylated–butylated MF resins are generally used. For lower temperature cure or air dry coatings, aliphatic polyisocyanates are used. A major advantage of polyesters over alkyds and most acrylic resins is the relative ease of preparing polyester resins suitable for very high solids and even solventless coatings (Section 25.2.2). Polyesters are also adaptable for use in powder coatings (Chapter 28).

25.2.1.3. Acrylics In general terms, the major advantages of acrylic binders (Chapter 8) are their low color, excellent color retention, resistance to embrittlement, and exterior durability at relatively modest cost. The best acrylics are quite photochemically stable and very hydrolytically stable. In general, their surface tensions are intermediate between alkyds and polyesters, and as a result, the susceptibility of acrylic based coatings to film defects is intermediate. Generally, their adhesion to metal surfaces is inferior to that of both alkyds and polyesters coatings; therefore, they are generally used over a primer.

Thermoplastic solution acrylic resins were used widely in OEM automotive coatings but have been replaced with thermosetting acrylics (TSAs) to reduce VOC emissions (Chapter 8). Most commonly, TSAs are hydroxy-functional, often with a minor amount of carboxylic acid functionality. They are cross-linked with MF resins or with polyfunctional isocyanates. Either Class I or Class II MF resins can be used; the choice usually depends on curing temperature requirements. Aliphatic isocyanate cross-linkers are more expensive than MF resins and present greater toxic hazards but cure at lower temperatures and with HALS stabilizers usually provide somewhat greater exterior durability and frequently have better environmental etch resistance.

25.2.1.4. Epoxies and Epoxy Esters Although the major uses for epoxy resins (Chapter 13) are in primers, significant volumes of BPA and novolac epoxy-based top coats are used in applications where exterior durability is not an issue. They are well suited to such purposes because adhesion of epoxy-based coatings in the presence of water or water vapor is generally superior to other types, and they are highly resistant to saponification. Applications such as beer and soft drink can linings and the insides of aircraft wings do not require exterior durability. Epoxy-functional acrylic resins cross-linked with polybasic acids give films with excellent exterior durability (Section 13.1.2).

Epoxy esters (Section 15.8) offer properties intermediate between alkyds and epoxies. An example of their use in top coats is in coating bottle caps and crowns. They exhibit the requisite combination of hardness, formability, adhesion, and resistance to water.

25.2.1.5. Urethanes Polyisocyanate cross-linkers (Chapter 12) have been mentioned in connection with alkyds, polyesters, and acrylics. They are widely used as cross-linkers because of low temperature curing and abrasion resistance combined with resistance to swelling of cured films with solvent. Urethanes can also be backbone links in resins that have reactive groups other than isocyanates. Hydroxy-terminated urethane resins (Section 12.8) can be cross-linked with polyisocyanates or MF resins. When MF resins are used, the coatings have the advantage of being one package coatings without a concern for the toxic hazards of free isocyanate. As with polyesters, there is no difficulty making low molecular weight resins where substantially all of the molecules have a minimum of two hydroxyl groups. Cost is higher than for polyesters, but the hydrolytic stability and therefore the exterior durability can be superior. However, the intermolecular hydrogen bonding of urethanes leads to higher viscosity at equal concentration solutions of equal molecular weight compared to polyester resins. Low molecular weight, hydroxy-functional urethanes can be blended with other generic types of hydroxyl-functional resins to modify coating properties.

Urethanes, especially those having primary carbamate $—O—CO—NH_2$ groups, cross-link with MF resins to give greater hydrolytic stability under acidic conditions than that of hydroxy-functional resins cross-linked with MF. Carbamate-functional acrylic, polyester, and silicone resins with MF cross-linking are useful in clear automotive coatings.

25.2.1.6. Silicone and Fluorinated Resins The highest resistance to both thermal degradation and photoxidation is obtained with silicones (Section 16.1) and fluorinated resins (Section 17.1.4). The cost of both is high, especially that of fluorinated resins. Silicone alkyds give greater exterior durability than alkyds for air dry coatings. In a compromise to obtain superior outdoor durability at an intermediate cost, silicone-modified polyesters and acrylics (Section 16.1.3) are relatively widely used. Fluorinated copolymer resins cross-linked with MF resin or aliphatic polyisocyanates have outstanding exterior durability.

25.2.2. Formulating Solventborne Coatings for Low VOC

The purpose of this section is to consider the various types of top coats, with emphasis on the potential for reduction of solvent use while achieving the required level of performance. Although thermoplastic resins are still being used, their use will continue to fall, owing to their high VOC. The majority of solventborne coatings currently used and expected to be used in the future are thermosetting coatings. Conventional thermosetting coatings have volume solids (NVV) on the order of 25 to 35%. Technical efforts on high-solids coatings since around 1970 have accomplished varying degrees of increases in solids of various types of coatings for various applications.

There is no single definition of high-solids coatings. For metallic automotive top coats (or base coats), high solids corresponds to about 45 NVV. For a highly pigmented primer, high solids might be 50 NVV. For clear or high gloss pigmented coatings, 75 NVV or even higher is possible. The situation is further complicated by the difficulty of exact measurement of, or even of defining, VOC of a coating (Section 18.9.1). For example, in some cases, solvents with functional groups may partially react with the cross-linker and hence not be evolved. On the other hand, there can be volatile by-products of cross-linking that should be included in VOC, and low molecular weight components may volatilize before cross-linking; the extent to which such emissions occur may vary with baking conditions.

A limitation on solids content is the increasing difficulty of achieving desired mechanical properties as molecular weight and average functionality per molecule $\bar{f}_n$ are decreased and molecular weight distribution is narrowed (Section 8.2.1). In a conventional thermosetting acrylic coating, one uses a resin with an $\bar{M}_w/\bar{M}_n$ on the order of 35,000/15,000, and depending on the end use, an $\bar{f}_n$ of 10 to 20. The cross-linker might have an $\bar{M}_w/\bar{M}_n$ on the order of 2000/800 and an $\bar{f}_n$ of 3 to 7. An acrylic resin that permits 45 NVV might have $\bar{M}_w/\bar{M}_n$ on the order of 8000/3000 with $\bar{f}_n$ of 3 to 6. As $\bar{f}_n$ is reduced, it becomes increasingly critical and difficult to control formulations and cure conditions to keep all film properties within the desired ranges.

As one aims for still lower molecular weights and functionalities for still higher-solids coatings, achieving high performance properties becomes even more difficult. For an NVV of 70, $\bar{M}_w/\bar{M}_n$ must be on the order of 2000/800 or less, with an average of a little over two hydroxyl groups per molecule. It is critical that essentially all molecules have at least two functional groups per molecule. Any molecules with only one functional group cannot cross-link and will leave dangling ends in the network; any molecules with no functional groups will be plasticizers, and if low enough in molecular weight, may partially volatilize in a baking oven. It is difficult to synthesize acrylic resins for very high solids coatings (Section 8.2.1). On the other hand, it is relatively easy to make polyurethane or polyester resins with an $\bar{M}_w/\bar{M}_n$ of 2000/800, or even lower, and with an average of a little over two hydroxyl groups per molecule where essentially all of the molecules have at least two hydroxyl groups (Sections 10.2 and 12.8).

Major progress is being made in solving the problems with conventional free radical polymerization by using controlled free radical polymerizations (CFRPs) (Section 2.2.1.1). A resulting SuperSolids automotive acrylic clear coat is in production; solids are reported to be 65%, with the possibility of future increases up to nearly 90%. At the same time both the scratch and mar resistance are substantially improved [2].

In conventional coatings, the *cure window* is relatively large; that is, it makes little difference if the baking temperature, baking time, or catalyst amount is off by ±10%. In high-solids coatings, the cure window is narrower [3]. If there are a large number of hydroxyl groups on each resin molecule and 10% are not reacted, the change in properties may be small. If, however, there are only a little over two hydroxyl groups per average molecule and 10% are left unreacted, a significant fraction of the molecules will be tied into the network in only one place, with detrimental effects on film properties. The problem may be minimized by using cross-linkers with a higher $\bar{f}_n$. Because of their greater average functionality, Class I MF resins generally offer broader cure windows than those of Class II MF resins (Section 11.3). The extent of self-condensation reactions of MF resins is particularly dependent on time, temperature, and catalyst concentration.

In using high-solids coatings, the applicator should be very careful in controlling the time and temperature in baking ovens and in following the coating supplier's recommendations. The formulator must be more careful in checking the film properties when the temperature is about 10°C above and below the standard temperature. In making recommendations of cure cycles to a customer, one should use pieces of the customer's metal to establish the baking schedule. The critical temperature for baking is that of the coating itself, not that of the air in the oven. Coatings applied to a heavy piece of metal heat up more slowly than do coatings on light gauge sheet metal. On sheet metal, the coating over a place where the sheet metal has been welded to a supporting member heats up more slowly than it does on the rest of the surface. High-solids coatings are more likely to be subject to variation in properties due to differences in coating temperature and time compared to conventional coatings.

To increase solids, polydispersity of resins can be decreased; however, this may narrow the breadth of the T_g transition range (Section 4.2), which may adversely affect the mechanical properties of films [4]. An approach to overcoming this problem is to blend resins with differences in composition, but still similar enough to each other to be compatible; for example, polyester–acrylic blends using low molecular weight hydroxy-terminated polyesters to reduce the viscosity and thereby increase the solids [5]. Resins and cross-linkers for high-solids coatings generally have an $\bar{M}_n$ well below 5000. In contrast to high molecular weight polymers, the entropy of mixing of different low molecular weight resins is large enough to be a significant factor favoring compatibility (Section 18.2). The effect of molecular weight is illustrated by 50 : 50 blends of several acrylic and methacrylic homopolymers that are compatible, when their $\bar{M}_n$ values are less than 5000 but incompatible when their $\bar{M}_n$ values are above 10,000 [6]. The broader compatibility of low-$\bar{M}_n$ resins permits formulation of high-solids coatings based on mixtures of resins different generic types. Not all blends of low-$\bar{M}_n$ resins are compatible, and there is the possibility that phase separation could occur as molecular weight increases in the early stages of cross-linking. Unpigmented films should be made and checked for transparency; haziness suggests phase separation may occur on a scale large enough to detract from appearance or properties.

Isocyanurates, unsymmetrical trimer, biuret, and allophanate polyisocyanates (Section 12.3.2) with lower molecular weights and hence lower viscosities have been made available. However, the lower viscosity of these polyisocyanates is only one factor affecting the VOC of coatings [7]. In some cases, the lower viscosity cross-linker also has a lower equivalent weight, which requires that the weight ratio of low viscosity cross-linker to higher viscosity polyol is decreased. For this reason, the lowest VOC could be obtained using a somewhat higher equivalent weight polyisocyanate, even though it had a somewhat higher viscosity. Aldimines and hindered diamines permit preparation of very high solids clear top coats (Section 12.4).

Research is now focused on *ultra high-solids* or *solvent-free coatings*. These are based on the use of low molecular weight oligomers or reactive diluents; the distinction between the terms is disappearing. VOC of two package polyurethane coatings can be reduced by replacing some of the hydroxy-terminated acrylate or polyester with a reactive diluent [7]. Examples of such coreactants are aliphatic diols and low molecular weight ester or urethane diols.

Polyesters afford the major opportunity for very low VOC coatings, since low molecular weight oligomers can be made such that all molecules have at least two reactive groups, usually hydroxyl groups. For example, 1,4-butanediol esters of mixed glutaric, adipic, and azelaic acids with an $\bar{M}_n$ of 300 have a viscosity at 25°C of 250 Pa•s [8]. Solvent-free coatings can be formulated with polyisocyanate cross-linkers. With MF resins, film hardness of baked films is too low; however, the coatings can be thinned with water (Section 18.4), permitting formulation with a variety of other components in solvent-free coatings [8].

An example of a "zero" VOC coating that uses water as a diluent is an epoxy–hydroxyl system [9]. Caprolactone polyols are used with 3,4-epoxycyclohexylmethyl–3,4-epoxycyclohexane carboxylate at a 2:1 epoxy/hydroxyl ratio, with a latent triflic acid derivative as catalyst.

VOC reduction is being aided by application methods that permit use of higher-viscosity coatings. Hot spray (Section 23.2.4), high speed electrostatic disks (Section 23.2.3), and supercritical fluid spray (Section 23.2.5) are examples. Improvements in transfer efficiency are making a significant contribution to reducing VOC emissions (Sections 23.2.1 and 23.2.3). For example, high volume low pressure air spray guns have a substantially superior transfer efficiency than that of conventional air atomization guns.

As solids increase, it becomes more difficult to avoid pigment flocculation [10]. The primary factor controlling stabilization of pigment dispersions is the thickness of the adsorbed layer on the surface of the pigment particles (Section 21.1.3). The very low molecular weight resins used in very high solids coatings are incapable of providing an adequate adsorbed layer. Furthermore, as the number of functional groups per molecule decreases, the solvent can compete more effectively for adsorption sites on the pigment surface, promoting flocculation. Hyperdispersants (Section 21.1.3) have been developed for use in high-solids coatings.

Another limiting factor for some high-solids coatings is that of surface tension effects. Generally speaking, as molecular weight gets lower, the equivalent weight must be lowered even further, since the number of reactions required to achieve high molecular weight will be greater. In most coatings, the functional groups are highly polar, such as hydroxyl and carboxylic acid groups. Increased levels of such groups give higher surface tensions. Furthermore, achieving high solids at a given viscosity with such resins generally requires using hydrogen-bond acceptor solvents rather than hydrocarbon solvents. Again, this results in higher surface tensions than that of most conventional coatings and therefore increased probability of film defects during application. When coating metal, the importance of clean surfaces increases as solids increase. When coating plastics, one must be careful to remove mold release agents. A broader range of plastic materials has to be surface treated to avoid crawling and achieve adhesion (Sections 6.5 and 31.3). Since the surface tension of a freshly applied high-solids coating is generally higher than that of a conventional coating, a larger fraction of contaminating particles floating in the air have lower surface tensions than that of the wet high-solids coating. Thus, cratering is more probable (Section 24.4).

Sagging is more of a problem with high solids than with conventional coatings [11]. This results from the slower rate of evaporation of solvents from high-solids coatings than from conventional coatings (Section 24.3). Although the reasons for this difference have not been elucidated completely, the consequences pose significant problems. Sagging of spray applied high-solids coatings cannot be controlled easily by adjusting the evaporation rate of the solvent in the coating or by changing the distance between the spray gun and the substrate. Sagging can be minimized by using hot spray (Section 23.2.4) or supercritical fluid spray (Section 23.2.5). For many applications, thixotropic flow properties must be built into a high-solids coating for spray application. Fine

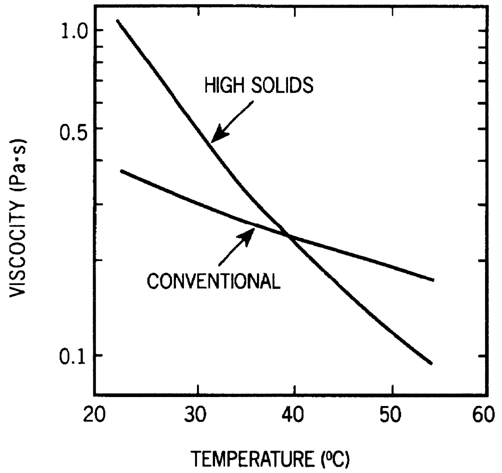

Figure 25.2. Viscosity as a function of temperature for a conventional and a high-solids resin solution. The high-solids solution is of a 1500 molecular weight polyester at 90% solids in ethylene glycol monoethylether acetate. The conventional solution is of a 20,000-molecular weight polyester at 25% solids in methyl ethyl ketone and ethylene glycol monoethyl ether acetate. (Adapted from Ref. [1], with permission.)

particle-size SiO_2, bentonite clay pigments, zinc stearate, and polyamide gel thixotropes are additives that can be useful. Another alternative is to include a modest fraction of highly reactive cross-linker that will cause a quick increase in viscosity; mixtures of isocyanates and MF resins can be used [12]. The problem of sagging in metallic coatings used on automobiles is particularly serious; microgel particles have been developed that are effective (Sections 24.3 and 30.1.2).

Even when sagging is not encountered during application, it can sometimes occur with high-solids coatings during baking. The temperature dependence of viscosity of high-solids coatings is greater than for conventional coatings, as illustrated in Figure 25.2. Before the cross-linking reactions have proceeded far enough to increase the viscosity, the increasing temperature during baking has already decreased the viscosity sufficiently to lead to sagging [1,11]. The phenomenon is called *oven sagging*.

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26

Waterborne Coatings

Before about 1950, almost all coatings were solventborne. Introduction of latex architectural paints was the first major step away from solventborne coatings; the driving forces were better performance, easier clean up, and reduced fire hazards. Since 1970, there has been a further trend away from solventborne coatings to reduce VOC emissions, and use of waterborne coatings in the United States now exceeds the volume of solventborne coatings. The trend is expected to continue as restrictions on VOC become more stringent. Most waterborne coatings contain some organic solvent. The solvents play a variety of important roles in resin manufacture, coating production and application, and film formation. Research efforts are under way to reduce and in some cases, eliminate the need for solvents.

The two largest classes of waterborne coatings are *water-reducible coatings* (Section 26.1) and *latex coatings* (Section 26.2); smaller amounts of *emulsion coatings* (Section 26.3) are also used. The terminology is not uniform [1]. We use the term *water-reducible* for resins made in solvent and reduced with water to form a dispersion of resin in water. Other authors refer to these resins as *aqueous dispersion* resins or *water-soluble resins*, but they are not really soluble in water. Some authors call latex coatings *emulsion coatings*; we recommend against this practice to avoid confusion of latexes (dispersions of solid polymer particles in water) with coatings that really are emulsions (dispersions of liquids in liquids). Latex resins are prepared by emulsion polymerization. Polyurethane latexes are called *aqueous dispersion resins*. There is growing use of blends of different types, for example, combinations of latex and water-reducible resins. Water is also used as a cosolvent in solventborne coatings, which we call *water thinning* (Section 25.2.2).

In relation to organic solvents, water has both advantages and disadvantages. Water presents no toxic hazard, is odor free, and is not flammable. Nonflammability reduces

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risks and insurance costs and permits use of less makeup air in baking ovens, reducing energy consumption in some cases. There are no emission or disposal problems directly attributable to use of water. With some formulations, cleanup of personnel and equipment is easier with waterborne coatings; however, in other cases, cleanup is more difficult. The cost of water is low; but it does not necessarily follow that the cost of waterborne coatings is low.

A wide range of solvents with different evaporation characteristics enables the formulator to fine-tune evaporation rates from solventborne coatings, but there is only one type of water. The heat capacity and heat of vaporization of water are high, resulting in high energy requirements for evaporation. With a given amount of energy available for evaporation, water evaporates more slowly than do solvents with similar vapor pressures, although the vapor pressure of water increases relatively rapidly with increasing temperature. Evaporation of water is affected by relative humidity (RH) and variations in RH when coatings are applied can lead to problems (Section 26.1).

The surface tension of water is higher than that of any organic solvent. In water-reducible coatings, pigments can be dispersed in solvent solutions of the resins before addition of water, and the surface tension can be reduced with solvents such as butyl alcohol or a butyl glycol ether. The surfactants in latex paints reduce surface tension, improving pigment wetting and enabling the coating to wet many types of surfaces. The presence of surfactants tends to give films having poorer water resistance; various approaches are being used to reduce or even eliminate the need for free surfactants.

Water increases corrosion of storage tanks, coating lines, ovens, and so on. This requires that corrosion resistant equipment be used in applying waterborne coatings, increasing capital cost. For example, mild steel lines may have to be replaced with stainless steel. Since it is electrically conductive, water requires special adaptations of electrostatic spray equipment, which increases cost (Section 23.2.3).

The largest fraction of water-reducible resins is used in OEM product coatings. Water-reducible electrodeposition coatings have such different formulation and application procedures that they are discussed separately in Chapter 27.

Latex systems are used in a majority of architectural coatings. The general principles of latex coatings are covered in Section 26.2, detailed discussion is postponed to Chapter 32. Small but increasing fractions of both OEM product coatings and special-purpose coatings are latex based.

26.1. WATER-REDUCIBLE COATINGS

Most water-reducible coatings are produced as high-solids solutions in water-miscible solvent(s). The resins have either carboxylic acid or amine groups that are at least partially neutralized with low molecular weight amines or acids, respectively. Pigment is usually dispersed in the partly neutralized resin solution, cross-linker is added along with additives such as catalysts, and the coating is diluted with water to application viscosity. The resin is not soluble in water or in the aqueous solution of the solvent that results. Instead, aggregates form with salt groups oriented at the water–particle interfaces and with low polarity parts of the resin molecules in the interior of the aggregates. The solvent partitions between the water phase and the aggregates. The aggregates are swollen by solvent as well as by water that associates with the salt groups and dissolves in the solvent. The cross-linker is dissolved in the resin–solvent aggregates, and the pigment also resides inside the aggregates. The aggregates exist in a dynamic equilibrium, with solvent moving freely from one to another and probably with aggregates fusing and separating.

When solutions of these neutralized resins are diluted with water, the change of viscosity with concentration is abnormal. Figures 8.1 to 8.3 show typical relationships between resin concentration and log viscosity when water-reducible acrylic resin solutions are diluted with water. As water is added, there is an initial rapid drop in viscosity. As more water is added, the viscosity plateaus and, frequently, with further addition of water, the viscosity increases. Still further addition of water leads to a rapid drop in viscosity. The solids of the coatings at application viscosity are usually lower than the solids of solventborne coatings. While the viscosity of the organic solvent solution of resin is Newtonian, the viscosity of the water-diluted system in the region of the peak or plateau is highly shear thinning. When diluted to application viscosity, flow is usually only slightly shear thinning. As explained in Section 8.3, this behavior is consistent with the formation of swollen aggregates.

As explained in Section 8.3, the pH of these systems is also abnormal. In the case of carboxylic acid–functional resins neutralized with a low-molecular weight amine, the pH is basic even though less than stoichiometric amounts of amine are frequently used. As application solids are approached on dilution, the viscosity, decreases rapidly as water is added and is very dependent on the ratio of amine to carboxylic acid. If a small excess of water is added inadvertently, the viscosity may be too low. However, this problem can usually be remedied by adding a small further increment of amine, which increases the viscosity.

Selection of the amine for neutralization is an important formulation consideration (Section 8.3). Amines are expensive, and they add to VOC emissions. Volatility and base strength are important. If there is insufficient amine, there will be macrophase separation of the coating. Therefore, it is desirable to select amines that stabilize the aggregate dispersion efficiently at low concentration. The principal factor controlling the required amine level appears to be water solubility of the amine. For example, the amount of tripropylamine required is substantially larger (on an equivalent weight basis as well as a weight basis) than the amount of triethylamine required. Still more efficient are aminoalcohols; *N*,*N*-dimethylaminoethanol (DMAE) is probably the most widely used amine. Somewhat less efficient but still more effective than trialkylamines are morpholine derivatives.

Commonly only about 20% of the volatiles are organic solvents and the VOC emitted per unit volume of coating, excluding water, are fairly low. In a water-reducible gloss acrylic coating, VOC is equivalent to the amount of solvent emitted by a solution acrylic with approximately 60 NVV. Air quality goals in the future will require still lower VOC emissions; research is under way.

Most types of resins can be chemically modified to make them water reducible. The most widely used resins are acrylics with both carboxylic acid and hydroxy functionality (Section 8.3). Water-reducible polyesters are used, but their hydrolytic stability is limited and low molecular weight cyclic oligomers can volatilize in baking ovens (Section 10.4). Since polyesters can be synthesized in the absence of solvent, it is possible to make solvent-free dispersions [2]. The resin is cast as a solid, is pulverized, and is stored as a solid until needed, delaying possible hydrolysis. When a coating is to be made, the powdered resin is stirred into a hot aqueous solution of dimethylaminoethanol to make a dispersion. Water-reducible alkyds (Section 15.6) are fairly popular in Europe, but their use is limited because of the difficulty in achieving adequate saponification resistance for package stability. Water-reducible epoxy esters (Section 15.8) and uralkyds

(Section 15.7) have better hydrolytic stability. Water-reducible urethanes have superior saponification resistance and a minimum of cyclic oligomers (Section 12.7). Solvent-free and low solvent water-reducible urethanes have also been reported [3]. Urethane resins can give films with excellent properties, but are generally more expensive than acrylic resins.

Coatings made with water-reducible resins have advantages and limitations. An important advantage follows from the high molecular weight that can be used, as high as that of resins used in conventional solution thermosetting coatings. This is possible because the viscosity at application dilution is almost independent of molecular weight. For example, one can use water-reducible acrylics with an $\bar{M}_w/\bar{M}_n$ on the order of 35,000/15,000 and an average of around 10 hydroxyl groups and 5 carboxylic acid groups per molecule along with a class I melamine–formaldehyde (MF) cross-linker and achieve properties essentially equal to those of a conventional solution acrylic enamel. The window of cure is comparable to that of the conventional thermoset acrylic. The problems related to molecular weight and functionality of high-solids coatings are not encountered. A disadvantage is that the application solids are low. Typically, such coatings are applied by spraying, roll coating, or curtain coating at around 20 to 30 NVV. The low solids means more wet film thickness has to be applied to achieve the same dry film thickness. On the other hand, in automotive metallic coatings, the low solids is an advantage because it is associated with better orientation of the aluminum pigment in the film.

Water-reducible resins, cross-linked with blocked isocyanates, have been reported for clear coats [4,5]. The combination of blocked isocyanate and MF resin cross-linking gives coatings having both mar and etch resistance.

The viscosity of water-reducible resin coatings depends strongly on the ratio of water to solvent. Relative humidity and temperature during application affect the ratio of the evaporation rates of water and solvent. If the humidity is above a critical level, water evaporates more slowly than even slow evaporating solvents such as 2-butoxyethanol (Section 18.3.6). In extreme cases, the viscosity of the coating during flash off after application can decrease, rather than increase, as evaporation continues. The result is delayed sagging [6]. Variations in humidity during application and drying can lead to problems. If the RH is over 70%, the rate of evaporation of water is very slow, and at 100% there is no net evaporation of water. In the mid-RH range, the effect can be reduced by a relatively modest increase in temperature, since RH decreases with temperature. However, if the humidity is very high, the only recourses have been to cool the air to condense out some of the water and then rewarm it, an expensive expedient, or to wait until the RH is lower. For factory applied coatings, it is generally desirable to formulate for best application at a relatively high RH, say 60%, since it is less expensive to increase RH than to decrease it.

Popping (Section 24.7) during baking of water-reducible coatings is more difficult to control than with solventborne coatings [7]. The probability of popping increases as film thickness increases. Since the solids are low and the rate of evaporation of water during spraying and flash off is low, the wet film thickness required to apply the same solids is higher than with solventborne coatings. The high heat of vaporization of water compared to solvents leads to a slower rate of heating of the coating and hence slower evaporation. Also, until the amine evaporates, there are polar salt groups that tend to retain water. When the coated article enters an oven, water evaporates fastest from the surface, so the viscosity of the surface layer increases. Subsequently, when the water remaining in the lower layers of the film volatilizes, some of the bubbles of water vapor either cannot break through the surface layer, leaving a bubble, or break through at a stage when the viscosity of the surface layer is so high that a crater cannot flow out. Popping is affected by the base strength and volatility of the amine. Popping can be minimized by spraying the coating in more, thinner coats (often called *passes*) so that there is a greater chance for evaporation as the film thickness is built up; by having longer flash off times before entering the baking oven; and by zoning the oven, such that the first part of the oven is at lower temperature, permitting water to diffuse out of the film before the viscosity at the surface increases unduly. In some installations, infrared ovens can be used to drive off most of the water before entering the baking oven. All these alternatives have relatively high capital or operating costs.

The greatest difficulties occur when spray applying thick coats. One cannot apply completely uniform films by spray. To assure that sufficient coating is applied on all areas, there will be some areas with substantially more than the average film thickness. Also, there is a greater chance of air entrapment with spray applied coatings. If the air bubbles do not break, the air in the bubbles expands when the coating is baked, ultimately leading to popping. Air entrapment is particularly severe with airless spray, since at the high pressure, more air dissolves in the coating and then comes out as pressure decreases on leaving the gun (Section 23.2.6). Siloxanes with a polyether terminal group have been reported to minimize air entrapment in waterborne coatings [8].

It has been shown that the problem of air entrapment can be reduced by using carbon dioxide rather than air for spraying [9]. The carbon dioxide largely evaporates during the time of flight between the spray gun and the substrate. Popping can be minimized by reducing T_g of the resins to the lowest level compatible with the film properties required. Use of some slow evaporating solvent such as 1-propoxy-2-propanol or the monobutyl ether of diethylene glycol in the formulation assists in reducing the probability of popping.

Thin coatings applied by roll coating or curtain coating seldom have a popping problem. The films are more uniform than spray applied films are and there is no air entrapment problem. With reasonable care about flash off times, curtain coating of relatively thick films can be accomplished without major problems. Water-reducible coatings are used on a large scale for such applications as can coatings and panel coatings.

One might think that the high surface tension of water would cause serious problems with crawling and cratering. This is usually not the case, presumably because orientation of nonpolar segments of solvent to the surface is rapid, reducing surface tension.

With air dry water-reducible alkyd coatings, equivalency of properties with solvent alkyd coatings has been difficult to achieve. Water-reducible alkyds can be made, as can modified alkyds such as silicone-modified alkyds, but their hydrolytic instability leads to limited storage life once the paint has been made and water added. With careful inventory control, they can be used for some industrial applications, but they are generally unsatisfactory for trade sales paints, for which a shelf life of two or more years is needed. Also, until the neutralizing amine required for water dilution evaporates from the film, the films are water sensitive. The time required to lose amine is related to both the volatility and the base strength of the amine. Ammonia is the most volatile amine and is widely used. However, the last of the amine is lost at a stage when volatile loss is controlled by diffusion rate through free volume holes, not by volatility. The time for amine loss may be reduced by using a combination of ammonia and a less volatile but relatively weak basic amine such as *N*-methylmorpholine. Even after the amine has evaporated, the films contain carboxylic acid residues and are sensitive to water and, particularly, to bases.

At one time it was widely assumed that waterborne urethane coatings that have free isocyanate groups would not be feasible, due to the reactivity of isocyanates with water. However, two package (2K) urethane coatings with adequate pot life for commercial use have been widely commercialized [10]. Reference [11] reviews 2K urethanes extensively. A water-dispersible, aliphatic, "hydrophilically-modified" polyisocyanate is used in one package, and the second package contains a hydroxy-terminated, water-reducible polyurethane with carboxylic acid groups from 2,2-dimethylolpropionic acid (Section 12.8). A 2 : 1 ratio of —N=C=O to —OH is used to offset possible reaction with water. Films cross-linked within a week at 25°C when the RH was 55% or lower. At high humidity, solvent resistance did not develop at 25°C, but warming to 31°C permitted cross-linking even at 80% RH. Acrylic polyols can also be used [12]. Pot life problems can be severe since water can diffuse into the dispersed particles of the isocyanate component, leading to cross-linking, which can preclude good coalescence. Such problems can be minimized by use of appropriate mixing and application equipment [12].

Alternatively, low viscosity polyisocyanates such as blends of HDI dimer and trimer can be used with aqueous polyurethane dispersions [13]. Very low viscosity HDI iminooxadiazenedione (unsymmetrical trimer) is reported to incorporate easily into 2K waterborne urethane coatings [14]. We discuss waterborne polyurethanes further in Section 12.7. Graft copolymer and semiblock copolymer aqueous dispersions prepared by catalytic chain transfer polymerization have the advantage of narrower molecular weight distributions compared with water-reducible acrylic resins made by free radical polymerization [15].

Waterborne primers are particularly important, since reducing VOC levels in solventborne primer formulations is particularly difficult (Section 25.1.3). Waterborne coatings are especially suited for dip coating applications (Section 22.3) because they eliminate fire hazards of solventborne dip coatings. For example, water-reducible maleated epoxy esters (Section 15.8) are used for spray or dip applied primers for steel. All electrodeposition coatings are water-reducible coatings (Chapter 27). Interior linings for beverage cans are water-reducible coatings, based on grafting acrylates, styrene, and acrylic acid onto BPA epoxy (Section 13.4).

26.2. LATEX-BASED COATINGS

Latexes have been used for many years in architectural coatings and are the major type of vehicle for these coatings. For certain household applications, such as flat wall paint, the advantages of latex paints over any solventborne paint are so large that solventborne paints are seldom marketed. Important advantages of interior latex paints include rapid drying, low solvent odor, absence of odor of oxidation by-products of drying oils and alkyds, easy cleanup, reduced fire hazard, and better long term retention of mechanical properties. For exterior paints, a major advantage is superior exterior durability of high-performance latex paints relative to drying oil or alkyd paints. On wood siding, blistering is reduced, since the latex films are more permeable to water vapor. On the other hand, adhesion of latex paints to chalky surfaces is inferior to that of solventborne paints (Section 32.1).

A further advantage of acrylic, styrene–acrylic, and styrene–butadiene latexes over alkyds is their superior resistance to saponification. Paints with shelf lives of many years are attainable. Latex paints generally show better adhesion to galvanized metal surfaces than do alkyd paints. They also generally show better performance over cement and concrete surfaces than alkyds, which tend to be hydrolyzed by the alkaline surfaces. Latex paints also give better coverage over porous cement surfaces (Section 32.1).

The polymers in latex coatings exist as discrete particles and do not move from one latex particle to another, although solvent and water molecules may do so. Latex coatings form films by coalescence of the polymer particles (Section 2.3.3). Coalescence can occur only if the film formation temperature is higher than the T_g of the polymer particles. Whereas initial coalescence proceeds rapidly at temperatures just a few degrees above T_g, completion of coalescence is relatively slow unless the temperature is significantly higher than T_g. For most architectural paints, slow final coalescence is not a real problem, so the T_g need be only a little below the film formation temperature. In baked industrial coatings, film formation should be complete by the time the coated article comes out of the baking oven; therefore, baking temperatures have to be significantly above the T_g.

There are limitations to latex paints, particularly in regard to the minimum film forming temperature (MFFT), which allows proper coalescence for film formation. To have a final film with a high enough T_g to resist blocking, it is common to use *coalescing solvents* in the formulation. The coalescing solvent dissolves in the polymer particles, reducing the T_g, permitting film formation at a lower temperature. After film formation, the coalescing solvent slowly diffuses out of the film and evaporates. Even with the use of coalescing solvents, however, there are limitations on the temperatures required for good film formation (Section 32.1).

Latex paints with less organic solvent or, in some cases, no VOC have been developed and marketed. Blends of latexes of different T_g and particle sizes [16,17] and latexes with particles having gradient T_g made by sequential polymerization (Sections 2.3.3 and 9.2) [18] have been used. Thermosetting latexes permit use of a low T_g polymer, facilitating film formation at relatively low temperatures; subsequent cross-linking gives the needed block resistance and other properties (Section 9.1.4). Some thermosetting latexes are used in two-package coatings for industrial use; pot life has to be long enough to permit coalescence before a significant degree of cross-linking occurs. For one package latexes, polymers with allylic substitutions that permit autoxidative cross-linking and polymers with trialkoxysilyl groups are being developed. Also, hybrid alkyd–acrylic latexes have been prepared by dissolving an oxidizing alkyd resin in the monomers used in the emulsion polymerization.

Polyurethane latexes are usually called *aqueous polyurethane dispersions* (PUDs) and are generally cross-linkable (Section 12.8). An important factor promoting their increasing use is that films of higher T_g polymers can be formed at ambient temperatures than with acrylic and other conventional latexes, hence, reducing or eliminating the need for coalescing solvents. The water acts as a plasticizer for the polyurethane, reducing the T_g of the polymer permitting film formation [19].

Latexes, water-reducible acrylic resins, and acrylated water-reducible polyesters can be blended with PUDs. Acrylic monomers can also be polymerized in PUDs to make hybrid acrylic–urethane resins. There have been three major approaches to preparing aqueous acrylic/urethane systems: (1) blending of PUDs and latexes (or other water-reducible acrylic resins) (Section 12.7.2), (2) polymerizing acrylic monomers in PUDs (Section 12.7.2), and (3) and cross-linking urethane–vinyl systems (Section 12.7.2.1).

In broad terms, acrylate/PUD blends combine the advantages of both acrylic latexes and PUDs. Acrylic latexes are lower in cost and have excellent exterior durability. The PUDs give films with higher abrasion resistance. The MFFTs of PUDs are lower than those of acrylic latexes having the same T_g, which permits reduction or even elimination of coalescing agents and hence reduction of VOC. Hybrid resins give films with higher tensile strength than acrylic films. Acrylated PUDs with functional groups can be cross-linked by a variety of cross-linkers. Such cross-linked films are of particular interest in automotive base coats.

Another limitation in the formulation of latex coatings is the difficulty of formulating high gloss latex paints (Sections 19.10.1 and 32.3). The main problem of formulating gloss coatings results from the random distribution of pigment and latex particles as the volatiles evaporate, so there is not the same chance of obtaining a pigment free or low pigment content upper surface of the film as with solventborne coatings. This problem can be minimized but not eliminated by using a small particle size latex. Gloss is also limited by the presence of surfactants in the dry film, which can lead to haze and blooming. Latexes with very low surfactant content or with surfactants that can polymerize are being developed to minimize or eliminate this problem (Section 9.1.1).

Latex coatings tend to be excessively shear thinning. When the viscosity at high shear rate is set appropriately for application, the viscosity at the low shear rates encountered in leveling tends to be high. This is one of several reasons that leveling of latex-based coatings tends to be poorer than that of solventborne coatings. Flat coatings with only fair leveling have acceptable appearance, but as gloss is increased, the unevenness of the films becomes undesirable. Substantial progress has been made by use of *associative thickeners* (Section 32.3).

Use of latexes has been more limited in OEM coatings, for many reasons. The problems of evaporation of water on a conveyor line and in ovens mentioned in Section 26.1 are part of the problem. There can also be a problem of popping with latex coatings. It is desirable to use a latex polymer with as high a T_g as possible to minimize the chances of coalescence of the latex particles at the surface of the film before the water has evaporated completely. Probably, the major limitation for industrial applications has been the flow properties of latex-based coatings. In addition, uncross-linked latexes lack the robust resistance to solvents, water, and mechanical damage that is required for many OEM applications. Leveling requirements for many industrial coatings are more rigorous than for architectural coatings. In general, latex coatings have exhibited relatively high degrees of shear thinning and, in many cases, thixotropy. In some cases, these flow characteristics result from flocculation of latex particles. Flocculation of latex increases low shear viscosity to a major degree; furthermore, it exacerbates the gloss problem. Use of associative thickeners minimizes this problem. Since most of the published work with associative thickeners has been done with latex paints for architectural end uses, discussion of them is deferred to Section 32.3. Combinations of latexes with water-reducible resins are used increasingly. Frequently, these combinations have better flow properties than latex coatings.

An advantage of latexes is that their high molecular weights provide mechanical properties that are fully satisfactory for many applications without need for cross-linking. Where good solvent resistance is needed, cross-linking is generally necessary. The viscosity of latexes is independent of molecular weight, so they can be applied at relatively high solids even though their molecular weight is high. In highly pigmented coatings, the fraction of internal phase volume becomes so large that the solids level has to be reduced; but the reduction is done primarily with water so that VOC emissions are minimal.

As pressure to reduce VOC emission increases still further, it is to be anticipated that there will be substantial increases in the use of latexes, particularly thermosetting latexes, in industrial applications of both OEM product coatings and special purpose coatings. For example, an emulsion of a 3,5-dimethylpyrazole blocked HDI isocyanurate modified so that it readily emulsifies in a hydroxy-functional acrylic latex has been suggested as a binder for clear coats [5].

Another method for cross-linking latexes is to copolymerize a few weight percent of diacetone acrylamide into the latex and then formulate the coating with adipic dihydrazide cross-linker; the cross-links are hydrazones formed from the carbonyl group on diacetone acrylamide and the dihydrazide [20]. Yet another method is to carry out the emulsion polymerization with hydroxyl-functional monomers in the presence of mixed-ether MF resins [21]. Both approaches are reported to give films with substantially enhanced hardness and solvent resistance.

26.3. EMULSION COATINGS

Although most waterborne coatings are based on water-reducible or latex binders, emulsion coatings have found some applications and may have potential for wider use.

Two package coatings in which one package is a BPA (or novolac) epoxy resin solution and the second is an amine-terminated cross-linking agent (Section 13.2.2) which contains a nonionic surfactant have had significant commercial applications [22–24]. The amine cross-linker package is diluted with water, and the epoxy resin solution package is added with vigorous stirring. The pot life is limited to a few hours, since the epoxy resin can react not only with the amine groups, but also, slowly, with water. Although pot life of solventborne epoxy–amine coatings is limited by viscosity increase, emulsion systems show little, if any, change in viscosity with age, since the viscosity is controlled by internal phase concentration, not by molecular weight, and because reaction with water does not lead to cross-linking. Instead, pot life is limited by reduced gloss of applied coatings or by inferior film properties. Such emulsion epoxy paints are used where hard, easily cleaned wall coatings are needed, for example, in hospitals and food processing plants. The residual surfactant reduces the corrosion protective properties for application to metal surfaces. Emulsion coatings based on aliphatic epoxy resins and aliphatic carboxylic acid-functional resins are reported to give superior pot life and improved properties [25]. An approach to eliminating surfactants is to use nitroethane as one of the solvents [26,27]. As discussed in Section 13.2.6, nitroethane forms a salt with an amine group of an amine-terminated polyamide, which then acts as a surfactant. When the film dries, the nitroethane evaporates, leaving a less water sensitive film. Such coatings are used in high performance applications such as aircraft primers (Section 33.4).

Amine salts of acrylic copolymers such as methacrylic acid/methyl methacrylate/ethyl acrylate/styrene (40 : 20 : 20 : 20) can be used as emulsifying agents for epoxy–phenolic coatings [28]. During baking, the carboxylic acid groups of the acrylic react with epoxy groups, incorporating the surfactant into the polymer structure, avoiding the ill effects of nonreactive surfactants on film properties. Another example is nitrocellulose lacquers emulsified into water for use as top coats for wood furniture (Section 31.1) [29]. The emulsions have a significantly lower VOC than solventborne lacquers, but longer times are required to achieve print resistance.

Alkyd emulsion paints have been formulated [30] and are used commercially, especially in Europe. Higher gloss can be obtained than with latex paints and there is not the problem of minimum temperature required for film formation versus blocking resistance experienced with latex paints. However, durability is poorer due to yellowing and embrittlement of alkyds. Long oil alkyds with anionic surfactants provide the most stable emulsions. Drying generally is slower than with solventborne alkyds. A contributing factor may be the partitioning of driers between the water and alkyd phases. Alkyds are emulsified into some latex paints to improve adhesion to chalky surfaces (Section 32.1).

Alkyd emulsions, formed initially as a water-in-oil emulsion, which subsequently inverts to an oil-in-water emulsion, are reported to have smaller as well as narrower distribution particle size and to be more easily formulated into paint. The alkyd is heated before addition of water; particle size varies with temperature. In general terms, the shorter the oil length of the alkyd, the higher the temperature for optimum emulsification. Superior film properties are obtained using an emulsifier with a polyunsaturated hydrocarbon chain to cross-link with the alkyd after application [31].

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27

Electrodeposition Coatings

Electrodeposition is an efficient method of applying high performance coatings. Electrodeposition coatings are a major class of waterborne coatings, which are used in largest volume as primers, but also in single and two coat systems. The general principle is relatively simple; development and initial commercialization were complex and difficult. Electrodeposition coating systems are anionic or cationic, alternatively anodic or cathodic, corresponding to deposition at the anode or cathode, respectively. E-coat, electrocoat, electropaint, ED, and ELPO are fairly common synonyms for electrodeposition coatings. Cationic E-coat is used worldwide for priming auto bodies, and its adoption in the 1970s and 1980s led to a major improvement in the corrosion resistance of motor vehicles. Reference [1] provides a review of electrodeposition coating.

In anionic coatings, negatively charged particles of coating in an aqueous dispersion are electrophoretically attracted to a substrate, which is the anode of an electrochemical cell. The coating particles are precipitated by hydrogen ions generated there by electrolysis of water. For cationic coating, the object is made the cathode, and positively charged particles of coating are attracted to the cathode and precipitated on its surface by hydroxide ions. In both types, thermosetting binders are used, and coatings are almost always baked. The coatings must be designed so that all coating components are attracted to the electrode at the same rate; otherwise, the composition will change with time. A vehicle in which pigments can be dispersed and cross-linkers dissolved must form a stable, electrically charged dispersion of aggregate particles when diluted with water. The pigment must be preferentially wet by the resin so that it does not migrate out of the resin aggregates. It is possible to electrodeposit polymer films from solutions of the salt of a polymer in water, but one cannot use a dissolved polymer as a binder for pigmented coatings; the resin, pigment, cross-linker, and other components would not be deposited in the same ratio over time. One can electrodeposit

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Organic Coatings: Science and Technology, Third Edition, by Zeno W. Wicks, Jr., Frank N. Jones, S. Peter Pappas, and Douglas A. Wicks

polymer films from a latex. But latexes cannot be used in pigmented coatings, since pigment particles and latex particles would be attracted to the substrate at different rates.

The coating is diluted to 10 to 20% solids with water. This relatively low solids is used for three reasons. When the coated object is brought out of the tank, it carries a layer of the bath liquid with it that must be rinsed off; losses are less, and rinsing is easier, if the solids are low. Furthermore, ultrafiltration (Section 27.4) is easier with lower solids. For coating products such as automobile bodies and appliances, the electrodeposition tanks are very large—up to 500,000 L. The tank is kept full at all times; therefore, part of the capital investment is the cost of a tank full of coating—the investment is lower with 10 to 20% solids than it would be with 50% solids.

A critical requirement for electrodeposition coatings is indefinite stability after dilution. As the coating is applied, coating solids are removed from the bath, and they have to be replaced continually to maintain the same composition in the tank. Ideally, the tank would never be emptied. Some material from the original loading will be in the tank for long times and must therefore be very stable to hydrolysis and mechanical agitation. The cross-linker must be stable in the diluted coating at a pH over 7 for anionic coatings and under 7 for cationic coatings. Stability to oxidation is critical, since air is mixed into the bath continually by the agitation. If an oxidizing type vehicle is used, an antioxidant that volatilizes in the baking oven is an essential additive.

27.1. ANIONIC ELECTRODEPOSITION COATINGS

Resins used in anionic systems are substituted with carboxylic acid groups that have an acid number in the range 50 to 80 mg of KOH per gram of resin. The pigments and other components are dispersed in the resin, and the carboxylic acid groups are partially neutralized with an amine such as 2-(*N*,*N*-dimethylamino)ethanol. To load the tank, the coating is diluted to about 10% solids with water. The degree of substitution with salt groups is designed to be such that the resin is not soluble in water but rather, forms aggregates on dilution. The aggregates are stabilized as a dispersion in water with salt groups on the outer surface of the particles. Even with less than the theoretical amount of amine to neutralize the carboxylic acid groups, the pH is above 7, due to entrapment of unneutralized COOH groups in the center of aggregate particles (Section 8.3).

In early work on electrodeposition primers for automobiles, maleated linseed oil (Section 14.3.5) was used as a vehicle. The anhydride moiety was bonded to the linseed oil molecules by carbon–carbon bonds that cannot be hydrolyzed, and hence the coating showed reasonable stability. However, adhesion to steel was relatively poor, and maleated linseed oil was soon replaced with maleated epoxy esters (Section 15.8), which had even better hydrolytic stability and provided superior adhesion to steel. The cross-linking obtained through the drying oil fatty acid esters in the epoxy ester was supplemented by using some melamine–formaldehyde (MF) resin as a cross-linker. Mixed methyl ethyl ether Class I MF resins (Section 11.2) are most appropriate for electrodeposition. Such resins have sufficient solubility in water to permit easy incorporation but are more soluble in the resin aggregates than in water, so it deposits in constant ratio as the bath is used over long times.

Carboxylic acid–substituted resins made by reacting moderate molecular weight (MW) polybutadiene with maleic anhydride have also been used as vehicles for anionic primers. Since the backbone linkages are all carbon–carbon bonds, there is no problem of hydrolysis in the bath.

Maleated epoxy esters are not appropriate for many top coat applications because their color stability and chalking resistance are poor. The most widely used resins for anionic electrodeposition top coats are acrylic copolymers made using acrylic (or methacrylic) acid and 2-hydroxyethyl methacrylate as co-monomers. The carboxylic acid groups permit formation of stable aqueous dispersions with electronegatively charged particles; the hydroxyl groups, as well as the carboxylic acid groups, serve as sites for cross-linking with MF resin.

The primary reaction occurring at the anode in anionic E-coats is electrolysis of water to yield hydrogen ions. The hydrogen ions neutralize carboxylate ions on the resin at the surface of the anode. Neutralization removes the charge that stabilizes the aggregates against coalescence. When the salt groups are neutralized, the surface is less polar; there is less swelling of the surface with water, so stabilization is eliminated and the particles coalesce on the metal surface.

$$2H_2O \longrightarrow 4H^+ + O_2 + 4e^-$$

$$RCOO^- + H^+ \longrightarrow RCOOH$$

Not all the salt groups have to be neutralized for precipitation to occur. When the film is formed, some salt groups, and hence ammonium ions, are trapped within the film. Side reactions can also occur at the anode. Iron can dissolve to form ferrous ions that are oxidized to ferric ions. The ferric ions can form insoluble salts with the carboxylic acids on the resin, leading to reddish-brown discoloration. Discoloration is not a problem for primers but is a limitation for making light colored or white electrodeposition top coats. Zinc phosphate conversion coatings generally reduce discoloration to acceptable levels. Anionic top coats can be used on aluminum, since aluminum salts do not affect the color of a coating. In fact, the protective oxide layer on aluminum is enhanced when it is the anode, so anionic E-coat is preferable to cationic for coating aluminum.

An important side reaction in electrocoating of phosphate conversion–treated steel is partial dissolution of the iron–zinc phosphate layer by hydrogen ions generated at the anode surface:

$$Zn_3(PO_4)_2 + 2H^+ \longrightarrow 3Zn^{2+} + 2(HPO_4)^{2-}$$

This partial removal of conversion coating has two potentially serious effects. Damage to the phosphate coating can lead to poorer adhesion to the steel surface and less corrosion protection. Also, the soluble ion concentration in the bath is increased, which leads to higher conductivity of the water phase. As discussed later, maintaining constant relatively low conductivity of the water phase is critical.

Electrolysis of water at the anode also generates oxygen. The oxygen can be generated at the metal surface after it has been coated, leading to film rupture as the bubbles of oxygen escape through the film. At the cathode, hydrogen gas and hydroxide ions are generated. The hydroxide ions neutralize the ammonium counterions:

$$4H_2O + 4e \longrightarrow 4OH^- + 2H_2$$

$$R_3NH^+ + {}^-OH \longrightarrow R_3N + H_2O$$

The amines formed are water soluble, and only a fraction of the amine is removed when the coated article is taken out of the bath. This leads to accumulation of amine in the bath. Methods of control of amine concentration are discussed in Section 27.4. An advantage of electrodeposition compared to other waterborne systems is that only a small amount of counterion is deposited on the substrate with the rest of the coating. Some anionic electrodeposition tanks have been run using potassium hydroxide as the neutralizing base.

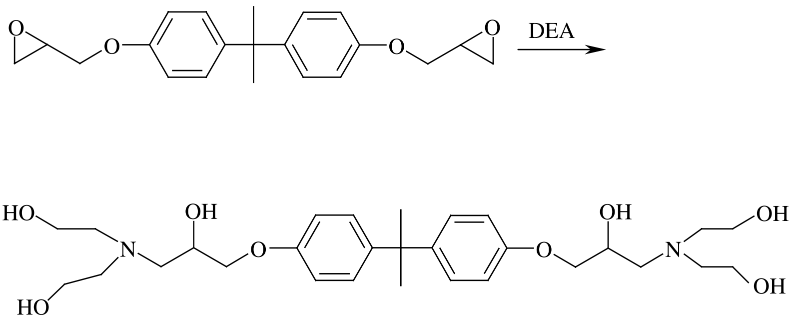
27.2. CATIONIC ELECTRODEPOSITION COATINGS

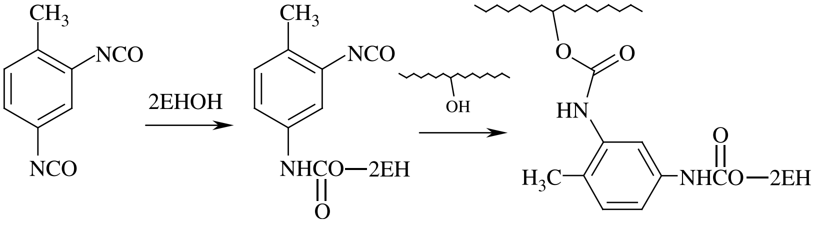
Cationic coatings have positively charged aggregates that are attracted electrophoretically to the cathode. The resins have amine groups neutralized by a low MW, water soluble acid such as formic, acetic, or lactic acid. Coatings stable at a pH a little below 7 are preferred; otherwise stainless steel or other expensive corrosion resistant piping and handling facilities should be used. Some suppliers recommend corrosion resistant equipment in all cases. Commercial cationic electrodeposition tanks are operated within a narrow pH range, 5.8 to 6.2.

The resins used in the formulation of cationic E-coat automotive primers are based on BPA epoxy resins.

- The epoxy resin is reacted with an aminoalcohol, such as diethanolamine (DEA) to yield a resin with amine and hydroxyl groups.
- The resin product is reacted with an isocyanate half-blocked with an alcohol (e.g., 2-ethylhexyl alcohol (2-EHOH) or 2-butoxyethanol) to make a self cross-linkable resin.
- Catalyst and pigment dispersions are added.
- The amine groups are neutralized with a volatile carboxylic acid such as acetic or formic acid.
- The coating is dispersed in water.

The blocked isocyanate cross-linking agent is stable in the slightly acidic water system, whereas MF resins are not. During baking, the blocked isocyanate reacts with a hydroxyl group to form a urethane cross-link. Older E-coat primers contained basic lead silicate as a catalyst, which interacted with the phosphate coating to enhance adhesion. Lead-free E-coats have replaced the older formulations.





The vast majority of cationic E-coats are cross-linked with blocked isocyanates. Upwards of 400 references, mostly patents, between 1980 and 1999 are given in a review of blocked isocyanates [2]. Many variations of epoxy derivatives are described in the literature.

2,4-TDI has the advantage of a large difference in reactivity between the para and ortho isocyanate groups allowing for the formation of predominantly monoblocked intermediate However, some deblocking of both isocyanate groups occurs during cure, releasing some free TDI, which can migrate into base coats causing discoloration. Non-yellowing primers can be made with aromatic isocyanates by reacting TDI half-blocked by the butoxyethoxyethoxy alcohol with BPA epoxy to make an oxazolidone, which is then used with a conventional modified epoxy resin [3]. In some, delamination occurs on exterior exposure between the E-coat and top coats; incorporation of HALS and a UV absorber in a 2-butoxyethoxyethyl alcohol-blocked TDI primer has been reported to overcome this problem [4].

MDI and polymeric MDI have the advantage over TDI in that they are less mobile than TDI, thus less likely to diffuse into base coats. E-coat dispersions are reported to be more stable using a polymeric MDI (12% 2,4′, 35% 4,4′, and 53% poly) blocked with methyl alcohol (or other alcohols) [5]. Partially reacting the MDI with polyether polyols before blocking gives coatings with greater flexibility. A cationic polyurethane dispersion (PUD), prepared from polymeric MDI partially blocked with 2-butoxyethoxyethyl alcohol, TMP, and *N*,*N*-dimethylaminopropylamine is neutralized with formic acid and dispersed in water to give a solvent-free cross-linker for E-coats [6].

In recent years primary focus has been on reducing the cure temperature by using other blocking agents and/or catalysts while maintaining the long term hydrolytic stability of the diluted coating. Since 2-EHOH was the standard for many years, it is used as the base for comparison. Based on patent citations, it appears that 2-butoxyethanol is the most widely used blocking agent today. Such glycol ether-blocked isocyanates cross-link at lower temperatures than those blocked with non-ether alkyl alcohols, since the reverse reaction of the glycol ethers to re-form the blocked isocyanates is slower. In addition, owing to lower volatility, glycol ethers remain in the film longer, promoting better flow and leveling. Glycol amides such as *N*,*N*-dibutylglycolamide have been disclosed as a blocking agent permitting lower temperature cure in E-coats than with 2-EHOH [7].

Methylethylketone oxime (MEKO)-blocked isocyanates are reported to give primers that cure in 20 minutes at 120°C [8]. Such oxime systems were widely used in Japan; but it has been shown that in the E-coat process, HCN is generated leading to dangerous waste discharges [9].

Considerable effort has been devoted to development of new catalysts for E-coats. There have been three driving forces: preparation of lead-free primers, reduction of curing temperatures, and increased hydrolytic stability. Dibutyltin oxide has been the most commonly used catalyst; it gives good stability, but it is insoluble and must be dispersed with the other pigments; it is not highly efficient, and it generally requires a lead compound as a co-catalyst. Trialkyltin compounds such as bis(trioctyltin) oxide (TOTO) are claimed to be effective catalysts especially when used with ZnO [10]. A patent discusses various possible catalysts and particularly recommends TOTO, which permits curing at 150°C [11]. It is claimed that with TOTO one can obtain thicker coatings, greater throw power, and better edge coverage. TOTO is low in toxicity and is a liquid that is easily incorporated into the coating, and can be used to make clear coatings.

Bismuth salts have been reported to be effective catalysts. Bismuth salts of lactic acid and dimethylolpropionic acid (DMPA) offer the advantage that the phosphate conversion coating does not need a chromate wash when the salts are used as catalysts for the E-coat primer [12]. The effectiveness of a series of catalysts on the cure of a cationic E-coat in which a glycol ether-blocked polymeric MDI was the cross-linker concluded that bismuth tris(isostearate), plus isostearic acid, gave the best cure response as well as superior resistance to hydrolysis [13]. See Ref. [2] for an extensive review of catalysts in cationic E-coats.

While aromatic isocyanates have been used in most cationic E-coat primers, problems arise if UV radiation reaches the primer surface as a result of inadequate coverage by the base coat. Photodegradation of the primer can lead to discoloration and possibly to delamination after outdoor exposure. Therefore, primers have been developed using aliphatic isocyanates that are more stable to photodegration. For example, caprolactam blocked IPDI/TMP prepolymer can be used as the cross-linker [14].

In cationic E-coating there is not the problem of acid dissolving the phosphate conversion coating that exists in the case of anionic deposition. Depending on zinc concentration in the treatment bath, different crystals can be deposited (Section 6.4.1). At relatively high zinc concentrations, the crystals are predominantly hydrated zinc phosphate, $Zn_3(PO_4)_2 \cdot 4H_2O$, called hopeite. Under zinc-starved conditions, the crystals have been identified as phosphophyllite, $Zn_2Fe(PO_4)_2 \cdot 4H_2O$ [16]. For E-coating steel the preferred treatment is phosphophyllite, not hopeite. On zinc-coated steels for E-coats, Zn–Ni, Sn–Mn, and Zn–Mn–Ni phosphate conversion treatments are used since straight zinc phosphate would give only hopeite [17].

A recent innovation has been the introduction of two-coat electrodeposition combinations for priming of automobiles. The first E-coat is electroconductive, which allows a second E-coat to be applied. The second E-coat is formulated to replace a spray-applied coating of a primer-surfacer, reducing application cost. A conductive E-coat primer, formulated with 2-EHOH-blocked TDI, an epoxy–amine resin, and electroconductive black pigment, has been disclosed [18].

E-coats based on BPA epoxies and TDI or MDI are used only as primers. If used as top coats, they would exhibit poor color retention and exterior durability. For top coats, acrylic resins with blocked aliphatic diisocyanates give better color retention and exterior durability. 2-(*N*,*N*-dimethylamino)ethyl methacrylate and hydroxyethyl methacrylate as co-monomers provide the amine groups for salt formation and the hydroxyl groups for cross-linking. The curing temperature required for alcohol-blocked aliphatic isocyanates to react with hydroxyl groups is high. One can use oxime-blocked isocyanates that cross-link at lower temperatures, but then the bath stability may be limited. Alternatively, one can make an acrylic resin using glycidyl methacrylate as a co-monomer; the pendant epoxy groups can be reacted with amines to yield secondary amines or mixed secondary and tertiary amines. Alcohol-blocked aliphatic isocyanates can be used to cross-link the secondary amine groups; high temperature bakes are required, but chemical stability in the tank is excellent.

Cationic E-coats have replaced anionic types as automotive primers owing primarily to superior corrosion protection. Amine-substituted cationic resin binders provide greater corrosion protection for steel, resulting, perhaps, from strong interaction between the amine groups and the substrate surface, thereby enhancing wet adhesion, the most critical factor in corrosion protection (Section 7.3.2). Wet adhesion of lead-free coatings is especially critical for corrosion protection, since lead-containing compounds, which inhibited corrosion in earlier E-coats, can no longer be used.

27.3. EFFECT OF VARIABLES ON ELECTRODEPOSITION

Deposition of coating is not instantaneous with application of current. Some time elapses before enough hydrogen ions (anionic E-coat) or hydroxide ions (cationic E-coat) are formed to neutralize enough charges on aggregate particles to cause precipitation. After this initial time interval, the rate of deposition is affected by the rate of electrophoresis of the aggregates. This rate is affected significantly by the impressed voltage; the higher the voltage, the faster the film deposition. Coatings are designed to coat in 2 to 3 minutes with 225 to 400 V; the high voltage is not needed to electrolyze the water, but rather, to increase the driving force for electrophoretic attraction of particles to the electrode and for adequate coating of recessed areas.

The first areas covered are the edges of the metal, since current density is highest there. As film thickness increases, electrical resistance increases, reducing the rate of deposition at those sections coated first. There is a limiting film thickness beyond which deposition of further coating stops or, at least, becomes very slow. After edges are coated, outer flat surfaces of the object are coated, followed by recessed and enclosed areas. The further back in a recess, the later the area is coated. Particularly for corrosion protective primers, it is desirable to have the entire surface of the steel coated, so it becomes important to coat the furthest recessed areas in the 2 to 3 minute dwell time in the tank.

The rate of deposition is also affected by the equivalent weight of the coating. The higher the equivalent weight, the greater the amount of coating precipitated by each hydrogen (or hydroxide) ion and therefore the faster the buildup of film thickness. On the other hand, it is critical to have a low enough equivalent weight so that there are sufficient polar salt groups to maintain stability of the dispersion of aggregates in the coating bath. The rate is also affected by the amount of soluble low MW ions present in the bath. These ions are attracted to the electrodes in competition with the aggregate particles. Since they are small, they move more rapidly in the electrophoretic field. Thus, concentration of soluble salts must be low and maintained close to constant.

A coating that deposits in recessed areas quickly is said to have a high *throw power* (called *throwing power* by some authors). Standard tests for throw power determine how far up into a pipe or an open-ended box the coating is applied at a standard voltage in a standard time. Throw power increases with higher impressed voltage and longer dwell times. However, if the voltage is increased to too high a level, there will be film rupture of the coating applied to the outer surfaces. At a sufficiently high voltage, the current breaks through the film, leading to local generation of gas under the film (oxygen in anionic electrodeposition and hydrogen in cationic electrodeposition), and bubbles of gas can blow out through the film, leaving film defects. It has been shown that, at higher voltages, electric discharges occur through the film during electrodeposition causing visible sparks [19]. These sparks may also be responsible for film ruptures. Sparking is reported to occur at lower voltages (240 V) when the substrate is galvanized steel than when the substrate is steel, about 300 V or higher. As conductivity of the deposited film increases, film rupture tends to occur at lower voltages. Direct current electricity obtained by rectifying AC electricity has a relatively wide variation in voltage; the current is said to *ripple*. The effect of rippling can be to break through at lower (average) voltage [20]. Model equations have been developed to permit predicting throw power and film build on complex shaped surfaces such as an automobile [21].

Throw power is affected by the conductivity of the bath; the higher the conductivity, the greater the throw power. However, there is a limitation; as the conductivity due to the presence of soluble salts increases, the rate of electrophoresis of coating aggregates decreases. Increased numbers of salt groups on the resin increase conductivity and hence throw power, but equivalent weight drops, which decreases the rate of deposition. Entrapment of conductive material in the film increases with a corresponding increase in the likelihood of film rupture. A compromise on conductivity must be reached. Conductivities used are in the range 1000 to 1800 microsiemens (μS); the older unit, mho, is still used; 1 $\mu S = 1$ μmho.

Film rupture and hence throw power are affected by variations in coating composition. If the viscosity of the aggregates precipitated on the surface is high, full coalescence is not achieved and a porous film results, giving high film conductivity and poor throw power. On the other hand, if the viscosity of the precipitated aggregates is very low, the films will be soft; then, if any electrolysis takes place below the surface, bubbles will break through easily and film rupture will be severe. A compromise must be made between the extremes. The glass transition temperature of the resin is a controlling factor, and correspondingly, the temperature at which the electrodeposition is carried out is important. Temperature of the bath must be controlled within a fairly narrow range, typically 32 to 35°C. Higher T_g resins can be used only if solvent is included in the formula. Many E-coats now use a small amount of solvent, but eliminating it is a desirable environmental goal. Solvents can affect the electrical conductivity of the deposited film, so care must be taken in their selection. Excess solvent leads to film rupture at lower voltage, which reduces throw power. Also, the partition coefficient must be such that almost all the solvent is dissolved in the aggregates, with very little in the water, or the solvent concentration in the bath will build up over time.

Pigment concentration also affects coalescence. If the PVC is near or above CPVC and the amount of solvent, if any, is small, the deposited film will not coalesce. Even if low enough to permit coalescence, the amount of pigment has a significant effect on leveling of the film. Since the film as applied has a low solvent concentration, its viscosity is very dependent on pigment concentration. Unless the PVC is low, in most coatings less than half of CPVC, leveling will be poor because of the high viscosity. Because of the low level of pigmentation compared to that of conventional primers, the gloss of electrodeposited primers is higher, especially if the pigment content is reduced to low enough levels to permit good leveling. The PVC also affects flow away from edges during baking; higher PVC reduces this problem, so a compromise between leveling and edge flow must be made.

27.4. APPLICATION OF ELECTRODEPOSITION COATINGS

A schematic diagram of an E-coat system is shown in Figure 27.1. The object to be coated is hung from a conveyer and carried into a dip tank. Both to return coating carried out of the tank by the object and to avoid local accumulation of excess coating on the object, the object is rinsed with ultrafiltrate as it comes out of the tank. At the rinsing stage, the coating film has not been cross-linked but is of sufficiently high viscosity to remain intact; only the bath liquid is washed from the surface of the coating. Concentration of coating in the bath must be kept constant by adding *makeup coating* continuously to replace coating solids removed by deposition. The heat exchanger maintains temperature within a narrow range.

The bath liquid is recirculated continuously through an ultrafiltration unit. Adoption of ultrafiltration was an essential factor in allowing large-scale cationic electrodeposition.

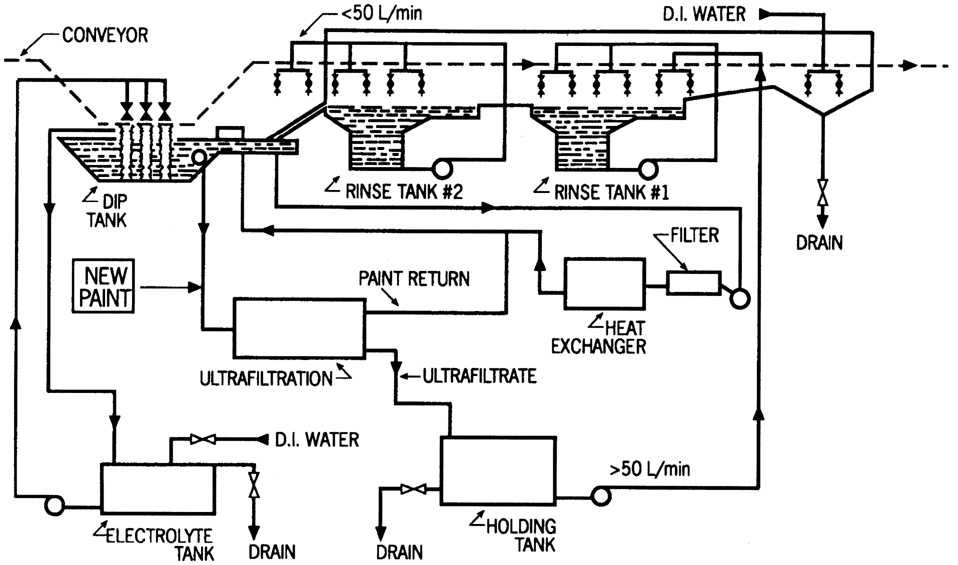


Figure 27.1. *Cationic automotive primer electrodeposition installation. (Adapted from Ref. [22], with permission.)*

The ultrafiltration membrane permits removal of excess water and water-soluble materials while not removing the aggregates containing the resin, pigment, and cross-linker. Ultrafiltration permits maintaining the concentration of soluble salts essentially constant so that there is constant conductivity.

Figure 27.1 also shows an electrolyte tank. This represents a system for controlling the concentration of solubilizing agent (acid for cationic coatings and amine for anionic ones). When coating is precipitated on the substrate surface, a corresponding amount of solubilizing agent is released. The concentration of solubilizing agent must be maintained at a constant level. A small amount of solubilizing agent is carried out of the bath with the coated product, and some is removed by ultrafiltration, but these losses of solubilizing agent are less than the amount being released by electrocoating. There are two ways of maintaining the balance. A sufficiently low level of solubilizing agent content is used in the makeup coating, and the remainder of the required level of solubilizing agent is the excess left in the bath. The other, more effective approach is to have the counter electrode in a microporous polypropylene box. The pore size of the membrane must be such that the aggregate particles cannot pass through the membrane, but water and carboxylate (or ammonium) ions can easily go through. In some cases it is necessary to use ion-selective membranes. The clear liquid in the box is recirculated to the electrolyte tank, where the concentration is monitored and corrected automatically. Maintenance of the proper level of solubilizing agent is critical. It is common to hear that the pH of the bath must be kept constant. Although this is true, the pH of these coatings is insensitive to the ratio of the weak acid and weak base (Section 8.3). Conductivity is a more important control criterion. The application lines can be highly automated, with feedback control of rate of addition of make-up coating, solubilizing agent, and water.

27.5. ADVANTAGES AND LIMITATIONS OF ELECTRODEPOSITION

Electrodeposition is used for applying coatings to a variety of products. Almost all new automobiles have electrodeposited primer coats. Many appliances are primed by electrodeposition. Aluminum extrusions, drapery fixtures, metal toy trucks, and steel furniture are a few of many examples of single coat electrodeposition applications.

Electrodeposition can be a highly automated system with low labor requirements, especially as compared to spray application. A startling example of a savings of labor has been reported in the use of cationic electrodeposition to apply an epoxy coating to air conditioners [23]. The former coating system of a flow coated primer and a spray applied acrylic top coat required 50 people, including those who did the required touchup and repair. The E-coat operation requires only one operator. Further savings result from elimination of coating losses from overspray. Coating utilization in excess of 95% is reported. The economic advantage of the combination of these factors is large in assembly line operations. However, the capital cost of the automated line is high, limiting applicability of highly automated lines to large production operations. The electrodeposition unit is the most expensive equipment in an auto assembly plant. Simpler installations are used for applications such as coating metal toys. Development of electrodeposition in the 1960s and 1970s was a long and expensive process, and even today it is expensive to start a new system and get it running smoothly.

Solvent content of E-coats is relatively low, so VOC emissions are low and fire hazard is reduced. Another environmental advantage over spray applied coatings is that there is no overspray sludge disposal (unless a poor job of formulating, coating production, bath maintenance, or control makes it necessary to dispose of 500,000 L of bad coating!). Since the solids of the deposited film are high, only 3 to 5 minute flash off time is required before entering the oven, an advantage relative to spray applied coatings.

Another advantage, assuming adequate throw power, is that complete coverage of surfaces is obtained. There can be differences in film thickness; for example, the recessed areas will generally have thinner deposits than the exposed face areas, but all of the surface will have some coating. Recessed and enclosed areas that cannot be coated by spray application can be coated by electrodeposition. Objects with many edges, such as drapery fixtures, can be coated better by electrodeposition than any other way. The edges are uniformly coated, in contrast to excess coating at the bottom edges of objects coated by dipping.

Sagging can be experienced when the electrocoated part is heated in an oven. However, due to the relatively high viscosity of the coating immediately on application, severe sagging is less likely than during spray or conventional dip application methods. Also, one is less likely to encounter the relatively large differences in film thickness between the top and bottom of the dipped object commonly experienced with conventional dip coating.

Uniform film thickness can lead to a problem, especially with relatively highly pigmented primers: the applied coating follows the surface contours of the metal closely, so a rough metal gives a rough primer surface. Some authors refer to this phenomenon of replication of the substrate surface profile as *telegraphing*. If there is minimal replication of metal scratches or a rough metal profile in the surface of the primer coat, some authors say the primer shows good *filling*. E-coat films are relatively thin, varying from 15 to 30 μm, depending on coating composition and application variables. When E-coat primers are sanded to smooth the surface and improve adhesion, only light *scuff* *sanding* is done. If necessary, heavier *spot sanding* will smooth out sags, runout, seeds, and so on, and remove dirt, weld balls, and weld spatter. However, spot sanding will often result in *sand-through* to expose metal. If so, the area must be patched with a *spot primer*, a catalyzed spray primer that contains corrosion inhibitors.

Substantial variations in smoothness of the primer surface can result from changes in E-coat primer composition [24]. Leveling can be improved by reducing the pigment content of the primer. With lower PVC, the viscosity of the coating after application and before cross-linking is lower. During baking, some leveling occurs before cross-linking increases the viscosity such that no further flow can occur. The lower viscosity can also permit undesirable flow; in some cases, edge coverage is reduced by flow away from the edges of the coated product. The edges heat up first, reducing the surface tension of the coating in that area, leading to flow over the adjoining higher surface tension area. Also, when the pigment content is decreased, gloss of the films is increased.

There can be a problem achieving adequate adhesion of top coats to the surface of electrodeposited primers. Adhesion is affected by the cross-link density of the E-coat; over-baking can lead to poorer intercoat adhesion. The gloss of electrodeposited primers is relatively high, and the smooth surface makes achieving intercoat adhesion more difficult. When the PVC is further reduced to promote leveling, the surface is still smoother to the further detriment of intercoat adhesion. For auto bodies, a primer–surfacer is usually applied over the E-coat primer. If the solvents are selected carefully, penetration into the electrodeposited film promotes intercoat adhesion. The primer–surfacer can have PVC $>$ CPVC to enhance adhesion of the top coat, and it can be sanded to smooth the surface without reducing adhesion. The primer–surfacer also improves adhesion of sealants and adhesives and protects the E-coat from UV degradation.

The substrate must be conductive; most applications have been for metal primers or for one-coat metal coatings. Two coat applications require that the first coat be conductive and are used in production in only a few instances.

Another limitation that electrodeposition shares with any other dipping system is the difficulty of formulation changeovers. If it is decided to change the color of an automotive primer, what do you do with 500,000 L of coating? At least once when this problem was faced, the coating supplier developed the new color primer to be compatible with the old color primer, so that the new coating could be introduced into the existing tank. Of course, for a period of time there was a slow change of primer color from the old color to the new color. This was not serious for a primer, but would not be acceptable for a top coat. Use of electrodeposition for top coats is limited to applications for which long runs of the same color are made (such as agricultural equipment, garden tractors, and lawn mowers) so that a line can be dedicated to a particular color. In small installations, such as for coating toys, one coating bath can be pumped out of the electrodeposition tank into a holding tank, where it must be kept continuously agitated, and another color is pumped into the tank. But these are relatively small tanks; the procedure would not be economically feasible with large tanks.

27.6. AUTODEPOSITION COATINGS

Autodeposition coating (also called autophoretic coating) is, as the name implies, a process in which coatings are applied without external electricity, in contrast to anionic and cationic electrodeposition. A paper has been published comparing the properties of steel coated by autophoresis with a cationic E-coat [25]. The coating is a stabilized poly(vinylidene chloride) latex bath containing a weak acid (hydrofluoric acid), an oxidant (hydrogen peroxide), deionized water, an accelerator (iron salt), surfactants, and additives. When a steel object to be painted is immersed in the coating bath, two reactions take place. The principal reaction is

$$Fe^0 + 2FeF_3 \longrightarrow 3Fe^{2+} + 6F^- \qquad (27.1)$$

A minor reaction is

$$Fe^0 + 2HF \longrightarrow Fe^{2+} + H_2(g) + 2F^- \qquad (27.2)$$

The ferrous ions precipitate the latex and pigment dispersion in the coating as an iron complex. The ferrous ions in the complex are oxidized to ferric ions by the hydrogen peroxide and hydrofluoric acid:

$$2Fe^{2+} + H_2O_2 + 2HF \longrightarrow 2Fe^{3+} + 2H_2O + 2F^- \qquad (27.3)$$

The FeF_3 is then available for a chain reaction via reaction (27.1).

Initially, the deposited coating is adherent and porous, allowing the acid to continue to penetrate to the substrate as the reaction continues. The first areas of the steel coated are the anodic areas of the steel, such as edges. As the initial anodic areas are coated, other areas of the steel become anodic and coating continues. After application, the coating is baked at 105°C to remove water and become cohesive.

The films from the autophoretic coating are rougher than those of cationic coating. Physical properties of the films are similar. Corrosion protection by intact autophoretic films is excellent, but when gouged through, the protection is inferior to the cationic primer. The resistance of the autophoretic coatings to brake fluid is inferior. Thus, cationic E-coat is preferable for coating car bodies, and autophoretic coating uses are limited to applications where the more limited corrosion protection is adequate: for example, seat structures, fans, head light casings, and the like. Only black coatings have been available.

Where the film properties are adequate, autophoresis has several advantages over E-coat: Bake temperatures are lower. Only thorough cleaning of the steel is required, not phosphate coating. Capital cost of application tanks and equipment is lower. Any active metal can be coated. The coatings have zero VOC.

In addition to poly(vinylidene chloride), a variety of other binders have been patented: vinylidene chloride, acrylic acid, methyl acrylate copolymer latex [26], an acrylic latex [27], a BPA epoxy resin with an IPDI uretdione prepolymer as a blocked cross-linking agent, and a resole phenolic resin with an acrylonitrile–butadiene latex [28]. Flexibilized BPA epoxy resins with caprolactam-blocked HDI isocyanurate are reported to give coatings with excellent adhesion and corrosion protection without the need for a phosphate conversion coating [29].

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28

Powder Coatings

Worldwide production of powder coatings in 2001 was estimated to be about 900,000 metric tons [1]. Powder coatings are used most extensively in Europe (43%) and Asia (26%); followed by North America (23%) and the rest of the world (8%). On a percentage basis, use of powder coatings grew rapidly from the 1970s through 2000; the growth rate slowed in the early 2000s [2].

The general principle is to formulate a coating from solid resins, pigments, and additives, to melt mix them under high shear to disperse pigments in a matrix of the major binder components, and to pulverize the resulting solid. The powder is applied to the substrate, usually metal, and fused to a continuous film by baking. Thermosetting and thermoplastic powders are available; the major portion of the market (>90%) is for thermosetting types.

28.1. BINDERS FOR THERMOSETTING POWDER COATINGS

Binders for thermosetting powder coatings consist of a mixture of a primary resin and a cross-linker, often called a *hardener*. The major types of binders are grouped somewhat arbitrarily into several classes, as shown in Table 28.1. The terminology has grown historically and has become confusing. *Epoxy powder coatings* include only coatings based on BPA and novolac epoxy resins with amine, anhydride, or phenolic hardeners. *Hybrid coatings* also contain BPA epoxy resins but are cross-linked with carboxy-functional polyester resins. Polyester coatings contain polyesters with various cross-linkers other than BPA and novolac epoxies; the term is used only for coatings that exhibit good to excellent exterior durability. Acrylic coatings contain acrylic resins with various cross-linkers. In addition, various blends, sometimes called *alloys*, of these classes are used. Blends are gaining

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Organic Coatings: Science and Technology, Third Edition, by Zeno W. Wicks, Jr., Frank N. Jones, S. Peter Pappas, and Douglas A. Wicks

TABLE 28.1. Classes of Thermosetting Powder Coatings

Common Name	Primary Resin Cross-Linker
Epoxy BPA (or novolac) epoxy	Polyamines, anhydrides, or phenolics
Hybrid COOH-functional polyester	BPA epoxy
Polyester	
COOH-functional polyester	Triglycidylisocyanurate or hydroxyalkylamide
OH-functional polyester	Blocked-isocyanate or amino resin
Acrylic	
Epoxy-functional acrylic	Dibasic acid
OH-functional acrylic	Blocked-isocyanate or amino resin
UV cure	
Acrylate-functional resin	Free radical
Epoxy-functional resin	Cationic

increasing importance, for example, in primers for auto bodies [3]. Among the factors in choosing a class of powder coating for an application are protective properties, exterior durability, and cost. Differences in exterior durability are indicated in Figure 28.1.

In powder coatings, it is necessary to control the balance of binder T_g, $\bar{M}_n$, $\bar{f}_n$, and reactivity [5]. It must be possible to process the material without significant cross-linking, and the resulting powder must not sinter (start coalescing) or start to cross-link during storage, but it must fuse during baking, level to form a desirable film, and cross-link. In general, the primary resins are amorphous polymers with a T_g high enough to avoid sintering of the powder and with an $\bar{M}_n$ of a few thousand. Recommended minimum binder T_g values are 40°C in Europe and 45 to 50°C in North America, reflecting the higher temperatures during shipment and storage in parts of North America. A typical powder coating having a T_g of 50°C could be melt processed at about 80°C and could be handled and stored at temperatures up to about 40°C. When heated in a baking oven, its viscosity would drop briefly

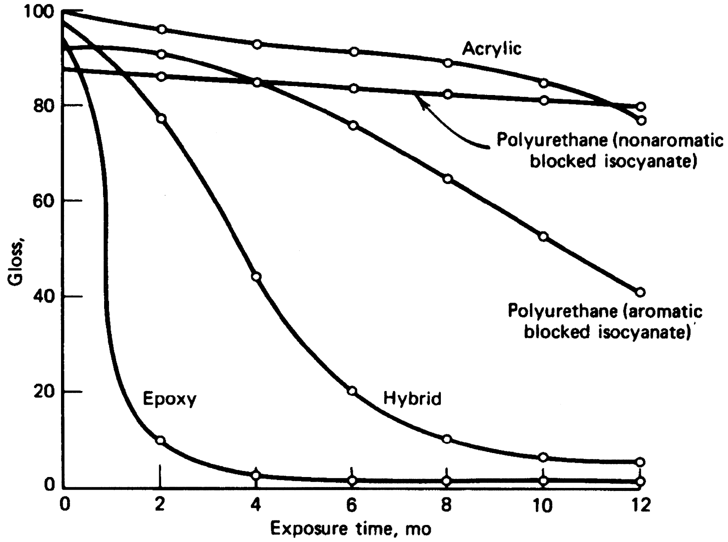


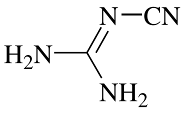
Figure 28.1. Florida outdoor exposure data on various types of powder coatings. (From Ref. [4], with permission.)

to about 10 Pa•s, allowing coalescence, flow, and leveling, and with continued heating for 15 minutes at a temperature in the range 130 to 200°C, it would cross-link. The T_g values referred to are those of the combination of the primary resin plus the cross-linker. The T_g required for the primary resin alone varies, depending on the cross-linker used with it. UV cure powder coatings can be cured at temperatures as low as 100°C.

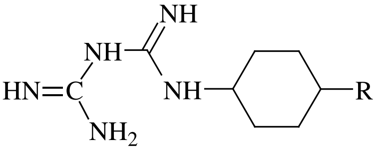
Because T_g is higher, powder coatings can attain good hardness at somewhat lower cross-link density than most liquid coatings designed for similar applications. This attribute tends to work in the favor of powder coatings, which often combine excellent hardness with excellent impact resistance.

28.1.1. Epoxy Binders

Epoxy powder coatings are the oldest and still one of the largest classes of thermosetting powder coatings. Decorative coatings have been based on BPA epoxy resins with *n* values of 3 to 5, usually made by the advancement process (Section 13.1.1). The trend, however, is to lower molecular weights (MW) with some epoxy resins having *n* as low as 2.5, to provide better flow in thin film applications. For protective coatings, *n* values range up to 8. The most commonly used cross-linkers are dicyandiamide (dicy) (Section 13.2.1) or a modified dicyandiamide. The curing reactions are complex [6]. Modified dicys are more soluble in epoxy resins and tend to form uniform films more readily. 2-Methylimidazole is a widely used catalyst.



Dicyandiamide



Modified dicyandiamide

Epoxy powder coatings have good mechanical properties, adhesion, and corrosion protection; however, their exterior durability is poor. Applications for decorative types include institutional furniture, shelving, and tools. Applications of protective epoxy coatings include pipes, rebars, electrical equipment, primers, and automotive underbody parts. Where enhanced chemical and corrosion resistance is needed, phenolic resins (Section 13.3.1) are used to cross-link epoxy resins, with 2-methylimidazole as catalyst. Novolac epoxy resins (Section 13.1.2) or blends of novolac and BPA epoxies give higher cross-link densities than BPA epoxies alone. All these coatings discolor and chalk on exterior exposure. Polycarboxylic acid anhydrides (Section 13.3.2), such as trimellitic anhydride, are sometimes used with BPA epoxy resins in applications for which greater resistance to yellowing and to acids and solvents is needed. The latter coatings are generally being replaced with hybrid coatings that have somewhat better exterior durability and less question of toxic hazard.

28.1.2. Hybrid Binders

BPA epoxy resins are cross-linked with carboxylic acid–terminated polyester resins with $\bar{M}_n$ of a few thousand. Such formulations are called *hybrid powder coatings*, implying that they are intermediate between epoxy and polyester coatings. Hybrid coatings have better color retention and UV resistance than epoxy powder coatings, but still do not have good exterior durability. Examples of end uses include water heaters, fire extinguishers, radiators, and transformer covers.

A variety of polyesters have been described. Most are derived from neopentyl glycol and terephthalic acid (TPA) with smaller amounts of other monomers to adjust the T_g to the desired level and give branching to increase the $\bar{f}_n$ above 2 (Section 10.6). An example is a polyester from neopentyl glycol (NPG) (364 parts by weight, 3.5 mol), TPA (423 parts, 2.55 mol), adipic acid (AA) (41 parts, 0.24 mol), and trimellitic anhydride (TMA) (141 parts, 0.74 mol) [7]. The acid number of the resin is 80 mg KOH per gram of resin. The relatively high trimellitic anhydride content increases $\bar{f}_n$, compensating for the low (about 1.9) $\bar{f}_n$ of the BPA epoxy. The primary cross-linking reaction is ring opening of the oxirane groups by carboxylic acids (Section 13.3.2). Esterification and transesterification reactions involving hydroxyl groups of the epoxy resin and homopolymerization reactions of oxirane groups may also play a role. A catalyst such as an ammonium or phosphonium salt, for example tetrabutylammonium bromide or choline chloride, permits baking temperatures in the range 160 to 200°C. Often, the polyester resins are supplied with the catalyst blended in.

A proprietary, modified BPA epoxy that exhibits greater flow with comparable sintering resistance compared to conventional BPA epoxies has been reported [8].

28.1.3. Polyester Binders

Depending on the cross-linker, carboxylic acid–functional or hydroxy-functional polyester resins are used. Flow properties of powder coatings containing carboxylic acid–terminated polyesters tend to be poorer than those made with hydroxy-terminated polyesters. Triglycidylisocyanurate (TGIC) (Section 13.1.2) has been widely used as a cross-linker for carboxylic acid–terminated polyesters with basic catalysts. TGIC based powder coatings have good exterior durability and mechanical properties. Examples of end uses are outdoor furniture, farm equipment, fence poles, and air conditioners. Although TGIC is expensive, the amounts required are relatively small because of its low equivalent weight. Typical binders contain 4 to 10 wt% TGIC and 90 to 96 wt% of carboxylic acid–terminated polyester. The polyesters used are generally less branched than those used in hybrid coatings because of the higher functionality of TGIC compared to BPA epoxies. One polyester, for example, is made from NPG (530 parts by weight, 5 mol), TPA (711 parts, 4.3 mol), isophthalic acid (IPA) (88 parts, 0.47 mol), pelargonic acid (58 parts, 0.37 mol), and TMA (43 parts, 0.22 mol); the acid number is 35 [7]. Such resins are prepared in a two-stage process to minimize the problems caused by the high melting point and low solubility of TPA (Section 10.6). Alternatively, dimethyl terephthalate is used in place of TPA and the polymer is formed by transesterification (Section 10.6). High equivalent weight (low acid number) is desirable, since this reduces the required amount of TGIC, but cross-link density decreases with the higher equivalent weight. There is an optimum for each application.

A study of a variety of catalysts for TGIC–polyester powder coatings was made to find a catalyst that will cure at a temperature of 120°C while still having adequate storage stability and flow. The work was aimed at a powder coated primer for use in coating aluminum alloy for aircraft. The properties of certain aluminum alloys change if exposed to temperature over 120°C. The most appropriate catalyst was found to be benzyltrimethylammonium chloride [9]. A combination of a fumaric unsaturated polyester and an allyl-functional polyester with TGIC and benzoyl peroxide as a free radical initiator is reported to cure at a temperature of 125°C [10].

A problem with NPG–TPA polyesters is that they can contain cyclic esters without functional groups; such compounds have been shown to bloom to the surface of polyester–TGIC coatings. A combination of NPG and 2-butyl-2-ethyl-1,3-propanediol with TPA and IPA gives a semicrystalline polyester with much less cyclic ester and no blooming when cross-linked with TGIC to make gloss coatings [11].

There has been increasing concern about toxic hazards of TGIC. Partly as a result, tetra(2-hydroxyalkyl)bisamides (Section 17.4) are being used as cross-linking agents for carboxylic acid–functional polyesters in exterior durable coatings [12]. These coatings also have good mechanical properties and flow. Water is evolved from the cross-linking reaction, which may limit the film thickness that can be applied without popping. Polyesters with terminal hindered carboxylic acid groups, cross-linked with tetra(2-hydroxyalkyl)bisamide, provided powder coatings with improved flow, less limitation on film thickness to avoid popping, and excellent acid rain resistance. A hindered COOH group increases flow due to the reduction of hydrogen bonding between COOH groups. The hindered COOH groups also reduce the cure rate, providing for improved leveling [13]. An example of such a polyester is made in three stages. First, NPG is esterified with TPA to give a hydroxy-functional polyester. Second, that polyester is reacted with IPA to give a carboxylic acid–terminated polyester. Then that polyester is reacted with hydroxypivalic acid to give a polyester terminated with tertiary carboxylic acid groups [14].

In North America, polyester coatings with blocked aliphatic isocyanates (Section 12.5) as cross-linkers for hydroxy-functional polyesters are widely used. The coatings have exterior durabilities equal to, or somewhat better than, TGIC cross-linked polyesters, and the superior mechanical properties and abrasion resistance typical of polyurethane coatings. Blocked isocyanate–polyester powder coatings generally show better flow than most powder coatings, perhaps because the unreacted cross-linkers or blocking agents released by unblocking are good plasticizers. Examples of their end uses are automobile wheels, lighting fixtures, garden tractors, fence fittings, and playground equipment.

Derivatives of isophorone diisocyanate (IPDI), bis(4-isocyanatocyclohexyl)methane ($H_{12}MDI$) isocyanurate, and tetramethylxylidene diisocyanate (TMXDI) low MW prepolymers (Section 12.3.2) are examples of blocked isocyanates that are solids. Blocked isocyanates from sterically crowded isocyanates such as TMXDI have the potential advantage of unblocking at a somewhat lower temperature [15,16]. Probably, the most widely used blocking agent is ϵ-caprolactam. Caprolactam-blocked $H_{12}MDI$–TMP prepolymer is reported to cure in 20 minutes at 160°C (20°C lower than with caprolactam-blocked IPDI or HDI), and give excellent exterior durability, flexibility, and impact resistance [17]. A disadvantage of caprolactam is build up of volatilized caprolactam in baking ovens. Also, there is pressure to reduce curing temperatures. Oxime blocking agents are being used, since they react at lower temperatures [16]. The sterically crowded blocked isocyanates from diisobutyl and diisopropyl oximes give the lowest cure temperatures [16]. Oxime-blocked isocyanate coatings tend to yellow during cure, especially if overbaked. Also, there is concern about toxic hazards with oximes. 3,5-Dimethylpyrazole and 1,2,4-triazole (and mixtures of the two) give blocked isocyanates that combine lower cure temperatures and no yellowing [18]. 3,5-Dimethylpyrazole-blocked $H_{12}MDI$ is reported to cure coatings at 150°C with excellent flow and leveling [17].

As cross-linkers, uretdiones (isocyanate dimers) have the distinct advantage that they cleave to give isocyanates, so that no blocking agent is evolved (Section 12.5). The cure temperatures without catalyst are high, and considerable work has been done on catalysis. Most recently it has been recommended that tetraalkylammonium carboxylates be used as catalyst along with TGIC to react with free carboxylic acid groups on the polyester that inhibit the cross-linking. The combination permits curing at 150°C [19]. A patent has been applied for in which an IPDI uretdione with the NCO groups partially reacted with TMP, benzyltrimethylammonium chloride as catalyst, and TGIC as an acid scavenger are used with a hydroxy-functional polyester in formulating a powder coating [20].

An amino resin, tetra(methoxymethylol)glycouril (TMMGU), is also used as a cross-linker for hydroxy-functional resins [21]. Since methyl alcohol is generated as a by-product, film thickness may be limited by popping or retention of bubbles in the cured film. Release of the methyl alcohol from the film can be aided by a variety of approaches that slow cross-linking, such as use of methyltoluenesulfonimide as a catalyst with a solid amine such as tetramethylpiperidinol as an inhibitor. Toluene sulfonamide–modified melamine–formaldehyde resins can also serve as cross-linkers for hydroxy-functional polyesters [22]. The reaction with these resins releases volatile by-products also; it is reported that buffering by a cure rate regulator, 2-methylimidazole, minimizes popping [23].

28.1.4. Acrylic Binders

A variety of acrylic resins can be used in powder coatings: Hydroxy-functional acrylics can be cross-linked with blocked isocyanates or glycolurils, and carboxylic acid–functional acrylics can be cross-linked with epoxy resins or with carbodiimides [24]. Hydroxyalkylamides have also been used to cross-link COOH-functional acrylic powders [25]. Controlled radical polymerization by ATRP of COOH-functional acrylic resins results in narrower MW distribution than by conventional free radical polymerization. (See Section 2.2.1.1 for a discussion of the polymerization process.) Such a resin had a $\bar{M}_w/\bar{M}_n$ of 1.25 compared with 1.95 for a similar resin made by conventional free radical polymerization. The melt viscosity at 180°C of the ATRP polymer was 11.2 Pa•s compared with 57.2 for the conventional resin. A powder coating using the ATRP polymer and bis(*N*, *N*-di-2-hydroxyethyl)adipamide as a cross-linker was compared with a similar powder coating made with the conventional free radical copolymer. The ATRP powder coating gave cured films with better leveling than the conventional polymer and had superior storage stability. The lower melt viscosity and hence narrow MW distribution of the ATRP polymer resulted in better leveling. The reduced amount of very low MW molecules reduced the fusion of the powder particles during storage [26].

The greatest interest has been in epoxy-functional acrylics made with glycidyl methacrylate (GMA) (Section 13.1.2) as a co-monomer and cross-linked with dicarboxylic acids such as dodecanedioic acid [$HOOC(CH_2)_{10}COOH$] [27] or carboxylic acid–functional resins [28]. An epoxy-functional acrylic for automotive primer–surfacer is said to require an $\bar{M}_n$ below 2500, a calculated T_g above 80°C, and a monomer composition such that melt viscosity is less than 40 Pa•s at 150°C [29]. Such a resin can be made with 15 to 35% GMA, 5 to 15% butyl methacrylate (BMA), with the balance being methyl methacrylate (MMA) and styrene. Such an acrylic evaluated for automotive clear coats had an $\bar{M}_n$ of 3000, an $\bar{M}_w/\bar{M}_n$ of 1.8, and a T_g of 60°C [28]. Epoxy-functional acrylic polymers can be synthesized by emulsion polymerization using cyclodextrin-assisted polymerization. Cyclodextrin is dissolved in water, the acrylic monomers are emulsified into the solution, and a redox initiator system is added. The product is a dispersion of the epoxy-functional acrylic, which is filtered and dried [30].

Acrylic powder coatings generally have superior detergent resistance and are used for applications such as washing machines. Acrylics tend to be incompatible with other powder coatings, requiring caution when changing coating types to avoid contamination, which can result in cratering. As with liquid coatings, acrylic powder coatings tend to have poorer impact resistance than polyesters [31].

28.1.5. Silicone Binders

The use of silicone and silicone/polyester resins in high heat resistance powder coatings has been reported. Silicone powder coatings require lower processing temperatures than other powder coatings. To avoid bubbling due to the escape of water during cross-linking, film thickness is limited to 2 mil or less. The coatings were cured at 232°C [32].

28.1.6. UV Cure Powder Coatings

Powder coatings have been developed that are cured by UV. (See Chapter 29 for discussion of UV curing.) This process permits rapid cure at lower temperatures [33,34]. Since the powder is stable in the dark, premature reaction during powder production is minimized. Both free radical– and cationic-cure coatings have been made. Free radical–cure coatings use acrylated epoxy resins (Section 29.2.4) and/or acrylated polyesters or unsaturated maleic polyesters as binders. The effects of annealing before UV cure of methacrylated BPA epoxy resin, acrylated BPA epoxy resin, silylated acrylated BPA epoxy resin, and an acrylated polyester have been investigated. The methacrylated BPA resin films annealed at 110°C were very inflexible. The acrylated BPA epoxy resin provided high MEK rub resistance and good smoothness when annealed at 170°C. The silylated acrylated BPA epoxy resin showed excellent smoothness and impact resistance when annealed at 90°C; however, the MEK rub resistance was lower than that of the other films. The acrylated polyester showed good smoothness when annealed at 190°C and was intermediate in other properties [35].

A UV cure powder coating for fiberboard formulated with an acrylated polyester and an acrylated BPA–polyphenoxy resin has been reported. The coating is sprayed on the fiberboard, which is backed up with a grounded copper plate. After fusing under IR the coating is UV cured [36].

Crystalline unsaturated polyesters with difunctional vinyl ethers have been recommended as a vehicle for UV cure powder coatings that are fused with IR at temperatures as low as 120°C followed by UV [37]. For example, a crystalline polyester from 1,6-hexanediol, fumaric acid, and terephthalic acid is used with the reaction product of HDI with 4-hydroxybutyl vinyl ether [38]. Semi-crystalline low MW polycarbonate diols esterified with methacrylic acid permit storing at 40°C and curing at 100 to 115°C. Synthesis of the resin is discussed in Section 17.9 [39].

Cationic UV cure coatings use BPA epoxy resins as binders. Photoinitiators must be incorporated in the formulation. After application, the powders are fused by passing under infrared lamps and then are cured by passing under UV lamps. Film formation with infrared lamps can be carried out at film temperatures below 120°C, and films UV cure in

1 second or less while still hot. This permits use on heat sensitive substrates such as wood and some plastics. Good leveling is possible because viscosity does not begin to increase until cure is initiated by UV. As with any other UV cure system, pigments can interfere with curing since the pigments may absorb UV, limiting the film thickness that can be cured. Although some pigmented UV cure powder coatings can be cured, the main interest has been for clear coatings.

28.2. BINDERS FOR THERMOPLASTIC POWDER COATINGS

The first powder coatings were thermoplastic coatings, but they now account for less than 10% of the North American market. Thermoplastic powder coatings have several disadvantages compared to thermosetting coatings. They are difficult to pulverize to small particle sizes; thus, they can be applied only in relatively thick films. To have good film properties the binders must have high MWs and/or strong intramolecular hydrogen bonding. As a result, when they are baked even at high temperatures they are viscous and give poor flow and leveling.

Vinyl chloride copolymers (PVC) and, to a more limited extent, polyolefins, polyamides (nylons), fluoropolymers, and thermoplastic polyesters are used as binders. High vinyl chloride–content copolymers (Section 17.1.1) are formulated with stabilizers and a limited amount of plasticizer, often a phthalate ester, so that the T_g is above ambient temperature. The partial crystallinity of PVC may help stabilize the powder against sintering. Vinyl powders are generally applied as quite thick films, 0.2 mm and higher, by fluidized bed application, discussed in Section 28.5.2. Dishwasher racks, handrails, and metal furniture are examples of end uses.

Polyolefin powders give coatings with low water absorption and excellent chemical resistance. They are used to coat lab and food-handling equipment. Nylon 11–nylon 12–based powder coatings exhibit exceptional abrasion and detergent resistance. They are used as antifriction coatings and as coatings for hospital beds, clothes washer drums, and other applications that must withstand frequent cleaning or sterilization and have good toughness and wear resistance. Fluoropolymers such as poly(vinylidene fluoride) and ethylene–chlorotrifluoroethylene copolymers are used for coatings that require exceptional exterior durability, such as aluminum roofing and window frames, and also for resistance to corrosive environments, such as equipment for chemical plants. The application of poly(vinylidene fluoride), nylon 11, and nylon 12 powders by high velocity thermal spray (Section 28.5.2) to aluminum and steel has been studied [40].

Thermoplastic polyester coatings are sometimes made using scrap or recycled poly (ethylene terephthalate). Polyolefin-based powder coatings are used, for example, in carpet backing, but the volume used in metal applications has been limited by generally inferior adhesion. Ethylene–acrylic acid (EAA) and ethylene–methacrylic acid copolymer resins that give coatings with substantially better adhesion [41,42] are available (Section 28.5.2).

28.3. FORMULATION OF THERMOSETTING POWDER COATINGS

The challenge facing formulators is satisfying a combination of conflicting needs: (1) minimization of premature cross-linking during production; (2) stability against sintering during storage; (3) coalescence, degassing, and leveling at the lowest possible baking temperature; and (4) cross-linking at the lowest possible temperature in the least possible time. Furthermore, flow and leveling must be balanced to achieve acceptable appearance and protective properties over the range of expected film thicknesses. Coatings that flow readily before cross-linking can form smooth films, but they may flow away from edges and corners because of the surface tension differential–driven flows that result from the faster heating of the edges (Section 24.3).

If the T_g of a coating is high enough, sintering can be avoided. However, coalescence and leveling at the lowest possible temperature are promoted by low T_g. Short baking times at low temperatures are possible if the resins are highly reactive and if the baking temperature is well above the T_g of the final cross-linked film. However, such compositions may cross-link prematurely during extrusion, and the rapid viscosity increase as the particles fuse in the oven limits the ability of the coating to coalesce and level. Compromises are needed. With current technology, a crude rule of thumb is that the lowest feasible baking temperature is 50°C above the melt extrusion temperature and 70 to 80°C above the T_g of the uncured powder. Thus, minimum baking temperatures are about 125 to 135°C for a powder with a T_g of 55°C.

Several studies have addressed the changes in viscosity during film formation [21,25,43–45]. Nakamichi used a rolling ball viscometer to measure viscosities of powder coatings on a panel during heating [43]. Results for three types of coatings are shown in Figure 28.2. In each case, viscosity is high immediately after fusion of the

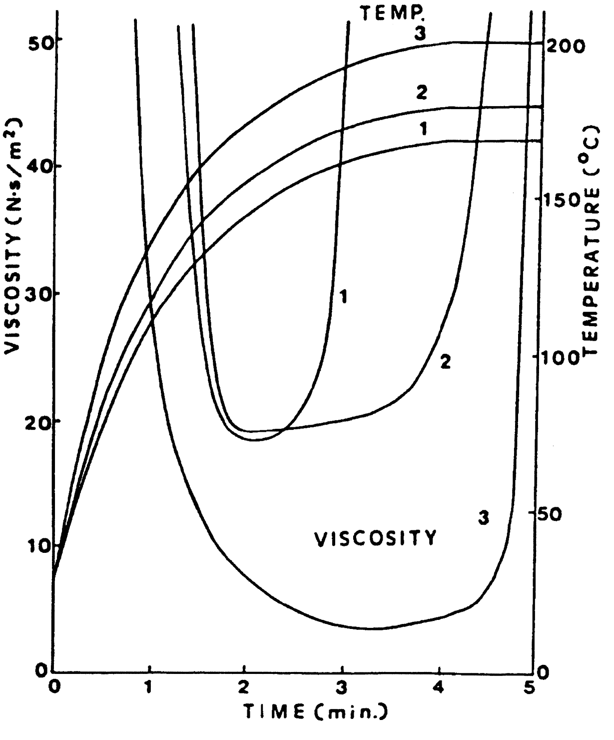


Figure 28.2. Non-isothermal viscosity behavior of powder coatings during film formation as functions of time and panel temperature. 1, Acrylic–dibasic acid type; 2, polyester-blocked isocyanate type; 3, epoxy–dicy type. (From Ref. [43], with permission.)

powder but drops off sharply with increasing temperature. Viscosity levels off as cross-linking reactions begin to increase the MW and then increases rapidly as the coating approaches gelation. Flow is governed by the lowest viscosity attained and by the length of time that the coating stays near that viscosity, called the *flow window*. In Figure 28.2, coating 2 will flow more than coating 1 even though the lowest viscosity is about the same because the reaction of coating 2 is slower and the flow window is longer.

Some authors discuss the temperature dependence of viscosity in terms of Arrhenius type relationships and discuss the activation energies for viscous flow. As indicated in Section 3.4.1, the dependency of viscosity on temperature does not actually follow Arrhenius relationships, but rather is dependent on free volume availability. The most important factor controlling free volume availability is $T - T_g$.

An area that needs more study is the important question of the driving forces for coalescence and leveling. Coalescence of latex particles has been studied extensively (Section 2.3.3), but not coalescence of powder coatings. The main driving force for coalescence may be the reduction of surface area driven by surface tension; in keeping with this hypothesis, it has been suggested that high surface tension promotes coalescence [44]. Low melt viscosity promotes leveling, but the mechanism involved is not well understood. It has been proposed that the driving force for leveling is surface tension as reflected by the Orchard equation (Section 24.2) [44]. The data obtained fit the Orchard equation reasonably well for relatively thin and/or fluid films, but thicker and/or somewhat more viscous films leveled better than predicted. It has been reported that surface tension differential flow can cause cratering of powder coatings and that addition of small amounts of additives such as poly(octyl acrylate) derivatives may overcome this problem [44]. In the same paper it was reported that epoxidized soy fatty acids and hydroabietyl alcohol reduce orange peel but do not affect cratering.

Reference [46] reviews the many factors affecting leveling of powder coatings. Liquid coatings that exhibit Newtonian viscosity level much better than thixotropic coatings. Blocked isocyanate coatings generally exhibit better leveling than other types since the blocking agent (caprolactam or oxime) plasticizes the film, lowering viscosity, until it evaporates. Particle size distribution of the powder affects surface smoothness; the largest particles should be no larger than two-thirds of the proposed film thickness. Film thickness has a major effect; if the film thickness is less than about 2 mil, particle size affects smoothness; above about 5 mil sagging is likely to occur. Surface tension, particularly surface tension differentials across the surface, can have major effects on leveling and cratering. Additives, particularly low-surface-tension polyacrylates, are widely used to promote leveling and reduce cratering. Commonly, these polyacrylates are adsorbed on the surface of silica to ease incorporation into the powder coating. The effectiveness of the additives depends not only on their chemical structure but also on MW and concentration. With one additive, a MW of about 6000 is more effective than a MW approaching 100,000. Concentrations must generally be kept below 1.5% since excess additive gives a tacky surface to the cured film. Higher concentrations of additive are effective if they are also hydroxy-functional so that they cross-link into the binder. The additives also reduce or eliminate cratering.

Severe cratering can be caused by cross contamination of one type of powder with another. Contamination can occur during powder production or application, for example, if a spray booth is inadequately cleaned when switching from one type of powder to another. A medium MW acrylic additive with a broad MW distribution is reported to solve this problem in some cases. In this case, the additive must be added in a premix, not adsorbed on silica, since the high MW fraction tends to adhere tenaciously to the surface of the silica.

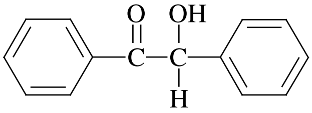
Surface tension also affects wetting of the substrate; if it is too high, poor wetting occurs, which leads to defects such as cratering. On the other hand, low surface tension affects leveling adversely. Furthermore, uneven surface tension on the surface of coatings leads to film defects. The problem is further complicated by the fact that surface tensions decrease with increasing temperature, and the extent of this decrease varies with structure. Surface tensions over a range of temperatures from 138 to 184°C have been studied by asymmetric drop shape analysis (ADSA) of epoxy resin and epoxy resin compounded with five acrylate additives and two polyester-modified methylalkylsiloxane additives. The acrylate additives reduced the high temperature surface tension of the epoxy resin with little difference between the acrylate additives. The siloxane additives decreased the viscosity further than the acrylates, especially siloxanes, in which the alkyl groups were short chain groups compared to those with long chain groups [47].

Dynamic mechanical analysis (DMA) (Section 4.5) is useful for characterizing cured films [22,41]. A DMA study showed that the T_g values of cured films of a series of decorative powder coatings, including a hybrid coating, a TGIC-polyester coating, and a blocked isocyanate–polyester coating, were all in the range 89 to 92°C [22]. The average MWs between cross-links, $\bar{M}_c$ (Section 4.2), for the cured films were in the narrow range 2500 to 3000. It is noteworthy that years of trial and error formulation in different laboratories with such disparate binders led to similar T_g and $\bar{M}_c$ values. On the other hand, a protective epoxy powder coating with a modified dicy cross-linker gave cured films with a T_g of 117°C and an $\bar{M}_c$ of 2200. These studies show that powder coatings are formulated with higher T_g and lower cross-link densities than are liquid coatings for the same end uses. Similar but not identical mechanical properties are attainable.

DMA can be a powerful tool for helping suggest starting points for development work on new binders for powder coatings for similar applications. Two different factors control the T_g of resins: chemical composition and MW. It has been reported that higher MW, more flexible resins are advantageous in that they can have adequate package stability and also flow more easily during baking than a lower MW resin of similar T_g that has more rigid chains [4].

Differential scanning calorimetry (DSC) is a very useful tool for T_g determination and measurement of cure response; its use for studying powder coatings is reviewed in Ref. [48]. It has also been recommended that a combination of modified dynamic load–thermal mechanical analysis, DSC, and TGA be used to determine melting point, onset flow, flow, and gel point [49]. DSC studies showed that pigmentation with TiO_2 had only a weak reinforcing effect and had essentially no effect on T_g, suggesting that pigment–binder interaction is weaker in powder coatings than in liquid coatings [22].

Very commonly, on the order of 0.1 to 1% benzoin (melting point 133 to 134°C) is included in the formulations of many types of powder coatings. It is said to improve the appearance of films and to act as an antipinholing agent and a degassing aid. Other additives with similar melting points are ineffective. The mechanism of benzoin's action has been the subject of much conjecture over the years. One study showed benzoin plasticizes the melt and increases the flow window of polyester–glycoluril formulations, indicating it can improve leveling; high levels (1.4 to 2.4%) were used [21]. Another study has shown that benzoin evaporates from the applied film during the first 6 to 8 minutes of cure and suggests to the authors voids left in the film facilitate degassing [50]. In another study it was proposed that the effect of benzoin is related to its air oxidation to benzil in the gas phase T_g. The study showed further that derivatives of benzoin such as *p*-chlorobenzoin are effective in degassing and lead to less yellowing of films than benzoin [51].



Benzoin

Wrinkle powder coatings have also been formulated with tetramethoxymethylglycoluril (TMMGU) (Section 11.4.3) cross-linkers using amine-blocked catalysts such as 2-dimethylamino-2-methylpropanol–blocked *p*-toluenesulfonic acid [21].

28.3.1. Low Gloss Powder Coatings

Since there is no volatile solvent, the volume of pigment in powders approaches the PVC of the final film. At a PVC near CPVC, the viscosity of the fused powder would be far too high for acceptable leveling. It has been shown that as pigmentation increases above a PVC of about 20, the problems of leveling increases, due to the increase in melt viscosity [31]. Thus, a common method for making low gloss liquid coatings by using a PVC that approaches CPVC (Section 22.1) can be used to only a limited degree in powder coatings, due to the increase in melt viscosity.

Low gloss and semigloss powder coatings have been prepared using approaches other than high PVC [52]. Some reduction in gloss can be achieved by incorporating polyethylene micronized wax with as much inert pigment as flow permits. In hybrid polyester powders, addition of organo-metallic catalysts along with wax is said to reduce gloss somewhat further. Low gloss hybrid polyester coatings are made by using a large excess over the stoichiometric ratio of epoxy resin with a high acid number polyester and curing at high temperatures. By selection of catalysts such as cyclohexylsulfamic acid (cyclamic acid) and stannous methane sulfonate, it has been found that smooth matte finishes can be obtained with tetramethoxymethyl glycoluril (TMMGU) cross-linked polyester coatings [21].

Another approach is to blend two different primary resins or two different cross-linkers with substantially different reactivities or with poor compatibility. For example, combination of a BPA epoxy resin, a carboxy-functional polyester resin, and a carboxy-functional acrylic were used with a BPA–amine adduct or a blend of imidazole and dicyandiamide as curing agent. The epoxy resin and polyester resins were compatible, the polyester and acrylic resins were reported to be relatively compatible, but the epoxy resin and acrylic resin were not compatible [53]. A prepolymer of dimethylolpropionic acid (DMPA), a diisocyanate blocked with caprolactam, and a hydroxy-functional polyester are used in low gloss powder coatings; the COOH groups from the prepolymer are cross-linked with a hydroxyalkylamide, TGIC, or GMA acrylics [17].

Addition of styrene–maleic anhydride copolymer to hybrid powder coatings together with tetrabutylphosphonium bromide catalyst gives a low gloss coating. The reduction in gloss is attributed to the dual cure system of anhydride–epoxy and COOH–epoxy reactions [54].

Low gloss (matte) powder coatings with excellent properties have been made with a bifunctional polyester having both OH and COOH functional groups, a GMA acrylic copolymer, caprolactam-blocked IPDI, and dodecanedioic acid [55]. The gloss can be controlled by the mole fraction of GMA in the acrylic resin. Gloss can be further reduced by mixing a small amount of small particle size fumed SiO_2 with the extruded powder formulation.

Generally speaking, the gloss reduction achieved by the methods described above may vary with film thickness and baking conditions. Thus, care during application is needed to achieve consistent gloss.

28.4. MANUFACTURE OF POWDER COATINGS

Manufacture of powder coatings poses production and quality control issues quite different from those of liquid coating manufacture.

28.4.1. Production

Most powder coatings are manufactured by the same process: premixing, melt extrusion (Figure 28.3), and pulverization (Figure 28.4). All major ingredients must be solids; some liquid additives are used, but they must first be melted into one of the solid components to make a *master batch* which is then granulated. The granulated ingredients, resins, cross-linkers, pigments, and additives are premixed in a batch process. A variety of premixers is used; it is essential that they provide a uniform, intimate mixture of the ingredients. The premix is fed through a hopper to an extruder in a continuous process. The barrel of the extruder is maintained at a temperature moderately above the T_g of the binder. In passing through the extruder, the primary resin and other low melting or low T_g materials are fused, and the other components dispersed in the melt. The extruder operates at a high rate of shear so that it can effectively separate pigment aggregates. The melt can be extruded through a die—either a slot to produce a flat sheet or a series of round orifices to produce *spaghetti*. More commonly, to reduce heat exposure, the melt is extruded through a die with a larger bore to produce *sausage* that is fed between chilled rollers to flatten it into a sheet and cool it.

Extruders have developed into sophisticated and rather expensive pieces of equipment. Two types are commonly used: single screw and twin screw; in both types, a powerful motor turns screws to drive the material through a barrel. The screws and barrel are configured to mix the material thoroughly and apply a high rate of shear. A popular single screw extruder uses a reciprocating action in addition to radial turning of the screw to effect mixing and dispersion. Twin screw extruders use a combination of screw segments and kneading segments. Both types of extruders are capable of excellent dispersion of most pigments. They operate with relatively high viscosity formulations at high shear rates and hence efficiently separate pigment aggregates (Section 21.4.6). However, there is a trade-off between separating pigment aggregates and production rate. Production capacity can be increased by pushing more material through the extruder per unit time. Residence time in the extruder is sometimes reduced to 10 seconds or less, but at some point, pigment dispersion, especially with some organic pigments, begins to suffer. Poor color development and color variability may result (Section 28.4.2). Polymeric dispersants used in pigmented powder coatings can substantially improve

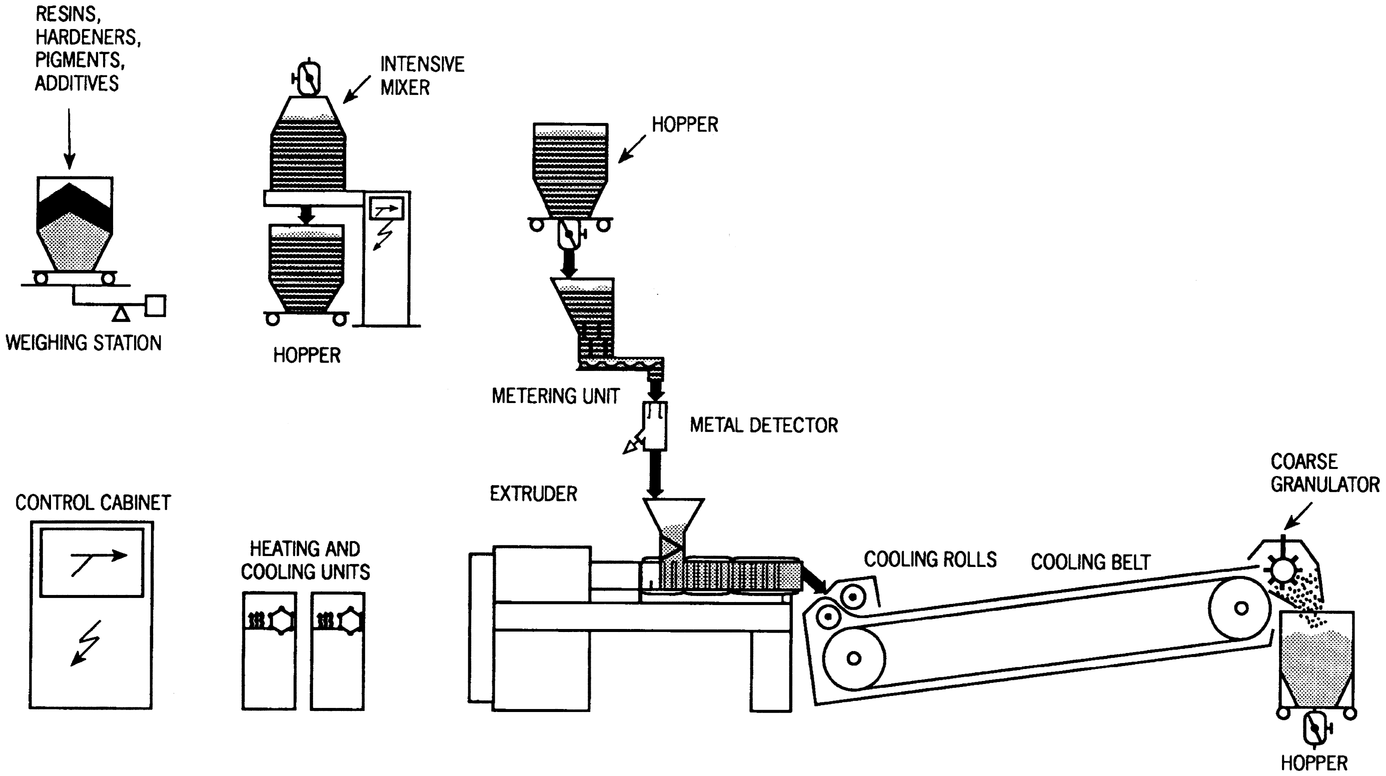


Figure 28.3. Line for premixing, melt extrusion, and granulation. (Adapted from Ref. [7], p. 242, with permission.)

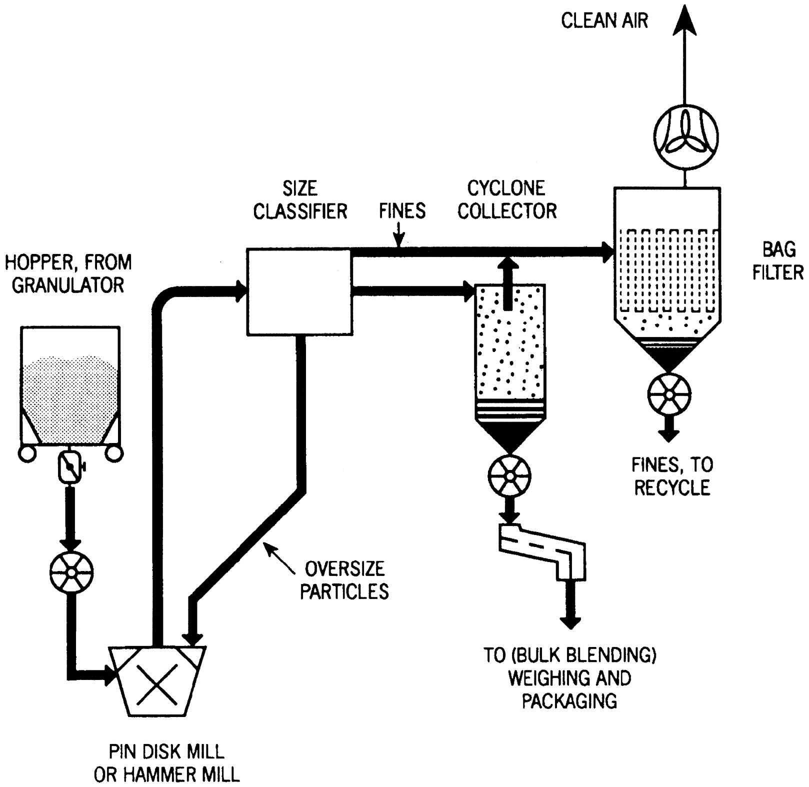


Figure 28.4. *Line for pulverization and classification. (Adapted from Ref. [7], p. 252, with permission.)*

pigment dispersion. For example, carbon black polymeric dispersants give increased jetness and pigment loading can be increased with lower melt viscosity. Similarly, TiO_2 pigmented powder coatings can be made with higher hiding at lower film thickness [56].

The granules are then pulverized. A variety of pulverizers is used. Some, such as *pin disk mills* and *hammer mills*, work on the principle of striking airborne granules with metal dowels or hammers mounted on a rapidly spinning disk. The newer *opposed jet mills* work by causing high velocity collisions of granules with one another. Opposed jet mills perform well for small (<12 μm) diameter powders needed for thin film application. Thermosetting extrudates are brittle and relatively easy to pulverize, but thermoplastics are generally quite tough and can be difficult to pulverize. For thermoplastics it is often necessary either to cool the mill with liquid nitrogen or to grind dry ice along with the granules so that the temperature is kept well below the T_g of the binder to offset the heating effect of the milling process. Even so, thermoplastic powders are generally available only in large particle sizes.

Some mills partially classify (i.e., fractionate) the powder, automatically returning oversize particles for further pulverization. Further size classification, by sieving and/or by an air classifier, is usually needed. The coarse particle fraction is sent back into the mill for further reduction in size. The fines are collected in a bag filter and recycled in the next batch of the same coating to be processed through the extruder. Finally, the classified powder is bulk blended for uniformity, packaged, and shipped to the customer.

A relatively new process uses supercritical CO_2 as a solvent during extrusion [57]. (See Section 23.2.5 for discussion of the use of supercritical CO_2 in other applications.) The powder coating materials and CO_2 are premixed under pressure and then fed to an extruder still under pressure. The extruder can be operated at lower temperatures than conventional processing permits, reducing the risk of premature cross-linking in the extruder, hence use of more reactive formulations. When the compound comes out of the extruder, the CO_2 flashes off, reducing the temperature and pulverizing a major part of the product. The product is classified; only the larger particle size fraction needs to be pulverized in the conventional manner. It is said that the process affords excellent pigment dispersion.

A suspension method of preparing powders has been recommended for making narrow size distribution GMA epoxy-functional acrylic or dicarboxylic acid powders for automotive clear coat powders [58]. An aqueous dispersion of a solution of the resins and cross-linkers is prepared, and the solvent is distilled off. The resulting suspension is centrifuged, washed with water, and dried. The particle size distribution is said to be much narrower than that of powders made by the conventional pulverizing process.

28.4.2. Quality Control

Close quality control of all components is required. In solvent-based coatings, the effect of small differences in MW or MW distribution can be readily adjusted by small variations in the solids of the coating. In powder coatings, there is no solvent in the formula with which to make such adjustments. The only way of maintaining consistent quality of powder coatings is to assure that the raw materials have no significant variation in MW and MW distribution as well as monomer composition.

In processing thermosetting compositions, care must be exercised so that no more than a minimal amount of cross-linking occurs at the elevated temperatures in the extruder. The rate of travel through the extruder should be as rapid as possible consistent with achieving the necessary mixing and dispersion of pigment aggregates. Reprocessing should be minimized. In an extreme case, reprocessed material could gel in the extruder. More commonly, reprocessing can lead to increases in MW, due to some cross-linking reactions, giving powders that show incomplete coalescence or poor leveling after application. Only a limited amount of fines from the micropulverizer should be put in any one batch of coating. If reprocessing is required, it is best to use a limited amount of the batch to be reprocessed in each of several new batches rather than reprocessing the batch alone.

Color matching is often the most troublesome aspect of powder coating production. It is more difficult than with liquid coatings, particularly with reprocessed powders. Generally, one cannot blend batches of powder to achieve satisfactory color matching; it must be done using the appropriate ratio of pigments in the extruder mix. In laboratory processing, it is feasible to make an extruder mix with an estimate of the ratio of colorants needed to match a color. The color of the coating is then checked against a standard. Color can be adjusted to match the standard by mixing into the initial batch the estimated additional quantities of pigments and running the coating through the extruder and pulverizer again. In the laboratory, a third hit might be possible. The number of hits required is kept to a minimum by using computer color matching programs (Section 19.9). In production, however, it is almost essential to have the mix right the first time. Potential problems can be minimized by extruding a small fraction of the production batch and then checking its color. If the color match is satisfactory, processing is continued. If the color needs adjusting, the initial fraction is granulated and returned to the hopper along with the additional amounts of pigments required. Some batch to batch variation of color is inevitable in pigment manufacture. For closely color matched powder coatings, the pigment manufacturer is requested to supply selected batches with narrow tolerance limits. In the case of large production runs, several extruder batches can be blended before pulverizing to average out batch to batch differences. With sufficient care, color reproducibility can be satisfactory for all but the most demanding end uses.

Other important quality control issues are particle size and particle size distribution. These important variables become increasingly critical as particle size is reduced for thin film (<50 μm) applications. Particle size distributions can be measured by passing the powder through a stack of graduated sieves and weighing the fraction retained on each sieve or by a variety of instrumental methods, such as laser diffraction particle sizing [59]. The important effects of particle size and its distribution on the handling and application characteristics of the powder are discussed in Section 28.5.1.

28.5. APPLICATION METHODS

Almost all thin-film powder coatings are applied by *electrostatic spray*. Other application methods, important for protective and thick-film powder coatings, include *fluidized bed, electrostatic fluidized bed*, and *flame spray*. See the general references listed at the end of the chapter for more extensive discussions.

28.5.1. Electrostatic Spray Application

Electrostatic spray (Section 23.2.3) is the major process for applying powder coatings. The powder is fluidized in a hopper and conveyed by a stream of air to an electrostatic spray gun. This gun consists of a tube to carry the airborne powder to an orifice at which an electrode is located. The electrode is connected to a high voltage (40 to 100 kV) low amperage power supply. Electrons emitted by the electrode react with molecules in the air, generating a cloud of ions, called a *corona*, around the orifice. The corona probably consists predominantly of HO^- and, perhaps, O_2^- ions. Powder particles come out of the orifice, pass through the corona, and pick up anions. The object to be coated is electrically grounded. The difference in potential attracts the powder particles to the surface of the part. They are attracted most strongly to areas not already covered, forming a fairly uniform layer of powder even on irregularly shaped objects. During application, size segregation of the particles has been observed, with the finer particles more prevalent near the substrate, presumably due to a combination of the higher charge on small particles and their fitting between larger particles [60]. The particles cling to the surface strongly enough for the object to be conveyed to a baking oven, where the powder particles fuse to a continuous film, flow, and cross-link. Heat can be furnished by either conventional convection ovens or by infrared (IR) lamps; use of induction heating has also been proposed. One comparison of alternative heat sources concluded that IR is least expensive and can be adjusted to provide more rapid cure [61].

The powder particles that do not adhere to the substrate (overspray) are recovered as a dry powder. This powder is usually recycled by blending with virgin powder. A schematic diagram of electrostatic spray application of powder coatings, including recovery of overspray, is given in Figure 28.5. Production spray guns are usually mounted on automated

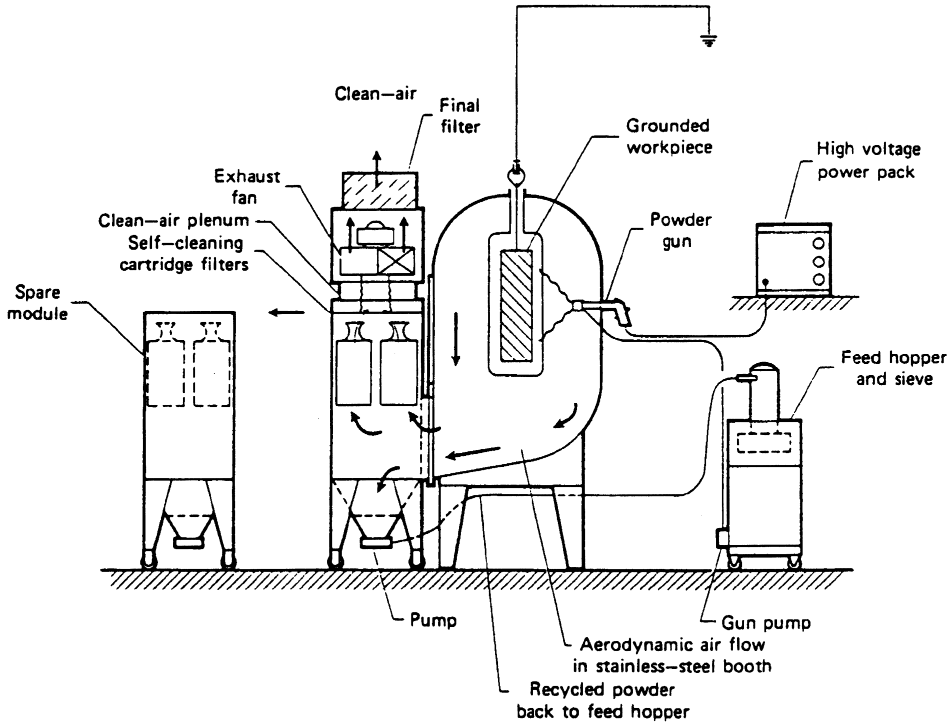


Figure 28.5. *Production equipment for electrostatic spray application of powder coating, showing the collection of overspray powder. (From Ref. [4], p. 18, with permission.)*

reciprocators; such equipment functions smoothly with minimal worker attention as long as a single color and type of powder are being applied.

A limitation of powder coatings is the difficulty of changing colors. When spraying liquid coatings, one can flush the gun with solvent and shift the feed lines to the guns from those feeding one color to those feeding another. In this way, successive objects on a conveyor line can easily be painted different colors. However, if changeover of powder coatings was attempted in this way, there would be sufficient dust in the air in the spray booth for color contamination both on the product and in the overspray collecting units. In production, the operation must be closed down, the booth cleaned, and the overspray collecting units changed to collect the next color. Although spray booths and overspray units have been designed to minimize cleanup time, it is still only economically feasible to make a reasonably long run of one color before shifting over to another color. Many important applications of powder coatings, such as fire extinguisher cases, are single color end uses, or are applications, such as metal furniture, for which runs of single colors are long enough to dedicate a spray booth to each of the limited number of colors involved.

Water-washed spray booths have been suggested to avoid the cost of installing special spray booths for shorter runs [62]. The overspray collected in the water is dispersed by a low foaming nonionic surfactant and flocculated with a melamine resin (Section 23.2.7).

In electrostatic spray, the charged powder particles wrap around the grounded object to a degree and coat exposed surfaces not in direct line with the spray gun. Nevertheless, in production, it is often desirable to use spray guns on both sides of the object, making it possible to coat uniformly such intricately shaped objects as automobile wheels and tube-and-wire metal furniture. The process is strongly affected by the Faraday cage effect (Section 23.2.3). As a result, it is difficult to get full coverage of areas such as interior corners of steel cabinets; the interior of pipes can only be coated with a spray gun inside the pipe.

Film thickness increases with increasing voltage and decreasing distance between the spray gun and the product being coated. Larger particle size powders tend to give increased film thickness. One can apply thicker coatings by heating the object to be coated before applying the powder. However, film thickness is limited by the fact that once a certain film thickness has been reached, the powder coating acts as an insulator and does not attract further particles. The insulating properties of the powder coating mean that defective coated parts generally cannot be recoated and must be stripped to be recoated. Coating over other coatings and over plastics frequently requires application of a conductive primer coating.

There is considerable room for improvement of the process and need for a better understanding of how it works. For example, there is no satisfactory physical explanation for why the powder clings to the object as well as it does [63]. One opportunity for improvement is to increase efficiency of charging by the corona of the electrostatic gun. It is estimated that only about 0.5% of the anions in the corona become attached to powder particles [64]. The rest are attracted to the nearest grounded object, where they at best do no good and at worst may reduce deposition efficiency and increase the Faraday cage effect [65]. Research on ways to improve this situation is under way; some experts think that if charging efficiency could be raised to 10%, deposition efficiency might become high enough to reduce overspray sufficiently that it would no longer be necessary to collect it.

Particle size and distribution have a critical effect on powder coating. The range of particle sizes must be limited; as a rule of thumb, the predominant particle diameter should be somewhat less than the intended film thickness, and the largest particles should be no more than twice the film thickness. Figure 28.6 shows a typical distribution, presumably for a powder coating to be applied at a thickness of around 50 μm [66].

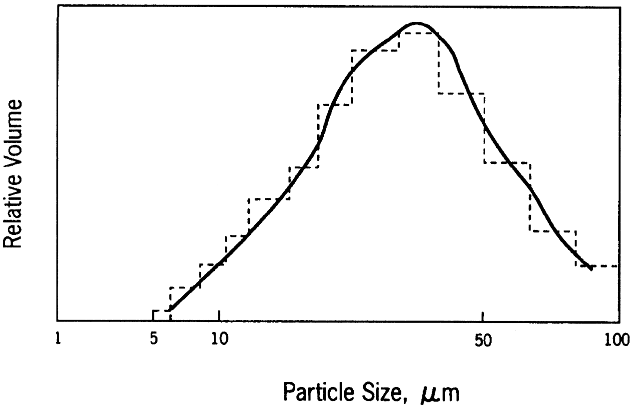


Figure 28.6. Particle size distribution of a typical white epoxy powder coating. (From Ref. [66], with permission.)

Very fine particles do not flow properly in hoppers and feed lines. In general, only 6 to 8 wt% of the particles are smaller than 10 μm in diameter. Small particles have a higher surface area/volume ratio and hence acquire a higher charge/mass ratio as they pass through the corona of an electrostatic gun. After charging, the particles are affected by three forces: the electrostatic field, air movements, and gravity. Theoretical calculations predict that gravity should be the predominant effect on very large particles and that air flow should predominate for the very small ones [67]. These theoretical predictions were confirmed by particle size analysis of overspray; with a typical powder, the overspray was rich in particle sizes below 20 and above 60 μm, indicating that the intermediate sizes were transferred most effectively. Small particles probably penetrate best into Faraday cages. Large particles flow better through the application system and retain their charge longer and therefore cling to the object better between application and baking. The dusts of very small (<1 μm) particles may present a toxic hazard if they are inhaled. On balance, it appears that particle sizes concentrated in the range 20 to 60 μm are best for powder coatings that are to be applied at film thicknesses of 30 to 60 μm.

Automotive clear coats with maximum smoothness are reported to result with fine particle size powders having a narrower size distribution [58,68]. However, application of such powders (averaging 10 μm) presents problems. Modification of application equipment has been reported to solve many of the problems [68]. Constant feeding of powder was accomplished by controlling temperature and humidity in the powder feed system and incorporating an agitator in the system to aid fluidization. Spitting of aggregates of particles was minimized by redesigning the gun nozzle. Transfer efficiency was improved by increasing charging efficiency, minimizing free ions, and adding an external electrode of intermediate charge to increase the electric field intensity near the part being coated.

Another means of applying electrostatic powder employs *triboelectric charging* of the powder particles. The particles are charged by the friction generated from streaming through a poly(tetrafluoroethylene) spray tube in the gun instead of a high voltage source generating a corona at the gun orifice. The mechanism is analogous to the buildup of a static charge on a comb when combing your hair. Since there is not the large differential in charge between the gun and the grounded work being sprayed, no significant magnetic field lines are established and Faraday cage buildup is minimal, facilitating coating hollows in irregularly shaped objects. Smoother coatings are obtained. On the other hand, throughput is slower and stray air currents can more easily deflect the particles between the gun and the object being coated. Triboelectric charging is widely used in Europe and is gaining popularity in North America. Guns are available that combine triboelectric and corona charging.

28.5.2. Other Application Methods

Fluidized beds are the oldest method of applying powder coatings. The equipment consists of a dip tank, the bottom of which is a porous plate. Air is forced through the porous plate and acts to suspend the powder in the dip tank in air. The flow behavior of air suspensions of powders resembles that of fluids, hence the term *fluidized bed*. The object to be coated is hung from a conveyor and heated in an oven to a temperature well above the T_g of the powder. The conveyor then carries the part into the fluidized bed tank. Powder particles fuse onto the surface of the object. As the thickness of fused particles builds up, the coating becomes a thermal insulating layer, so that the temperature at the surface of the coating becomes lower, finally reaching the stage at which further particles do not stick to the surface. The last particles that attach to the coated surface are not fused completely, so the conveyor must then carry the object into another oven, where the fusion is completed. Film thickness depends on the temperature to which the part is preheated and on the T_g of the powder. Thin films cannot be applied in this fashion. Most commonly, the method is used for applying thermoplastic coating materials.

Electrostatic fluidized beds are similar, but electrodes are added to generate ions in the air before the object passes through the powder. The object to be coated is grounded. The process is illustrated schematically in Figure 28.7. Powder is attracted to the object by electrostatic force, as in electrostatic spray. The object can be heated when thick films are desired, but heating is not necessary. This method is used to apply thermoplastic and some thermosetting powders: for example, electrical insulation coatings. There is no overspray and powder losses are minimal; color change-over is also easier. Thinner films can be applied compared to conventional fluidized bed coating. However, very thin films are hard to apply, there is a strong Faraday cage effect, and it is difficult to coat large objects uniformly.

Powder coil coating is also practiced. In some cases, the powder is applied to the coil strip by electrostatic spray [34]. In another process, an electrostatically charged strip is passed through a cloud of powder, then to the oven for fusing [70]. The method makes possible coating of perforated or preembossed metal and has the advantage of no VOC emissions. Capital cost is said to be lower, but line speeds are somewhat slower than with conventional coil coating.

Flame spray is another technology for applying thermoplastic powder coatings [41,42,71]. In a flame spray gun, the powder is propelled through a flame, remaining there just long enough to melt. The molten powder particles are then directed at the

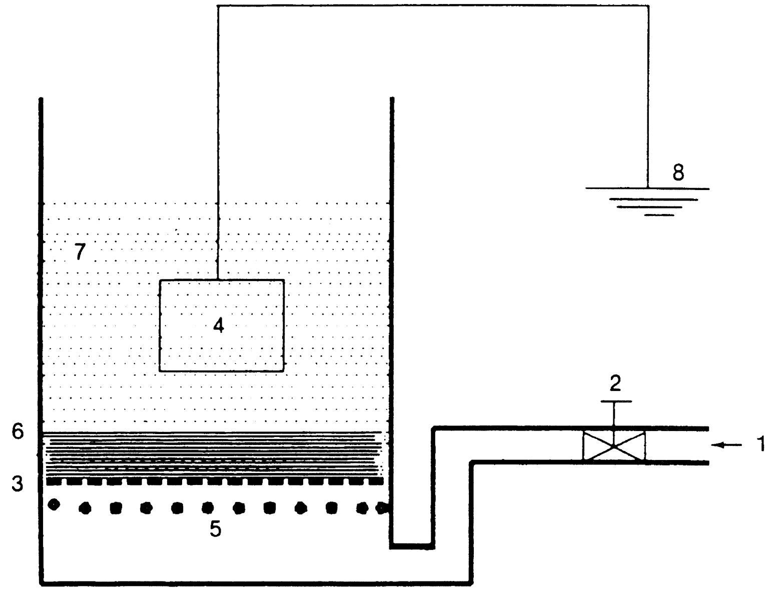


Figure 28.7. *Electrostatic fluidized bed coating apparatus. 1, Air inlet; 2, air regulator; 3, porous membrane; 4, object to be coated; 5, electrodes; 6, fluidized powder; 7, cloud of charged powder; 8, ground. (From Ref. [69], with permission.)*

object to be coated. The flame heats and melts the polymer and heats the substrate above the melting temperature of the polymer so that the coating can flow into irregularities in the surface to provide an anchor for adhesion. The combination of flame temperature (on the order of 800°C), residence time in the flame (small fractions of a second), T_g of the coating, particle size distribution, and substrate temperature must be carefully balanced. Particle size distribution must be fairly narrow; very small particles pyrolyze at 800°C before larger particles can melt.

Poly(vinylidene fluoride), ethylene–chlorotrifluoroethylene, perfluoroalkoxyalkane, and fluorinated perfluoroethylenepropylene have been applied by flame spray to steel and showed excellent salt spray corrosion resistance. The chemical resistance of perfluoroalkoxy alkane polymer was particularly outstanding [72].

In contrast to other methods of application, flame spray permits application in the field, not just in a factory. Examples of commercial or experimental applications include drum linings, metal light poles, bridge rails, concrete slabs, and grain railcars, among others. Since the application is not electrostatic, nonconductive substrates such as concrete, wood, and plastics can be coated. The coating need not be baked, so substrates that will withstand just the temperature from the impinging spray can be coated by this method. Since the coatings are thermoplastic and are not applied electrostatically, it is possible to use powder to repair damaged areas of coating, which is generally not possible with other powder coating methods.

Disadvantages of flame spray application include limitations on the service temperatures of objects coated with thermoplastic coatings (75°C in the case of EAA-based coatings) (Section 28.2) and the need for careful control of application variables [41]. Overheating the polymer can lead to thermal degradation and hence to poor coating performance, with no visual indication of degradation until the polymer begins to pyrolyze. Adhesion to steel is also affected by application variables [42]. The carboxylic acid groups promote adhesion, but coatings are subject to cathodic delamination (disbonding) because of the acid groups.

28.6. ADVANTAGES AND LIMITATIONS OF POWDER COATINGS

In this section, advantages and limitations of powder coatings are compared to solventborne or waterborne coatings. The primary advantages may be summarized as follows: VOC emissions are low; flammability and toxicity hazards are substantially reduced; thick films of 100 to 500 μm can be applied in a single operation; and energy consumption can be reduced. At first blush, the low energy requirements of powder coatings are surprising, since their baking temperatures are generally higher than those of most solventborne baked coatings. However, with little or no volatiles being emitted into the oven, the air in the oven can be recirculated with almost no make-up air. In contrast, with solventborne coatings the solvent concentration in the air in the oven must always be kept well below the lower explosive limit, resulting in the need to heat a substantial volume of make-up air. Also, air flow through the spray booth can be lower with powder coatings because it is no longer necessary to keep the solvent concentration in the air below a safe concentration for people to be in the spray booth. In winter, the cost of heating air flowing at a high rate through a spray booth can be high. Since there is no drying or flash off time, parts can be hung closer to one another on the conveyor. There is no sagging or dripping.

An important further factor reducing the overall cost of powder coatings is that the overspray powder can be collected in filter bags from the spray booth and reused. This not only increases paint utilization, but also eliminates the cost and difficulty of disposing of the sludge obtained from the water wash spray booths used with liquid paints.

Important limitations of powder coatings are:

1. *Explosive hazards*. Whereas the absence of solvents eliminates the flammability problem, suspensions of powder in air can explode. Consequently, manufacturing and application facilities must be designed to avoid powder explosions. With good engineering and good housekeeping, the processes can be operated safely. Triboelectric charge systems are less likely to initiate explosions than corona charge spray guns, which can spark if brought near a grounded conductor.

2. *Inability to coat large or heat sensitive substrates*. With electrostatic spray and fluidized bed methods, only baked applications can be considered, and since the baking temperature must be fairly high, only substrates that can withstand the baking cycle can be used. This limits applications of conventional thermosetting powder coatings almost entirely to metal substrates. UV cure powder coatings can be used on some heat sensitive substrates, and as noted in Section 28.5.2, flame spray can be used for some other applications.

3. *Appearance limitations*. Broadly speaking, powder coatings can have good appearance, but some of the appearance effects attainable with liquid coatings are difficult or impossible to match with powders. Color matching is more difficult than with liquid coatings, and color reproducibility can also be difficult. Since there is no solvent loss, there is not the degree of shrinking during film formation required for metallic coatings to show the color flop typical of automotive coatings. One can make powder coatings that contain aluminum flake pigments; they sparkle but display little color flop. As discussed in Section 28.3, a compromise between leveling and edge coverage is inevitable. The usual result is that the formulator must settle for a film with some orange peel to get acceptable edge coverage. The thinner the film, the more difficult the problem becomes. As also discussed in Section 28.3, there are problems making and controlling gloss of low and medium gloss powder coatings.

Achieving satisfactory appearance is a major obstacle to development of powder clear coats for autos and trucks [73]. Uniform film thickness must be applied to the entire car body because leveling of powder coatings is quite sensitive to variations in film thickness. This requires close control of powder flow rates; which is an engineering challenge. Films thinner than 1.0 mil are difficult to achieve because of pinholing. The entire operation, including reclamation of overspray, must be scrupulously clean to avoid dirt particles, which are especially noticeable in clear coatings. It is difficult to coat objects with outside sharp corners and inside corners tend to get low film thickness, due to the Faraday cage effect.

4. *Materials limitations*. Since all major components must be solids, a smaller range of raw materials is available to the formulator. Furthermore, it is not possible to make thermosetting powder coatings for which the T_g of the final film is low. This limits the range of mechanical properties that can be formulated into a powder coating.

5. *Limits of production flexibility*. Economics of production and application suffer badly whenever frequent color changes are needed. Cleanup between color changes is time consuming. Powder coatings are best suited to reasonably long production runs of

the same type and color of powder. Water-washed spray booths permit shorter runs, but the advantage of recycling overspray is lost. New engineering designs have reduced the problem of color changes.

Some of the limitations of powder coatings can be overcome by making aqueous dispersions (slurries) of powders. This eliminates the potential for powder explosions, broadens the range of application methods, and reduces storage stability problems. The T_g of the powder no longer needs to be high to avoid sintering, and therefore more flexible coatings can be formulated and lower baking temperatures can be utilized. Settling problems can be minimized and appearance improved by using smaller particle size, less than 10 μm, in the slurries. However, new challenges are added. Aqueous dispersions must be stabilized without undue sacrifice of properties due to the presence of surfactant, and spray rheology must be controlled. Aqueous powder dispersions are being used in automotive clear coats.

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29

Radiation Cure Coatings

Radiation cure coatings cross-link by reactions initiated by radiation, rather than heat. Such coatings have the potential advantage of being indefinitely stable when stored in the absence of radiation; following application, cross-linking occurs rapidly at ambient temperature on exposure to radiation. Rapid cure at ambient temperature is particularly significant for heat sensitive substrates, including paper, some plastics, and wood. See Section 28.1.6 for a discussion of UV cure powder coatings.

Two classes of radiation cure coatings are (1) UV cure coatings, in which the initial step is excitation of a photoinitiator (or photosensitizer) by absorption of photons of UV–visible electromagnetic radiation, and (2) EB (electron beam) cure coatings, in which the initial step is ionization and excitation of the coating resins by high energy electrons. Cross-linking is initiated by reactive intermediates that are generated from the photo-excited photoinitiator in UV curing and from excited and ionized resins in EB curing. Infrared and microwave radiation are also used to cure coatings, but these systems are not included here, since the radiation is converted to heat, which initiates thermal curing.

While the physical volume of radiation cure materials used in the United States is relatively small, perhaps 50,000 metric tons per year, their economic importance is disproportionate to their volume. They are essential to the production of computer chips, optical fibers, printed circuit boards, and printing plates, and they are used in a variety of other economically important applications, including dental and medical applications.

29.1. UV CURING

Two classes of polymerization reactions are used in UV curing: free radical and cation-initiated chain-growth polymerization. Although there have been attempts to use

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Organic Coatings: Science and Technology, Third Edition, by Zeno W. Wicks, Jr., Frank N. Jones, S. Peter Pappas, and Douglas A. Wicks

photoreactions in which the radiation leads to generation of a reactive functional group, this approach is not useful for coatings. In such reactions, each photon absorbed can effect only one cross-linking reaction. In chain reactions, absorption of a single photon can lead to the formation of many cross-links.

A key requirement for UV curing is a UV source that produces high intensity UV radiation at low cost without generating excessive infrared radiation. Major radiation sources in commercial use are medium pressure mercury vapor lamps. Such *electrode lamps* are tubes up to 2 m long; power outputs of 80 W cm^{-1} are in wide use; and lamps with outputs up to 325 W cm^{-1} are available. The radiation has continuous wavelength distribution with major peaks at 254, 313, 366, and 405 nm, among others. Visible radiation and a minor but not insignificant amount of infrared radiation that causes some heating is also emitted. The wavelength distribution of radiation from a medium pressure mercury vapor electrode lamp is shown in Figure 29.1.

Radiation is emitted in all directions around tubular lamps, and its intensity drops off with the square of the distance from the source. To increase the efficiency of absorption, lamps are mounted in an elliptical reflector with a focal length such that the maximum intensity of radiation is focused at the distance between the lamp and the coated surface being cured. A limitation of UV curing is that the distance between the lamp and the coating on various parts of the object being coated must be fairly uniform. Hence, UV curing is most easily applicable to coating flat sheets or webs that can be moved under the UV lamps or cylindrical objects that can be rotated under or in front of the lamps. Since thermal energy is also produced, the lamp housing must be water and air cooled. UV radiation is hazardous and can lead to severe burns. **It is essential to avoid exposure of eyes to the radiation**. The lamps are housed in enclosures; when the enclosure is opened, the current to the lamps is turned off automatically. Depending on the radiation source, a greater or lesser amount of ozone is generated. Since ozone is toxic, the UV unit must be ventilated. (These and other safety considerations in radiation curing are reviewed in Ref. [1].)

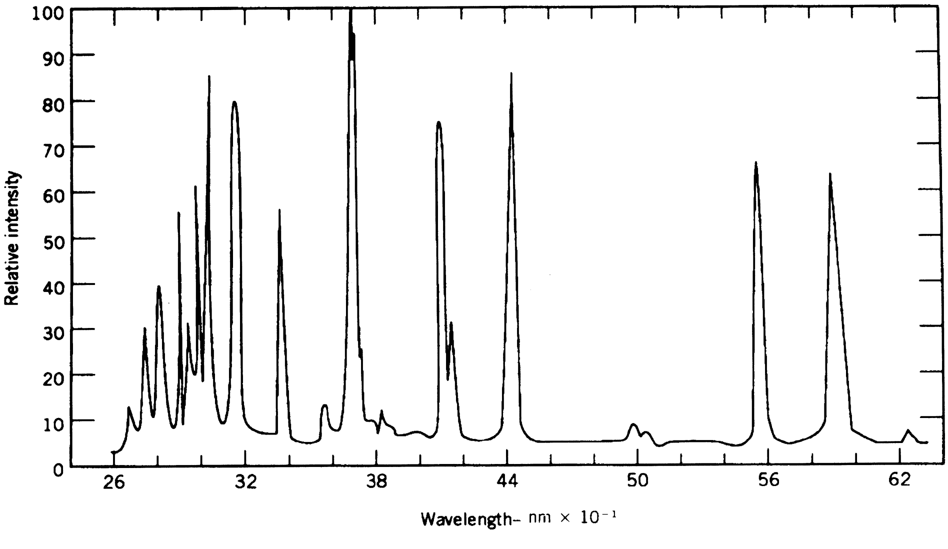


Figure 29.1. Energy distribution of radiation from a medium pressure mercury vapor lamp. (From U.S. patent 3,650,699, as cited in Ref. [2], with permission.)

In some cases, there are advantages of using other wavelength distributions, especially those with increased fractions of radiation in the very near UV–visible region. Changes in distribution can be made by doping the lamp with traces of other elements besides mercury or by having fluorescent coatings on the lamp tube that absorb short UV and emit longer UV radiation.

Electrodeless lamps, powered by microwaves, also enjoy substantial commercial use. Electrodeless lamps are more suitable for doping, since the lifetime of lamp electrodes is generally reduced by dopants. Electrodeless lamps have the further advantage of essentially instantaneous start-up and restart. On the other hand, electrodeless lamps are more expensive. (For further discussion of UV sources, see Ref. [2].) The utilization of DC power supplies for both electrode and electrodeless lamps has been shown to result in constant radiation, which is reported to enhance the efficiency of polymerization relative to pulsed radiation [3].

Excimer lamps emit very narrow bands of UV [4,5]. They use silent electrical discharge through two quartz tubes and an enclosed gas volume. Electronically activated molecules are produced in the gas phase and decompose within nanoseconds to produce photons of high selectivity. The narrowness of distribution is comparable to that of lasers, but in contrast to laser sources, the radiation is incoherent and can therefore be used for large area applications. Different excimer lamps are available or in commercial development that have principal emissions at 172, 222, 308, and 351 nm. The high intensity of very narrow wavelength distribution can provide rapid cures. The 172 nm excimer lamps are reported to activate acrylates directly [5]. Xenon chloride excimer lamps that produce energy at 308 nm have been shown to effect UV cure in shorter times than do mercury vapor lamps at equal photoinitiator concentration or at equal speed with lower initiator concentration [6]. The 308 nm excimer lamps are reported to be particularly effective for cationic curing using triarylsulfonium salt photoinitiators that absorb in that region [7].

For initiation via any lamp source, there must be absorption of radiation by the photoinitiator (or, as discussed later, by some substance that leads to the generation of an initiator). The fraction of radiation absorbed within a coating film, I_A/I_0, is related to the molar absorptivity ε, concentration of photoinitiator C, and optical path length of radiation in the film X. Assuming that no other absorber is present and neglecting surface reflection, the fraction of radiation of a given wavelength absorbed is expressed as

$$\frac{I_A}{I_0} = 1 - 10^{\varepsilon CX} \tag{29.1}$$

The molar absorptivity ε can be concentration dependent, so the range of concentration over which the equation is valid may be limited. Molar absorptivity varies with wavelength, so the fraction of radiation absorbed also varies with wavelength. Also, the intensity of radiation from the source varies as a function of wavelength. The total number of photons absorbed per unit time depends on the combination of these factors. When a photoinitiator absorbs a photon, it is raised to an excited state, which leads to generation of an initiating species. But there are also other possible fates of the excited state photoinitiator. It may emit energy of a longer wavelength; that is, it may fluoresce or phosphoresce. It may be quenched by some component of the coating or by oxygen. It may undergo other reactions besides those that lead to initiator generation. The efficiency of generation of initiating species is an important factor in the selection of a photoinitiator.

Whereas most photoinitiators absorb a single photon, efficient two-photon absorbing photoinitiators have been developed which can generate free radical [8] or cationic [9] initiator species. Such photoinitiators are particularly useful for three-dimensional applications, including three-dimensional microfabrication and optical data storage systems.

The rate of polymerization reactions is related to the concentration of initiating radicals or ions. It would therefore seem that the higher the initiator concentration, the faster the curing. As one increases from very low concentrations to somewhat higher concentrations, the rate of cure increases. However, there is an optimum concentration. The rate of cure in the lower part of the film decreases above this concentration. If the concentration is high enough, such a large fraction of the radiation is absorbed in the upper few micrometers of the film that little radiation reaches the lower layers. Since the half-life of free radicals is short, they must be generated within a few nanometers of the depth in the film where they are to initiate polymerization. Although the half-life of the acid species in cationic cure coatings is substantially longer, migration may be limited by diffusional constraints as polymerization and cross-linking proceed.

Optimum photoinitiator concentration is dependent on film thickness: The greater the film thickness, the lower the optimum concentration. Lower concentration is favorable from the standpoint of cost, since the photoinitiator is generally an expensive component. However, comparing the cure speeds of films of different thicknesses, each containing the optimum concentration of photoinitiator for its thickness, the time required to cure a thick film is longer than to cure a thin film. This follows since less radiation is absorbed in any volume element with increasing film thickness. The problem is further exacerbated when surface cure is oxygen inhibited, as is the case with free radical polymerization. (Oxygen inhibition is discussed in Section 29.2.3.) In general, one should determine the concentration of photoinitiator just sufficient to give the required extent of cure at the surface; this concentration gives the maximum rate of cure for that film thickness of that system at the lowest possible cost.

The problem of achieving both surface and through cure can be ameliorated by using a photoinitiator or a mixture of photoinitiators having two absorption maximums with distinctly different molar absorptivities near different emission bands of the UV source. The emission band that is highly absorbed by the photoinitiator(s) is absorbed more strongly near the surface, and less UV is available for absorption in the lower layers. This band is most important for counteracting oxygen inhibition (Section 29.2.3) but does not contribute substantially to through cure. The weaker absorption of a second emission band is more uniform throughout the film to provide through cure.

Another factor that affects absorption of UV by a photoinitiator is the presence of competitive absorbers or materials that scatter UV radiation. In designing vehicles for UV cure systems, it is desirable to minimize their absorption of UV in the range needed for excitation of the photoinitiator. Pigments can cause problems by absorbing and/or scattering UV radiation; the effects of pigmentation are discussed in Section 29.4.

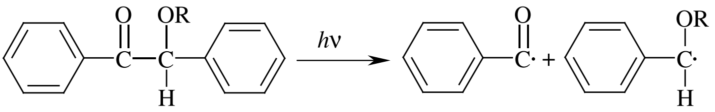
Although film thickness is one variable that affects path length, it is not the only one. If the same coating is applied over a black substrate and over a highly reflective metal substrate, the rate of cure over the metal substrate is close to twice as fast as over the black substrate. UV radiation that passes through the film to the black substrate is absorbed, but that reaching a smooth metal substrate is reflected and passes through the film twice; the path length is twice the film thickness, so there is almost twice the opportunity for absorption.

29.2. FREE RADICAL INITIATED UV CURE

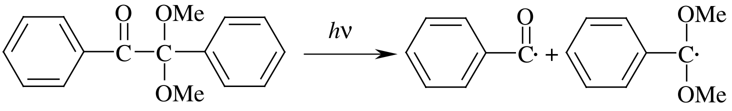
In coatings cured by free radical initiated UV, free radicals are photogenerated and initiate polymerization by adding to vinyl double bonds, primarily acrylates. Two classes of photoinitiators are used: those that undergo unimolecular bond cleavage and those that undergo bimolecular hydrogen abstraction from some other molecule.

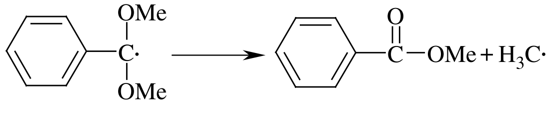
29.2.1. Unimolecular Photoinitiators

A range of unimolecular photoinitiators has been studied [10]. The first ones used on a large scale commercially were ethers of benzoin. Benzoin ethers undergo cleavage to form benzoyl and benzyl ether radicals:

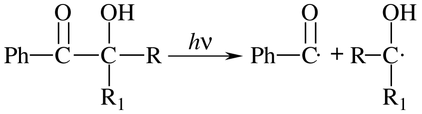


Both these radicals can initiate polymerization of acrylate monomers [11]. There is doubt whether the benzyl ether radical can initiate the polymerization of styrene [10]. The package stability of UV cure coatings containing such benzoin ethers tends to be limited. Apparently, this is due to the ease of abstraction of the hydrogen on the benzyl ether carbon. Any organic material contains traces of hydroperoxides that slowly decompose. The resulting radicals can abstract the benzylic hydrogen, leading to initiation of polymerization and hence poor package stability. Package stability is improved if the benzylic carbon is fully substituted. Accordingly, the ketal, 2,2-dimethoxy-2-phenylacetophenone, is an effective photoinitiator with good package stability. Photocleavage produces benzoyl and dimethoxybenzyl radicals. The latter is a sluggish initiator; however, it can undergo further cleavage to the highly reactive methyl radical; the extent of this cleavage increases with increasing temperature.



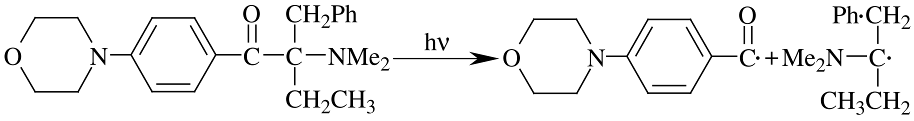


2,2-Dialkyl-2-hydroxyacetophenones (α-hydroxyacetophenones) are also commercially important photoinitiators with good package stability, including 2-hydroxy-2-methyl-1-propan-1-one (HMMP) shown below where R═R_1═CH_3, and 1 benzoylcyclohexanol, where R and R_1 form a cyclohexane ring. These photoinitiators tend to give less yellowing than do phenyl-substituted acetophenones, including benzoin ethers as well as the ketal above, probably because benzylic radicals are not generated by photocleavage.

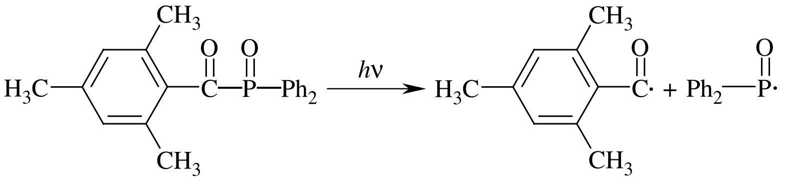


$$\mathrm{Ph{-}}\overset{\displaystyle O}{\overset{\|}{C}}\mathrm{-}\underset{\displaystyle R_1}{\underset{|}{\overset{\displaystyle OH}{\overset{|}{C}}}}\mathrm{-R} \xrightarrow{h\nu} \mathrm{Ph{-}}\overset{\displaystyle O}{\overset{\|}{C}}\cdot + \mathrm{R{-}}\underset{\displaystyle R_1}{\underset{|}{\overset{\displaystyle OH}{\overset{|}{C}}}}\cdot$$

All these photoinitiators have an acetophenone chromophore, the absorptivity of which is enhanced by electron donating substituents on the benzoyl ring. This is exemplified by the morpholino-substituted photoinitiator 2-dimethylamino-2-benzyl-1-(4-morpholinophenyl)-butan-1-one, which is recommended for pigmented coatings [12,13]. Yellowing can be a problem in clear coatings.



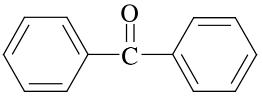
Acylphosphine oxides are another class of unimolecular photoinitiators. Several acylphosphine oxides are available: for example, diphenyl-2,4,5-trimethylbenzoylphosphine oxide. Irradiation generates the corresponding benzoyl and phosphinyl radicals. Acylphosphine oxides tend to be nonyellowing and give good package stability.



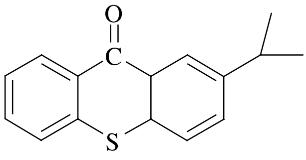
Bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentylphosphine oxide (BAPO) on irradiation is reported to generate four radicals that can initiate polymerization [14]. The strong absorption of near UV–visible radiation makes possible curing of relatively thick films of white pigmented coatings. Although BAPO is yellow, photocleavage results in reduced absorptivity (bleaching), so BAPO can be used in white coatings. The absorption spectrum can be broadened by using a blend with HMMP, providing combined surface and through cure at lower cost.

29.2.2. Bimolecular Photoinitiators

Photoexcited benzophenone and related diarylketones, such as xanthone and thioxanthones, do not cleave to give free radicals, but can abstract hydrogens from a hydrogen donor to yield free radicals that initiate polymerization. Thioxanthones such as 2-isopropylthioxanthone are used when their high absorption in the very near UV is desirable to permit absorption in the presence of pigments or dyes that absorb UV strongly in the longer wavelength UV range.

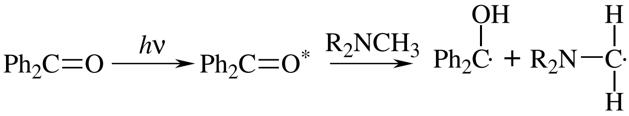


Benzophenone



2-Isopropylthioxanthone

Widely used hydrogen donors are tertiary amines with hydrogens on α carbon atoms such as 2-(dimethylamino)ethanol (DMAE) and in printing inks, methyl *p*-(dimethylamino)benzoate. It has been shown that the accompanying ketyl free radical does not initiate polymerization. Use of *N*-phenylphthalimide as a photosensitizer with isopropylthioxanthone and *N*-methyl-*N*,*N*-diethanolamine accelerates photocuring of acrylates at least twofold [15]:



$$Ph_2C{=}O \xrightarrow{h\nu} Ph_2C{=}O^* \xrightarrow{R_2NCH_3} Ph_2\overset{OH}{\overset{|}{C}}\cdot + R_2N{-}\overset{H}{\underset{H}{C}}\cdot$$

An advantage of bimolecular initiators with amine co-initiators is reduced oxygen inhibition, discussed in the next section. A disadvantage is that excited states of these initiators are generally longer lived than those of unimolecular photoinitiators and therefore more readily quenched by oxygen as well as by vinyl monomers with lower triplet energies.

N-Alkylmaleimides have been shown to be photoinitiators for the polymerization of acrylates. The effectiveness is enhanced by using benzophenone as a photosensitizer and an amine. For example, a combination of *N*-methylmaleimide, benzophenone, and methyldiethanolamine in 1,6-hexanediol diacrylate gave essentially the same exotherm and peak time as 2,2-dimethoxy-2-phenylacetophenone, and substantially higher than benzophenone and amine. However, the maleimides are toxic [16].

29.2.3. Oxygen Inhibition

Oxygen inhibits free radical polymerizations. In coatings, this inhibition is particularly troublesome, since coating films have such a high ratio of surface area, where oxygen exposure is high, to total volume. Oxygen reacts with the terminal free radical on a propagating molecule to form a peroxy free radical. The peroxy free radical does not readily add to another monomer molecule; thus, the growth of the chain is terminated. The terminal radical from methyl methacrylate has been shown to have a rate constant for reaction with oxygen that is 10^6 times that for reaction with another monomer molecule. Furthermore, the excited states of certain photoinitiators are quenched by oxygen, thereby reducing the efficiency of generation of free radicals.

Several approaches are available to minimize this problem. Curing can be done in an inert atmosphere, but this is relatively expensive. The most economical inert atmosphere approach is to use a CO_2 atmosphere. CO_2 is relatively inexpensive and its high density makes it easier to contain. It permits reduction in photoinitiator concentration and use of slower curing reactants [17].

High intensity UV sources minimize but do not eliminate the problem with fast curing systems. In effect, free radicals can be generated so rapidly that their high concentration can deplete the oxygen at the film surface, permitting other radicals to carry on the polymerization before more oxygen diffuses to the surface.

A formulating solution is to incorporate paraffin wax in the coating. As the coating is applied and cured, a layer of wax comes to the surface of the coating, shielding the surface from oxygen. Although effective, the residual wax detracts from the appearance of the film and makes recoating difficult.

Another common approach is to add a chain transfer agent, including tertiary amines, having α-CH groups; alkyl ethers, having α-CH groups; and thiols. Although peroxy free radicals are poor initiators, they readily abstract H atoms from such chain transfer agents, and the resulting α-amino, α-ether, or thiyl radical can initiate a new growing polymer chain.

Free radicals on carbon atoms alpha to amines and ethers also react rapidly with oxygen. Thus, amines and ethers not only act as chain transfer agents but also serve to deplete oxygen levels. Accordingly, benzophenone–amine initiating systems substantially reduce oxygen inhibition. Oxygen inhibition can also be reduced using unimolecular photoinitiators by adding small amounts of an amine. This process is useful when low-intensity lamps or short exposure times are employed.

29.2.4. Vehicles for Free Radical Initiated UV Cure

In the first UV cure coatings, styrene solutions of unsaturated polyesters (Section 17.3) were used along with benzoin ether photoinitiators. However, styrene is sufficiently volatile that a significant amount evaporates between application and curing. Furthermore, the rate of polymerization is relatively slow compared to that of acrylate systems. However, the cost is low, and they continue to find some applications.

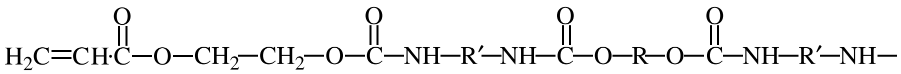
Most current coatings use acrylated reactants. Acrylate rather than methacrylate esters are used, since acrylates cure more rapidly at room temperature; they are also less oxygen inhibited. Furthermore, polymerization of acrylates tends to terminate by combination, whereas methacrylate polymerization terminates largely by disproportionation. The extent of cross-linking and higher molecular weights (MW) are favored when termination of growing radicals occurs by combination.

In general, the vehicle consists of three types of acrylate esters: multifunctional acrylate-terminated oligomers, multifunctional acrylate monomers, and acrylate monomers. The monomers range from mono- to hexafunctional. Many formulas include mixtures of mono-, di-, and trifunctional acrylates. The monomers are also called *reactive diluents*. Multifunctional oligomers contribute to high rates of cross-linking, owing to their polyfunctionality, and in large measure control the properties of the final coating, due to the effect of the backbone structure on such properties as abrasion resistance, flexibility, and adhesion. Their viscosity is too high alone and monomers are required to reduce viscosity for application. Multifunctional acrylate monomers also give fast cross-linking, owing to polyfunctionality, but have lower viscosities than oligomers. Viscosity is lowered further by most monofunctional acrylates, but the rate of cross-linking is reduced.

Quantitative kinetic studies of photopolymerization can be carried out by methods such as photo-differential scanning calorimetry [4] and real-time infrared spectroscopy. Conventional infrared and Raman spectroscopy are also valuable. Kinetic studies furnish useful insights, but because of the large number of variables involved, a complete quantitative description of UV curing processes is difficult to construct, especially with practical formulations containing three types of acrylates.

It would be desirable to react all of the acrylate groups during photopolymerization to eliminate residual double bonds that might cause undesirable long-term changes in film properties. In practice, this is usually not possible, but it is often possible to polymerize a large fraction of the acrylate groups. The *extent of conversion* of the double bonds is affected by the choice of components; in general terms, extent of conversion increases with an increase in monofunctional monomer, presumably because the small monomer molecules can diffuse through the film during the reaction. Extent of conversion is also affected by free volume availability; in general, conversion is increased by use of components that give low T_g films. As polymerization proceeds, T_g of the binder increases. If, as is commonly the case, T_g approaches the temperature at which curing is being carried out, the rate of reactions slows. Reactions become very slow at temperatures only a little above $T_g = T_{cure}$. Since there is heat from the radiation source and a reaction exotherm, T_{cure} is somewhat above ambient temperature. (See Ref. [4] for a review of cross-linking rates and extents of conversion of various systems.)

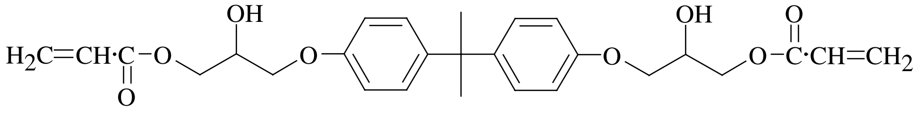
Acrylated oligomers are prepared from a variety of starting oligomers. The properties of films made from the acrylated oligomers are affected by the average number of acrylic double bonds per molecule, MW, and by the structure of the "core" oligomer. For example, acrylated urethane oligomers tend to give coatings with a good combination of hardness and elasticity. Any polyol or hydroxy-terminated oligomer can be reacted with excess diisocyanate (OCN—R′—NCO) to yield an isocyanate-terminated oligomer. This oligomer can then be reacted with hydroxyethyl acrylate at ambient or moderately elevated temperature to yield an acrylated urethane oligomer. It has been shown that the gloss retention on exposure to UV of UV cure coating films decreases as the MW of the diol from which the urethane diacrylate is prepared increases. It is proposed that this reflects a higher cross-link density with the lower MW oligomers [18].



$$H_2C{=}CH{\cdot}\overset{\overset{O}{\|}}{C}{-}O{-}CH_2{-}CH_2{-}O{-}\overset{\overset{O}{\|}}{C}{-}NH{-}R'{-}NH{-}\overset{\overset{O}{\|}}{C}{-}O{-}R{-}O{-}\overset{\overset{O}{\|}}{C}{-}NH{-}R'{-}NH{-}$$

Acrylated urethane oligomer (terminal group)

Another route is to react oxirane groups of epoxy resins with acrylic acid. The ring-opening reaction yields the acrylic ester and a hydroxyl group as shown. Like conventional epoxy resins, the acrylated epoxies tend to give coatings with good toughness, chemical resistance, and adhesion.



Acrylated epoxy oligomer

Various catalysts (e.g., triphenyl phosphine) are used, so the reaction is carried out at as low a temperature as possible. Care is required to avoid polymerization of the acrylic acid or esters during the process. Inhibitors are added to trap free radicals. Some inhibitors, notably phenolic antioxidants, are effective only in the presence of oxygen, so the reaction is commonly carried out under an atmosphere of air mixed with inert gas. Variations in reaction conditions and catalyst composition can result in significant differences in the product. The most widely used epoxy resin is the standard liquid BPA epoxy resin ($n = 0.13$), yielding predominantly the acrylated diglycidyl ether of BPA. Epoxidized soybean or linseed oil also react with acrylic acid to give lower T_g oligomers with higher functionality.

Acrylated melamine–formaldehyde (MF) resins have been prepared by reacting etherified MF resins with acrylamide. These resins have the potential to cure in two ways: by UV curing through the acrylate double bonds, and thermally by residual alkoxymethylol groups on the MF resin. It is reported that UV curing followed by thermal curing provides films with increased hardness, improved stain resistance, and improved durability [19].

Many multifunctional acrylate monomers have been used; examples are trimethylolpropane triacrylate, pentaerythritol triacrylate, 1,6-hexanediol diacrylate, and tripropyleneglycol diacrylate. Care must be used in handling them because many are skin irritants and some are sensitizers [1]. A range of monofunctional acrylates has been used. Those with lowest MW tend to reduce viscosity most effectively, but they may be too volatile. Ethylhexyl acrylate has sufficiently low volatility. Ethoxyethoxyethyl acrylate, isobornyl acrylate, 2-carboxyethyl acrylate, and others are also used. Small amounts of acrylic acid as a co-monomer promote adhesion. 2-Hydroxyethyl acrylate has low volatility, high reactivity, and imparts low viscosities, but its toxic hazard is too great in many applications. *N*-Vinylpyrrolidone (NVP) is an example of a non-acrylate monomer that copolymerizes with acrylates at speeds comparable to that of acrylate polymerization; NVP is particularly useful because the amide structure promotes adhesion to metal and reduces oxygen inhibition; but it also introduces a possible toxic hazard.

Decker found that monomers with carbamate, oxazolidine, or carbonate ester groups in addition to the acrylate functionality give faster curing (by as much as 100-fold) and more complete conversion than did simple acrylates [12]. Addition of a reactive acrylated carbamate monomer to more slowly polymerizing traditional acrylate monomers dramatically increased overall reactivity. Factors affecting the inherent reactivity of such monomers have been investigated intensively [13,20,21]. Three theories have been advanced: (1) hydrogen abstraction/chain transfer that would essentially increase the monomers' functionalities, (2) hydrogen bonding, and (3) electronic and resonance effects. A recent study of monomers with methyl groups blocking potential sites for hydrogen abstraction [20] provided evidence in favor of theory 1 as the dominant factor, although theories 2 and 3 are not excluded.

$C_6F_{13}(CH_2)_2OCOCH{=}CH_2$ as a monomer in an epoxy–acrylate oligomer as a UV cure coating for wood paneling provides high hydro- and oleo-phobicity, improved chemical resistance, and better scratch resistance than do coatings without the fluorine monomer [22].

The combination of unsaturated polyesters with vinyl ether resins has been reported to UV cure at rates comparable with those of acrylates [23]. It is also reported that 1-propenyl ethers can be UV cured at rapid rates. They are made by isomerizing the corresponding allyl ethers [24]. Maleated resins [25] as well as maleimides [4] can also be used for copolymerization with vinyl ethers. Maleimide–vinyl ether compositions have also been reported to cure at rates comparable to those of acrylates without the use of photoinitiators. This is possible because maleimides absorb in the 300 to 310 nm region, so the monomer serves as its own photoinitiator. Initiating free radicals are reported to arise from hydrogen-abstraction by the photoexcited maleimide. These compositions are particularly efficient with high intensity lamps that emit primarily at 308 nm, where the maleimides have peak absorbance [4].

Other UV cure copolymer compositions are amine–enes [26] and thiol–enes. However, applications have been limited: in the former case by relatively slow cure rates, and in the latter by the odor of thiols. Recent years have seen a resurgence of interest in thiol–enes because "they exhibit all of the advantages of typical photopolymerizations . . . and have excellent mechanical properties. In addition, thiol–ene polymerizations have the advantages of being relatively uninhibited by oxygen, exhibit delayed gelation, and enable radical polymerization of a wide range of thiol and vinyl functional group chemistries" [27]. Typical thiol–ene formulas contain a tri- or tetra-functional thiol, an *ene* (a compound with two or more C=C double bonds), and a photoinitiator. Vinyl ethers and highly reactive norbornene derivatives are especially useful ene components [28]. For example, a mixture of trimethylolpropane tri-3-mercaptopropionate with pentaerythritol trivinyl ether can be UV cured in air with very little oxygen inhibition. Other vinyl ether–thiol systems can be cured in air by sunlight [29].

Propagation of thiol–ene cure involves addition of a RS· radical to the ene to form a carbon centered radical followed by chain transfer to RSH to form another RS· radical. The process follows step-growth kinetics rather than the chain growth kinetics of conventional photopolymerization.

29.2.5. Waterborne UV Cure Coatings

Waterborne UV cure coatings are reported to have several advantages over conventional UV coatings. Since the resin is dispersed in water, no reactive diluent is needed. There is no emission of volatile, possibly toxic monomer. The viscosity of the coating is independent of MW, so that low viscosity for spraying is obtained by adjusting the solids with water. The high MW means that fewer reactions of double bonds are needed, hence the film shrinkage is much lower, which in turn improves adhesion to substrates such as metal. Reaction of fewer double bonds is also expected to result in reduced restricted shrinkage and therefore less internal stress in the cured coatings. The main drawback is that the water must be flashed off before exposure to the UV source.

The water is evaporated in an oven at 80°C, followed by UV curing; the higher temperature leads to faster, more complete cure. Since the dispersions are stable at high dilution, overspray caught in a water wash spray booth can be recovered by ultrafiltration. It is reported that it is not even necessary to add further photoinitiator to the recovered coating. Furthermore, the UV cure dispersion can be blended with other waterborne coatings, thus permitting enhanced exterior durability [30,31]. Acrylated PUDs have been used as vehicles for waterborne UV cure coating on wood paneling. Extractables after curing are very low, due to the absence of unreacted low MW reactants. Adhesion is reported to be excellent due to reduced shrinkage during cure due to the lower ratio of double bonds compared to that of conventional UV cure coatings. Low gloss coatings can be made by addition of silica pigment to the formula since the evaporation of water carries pigment to the film surface, and shrinkage due to water evaporation provides a low gloss surface. After application, but before cure, the water is removed by force drying, which means that nonvolatile photoinitiators must be used. 1-Benzoyl hydroxycyclohexyl phenyl ketone was reported to give excellent results. Water soluble photoinitiators are also available. The heating required to evaporate the water has the desirable side effect of increasing conversion, reducing the residual double bonds [32].

Decker and co-workers studied ways to speed up UV curing of water-based acrylic–PUD coatings [33]. They recommend curing the coating while it is still hot following water removal; otherwise, mobility restrictions will retard cure. Another important factor is selection of the base needed to stabilize the PUD; volatile tertiary amines are recommended; most of these amines presumably evaporate during water flash-off. Nonionically stabilized acrylated PUDs do not require an amine to stabilize the dispersion [34].

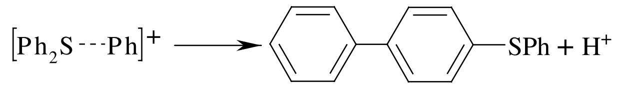
Waterborne UV cure coatings based on acrylated polyesters have been disclosed. An emulsifying polyester and a water insoluble polyester, both acrylated, are mixed, neutralized with aqueous ammonia, and dispersed in water. A photoinitiator (HMMP) is added. The coating is applied to wood, flashed off, and UV cured. The films obtained have excellent properties, and the grain of the wood is not raised [35].

29.3. CATIONIC UV CURE

Photoinitiators for cationic polymerization are typically onium salts of very strong acids [4,36,37]. Iodonium and sulfonium salts of hexafluoroantimonic and hexafluorophosphoric acids are examples. Irradiation of diaryliodonium and triarylsulfonium salts yields strong protic acids of the corresponding counter anions, as well as radical cations; both initiate cationic polymerization. Biscumyliodonium tetrakis(pentafluorophenyl)borate is reported to give substantially faster cure rates than obtained with other onium salts [38].

Onium salts can also be utilized as photoinitiators for free radical polymerization as well as for concurrent cationic/free radical polymerization, since free radical species are also formed in their photolysis. These reactions are shown for a triphenylsulfonium salt (anion omitted) following the primary unimolecular bond cleavage.

$$\mathrm{Ph_3S^+} \longrightarrow [\mathrm{Ph_2S} \cdots \mathrm{Ph}]^+$$



+ ortho and meta isomers

$$[\mathrm{Ph_2S} \cdots \mathrm{Ph}]^+ \longrightarrow \mathrm{Ph_2S^{+\cdot}} + \mathrm{Ph\cdot}$$

Diaryliodonium and triarylsulfonium salts absorb radiation only weakly above 350 nm; however, their spectral response can be extended into the near UV–visible as well as into the mid-visible range by use of photosensitizers [17,37]. Anthracene-bound sulfonium salts exhibit substantially higher reactivity than bimolecular anthracene-sensititized sulfonium salts in epoxy-based UV cure coatings and photoresists, which has been attributed to greater efficiency of intramolecular sensitization as mobility diminishes in such compositions [39].

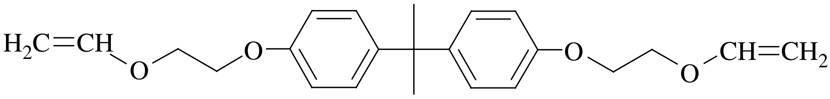
Reported to be particularly effective are 308-nm excimer lamps using triarylsulfonium salts as photoinitiators [7]. Diphenyliodonium salts have limited solubility and are toxic. Substituted derivatives such as bisdodecylphenyliodonium hexafluoroantimonate have both higher solubility and lower toxicity [38].

29.3.1. Vehicles for Cationic UV Cure

Homopolymerization of oxirane groups (equations in Section 13.3.6) is the major type of cationic polymerization used commercially. The counterions must be very weak nucleophiles: in other words, anions of very strong acids. Hexafluoroantimonates, hexafluorophosphates, and the recently introduced borate derivatives are particularly effective. In contrast to free radicals, cations do not react with each other. Consequently, in the absence of nucleophilic anions, cation initiated cross-linking can continue after exposure to the radiation source until the reactive cations become immobilized. Reactions with water and alcohols terminate polymer growth. Nevertheless, cross-linking occurs even if only one pair of epoxy groups reacts before reaction with water; furthermore, the termination reaction is accompanied by regeneration of a proton, corresponding to chain transfer. The absence of oxygen inhibition further distinguishes cationic from free radical polymerization.

Bisphenol A (BPA) epoxy resins react slowly at ambient temperatures. Higher temperatures promote the reaction; optimum cure temperatures are about 70 to 80°C. Rapid curing of coatings based on BPA epoxy resins can be effected by using a combination of UV and infrared sources. Cycloaliphatic epoxides, such as 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexane carboxylate show higher reactivity, which results from the added ring strain due to the fused epoxy ring system that promotes ring opening of the oxonium ion during the propagation step. Their low viscosity makes such epoxides useful as reactive diluents. Epoxy-functional silicone polymers have been recommended for use in UV cure release coatings [38].

Vinyl ethers and styrenes, particularly *p*-alkoxystyrenes, rapidly polymerize cationically. Cationic photopolymerization of vinyl ethers is more rapid than polymerization of epoxy-functional reactants [4,36]. Less photoinitiator is required; moreover, multifunctional vinyl ether monomers are said to show a very low order of toxicity. Vinyl ether monomers are interesting in their own right and are also useful as a highly reactive component in epoxy resin coatings. An example of a divinylether monomer, reported to have a very high rate of polymerization, is the divinylether derived from the reaction product of chloroethyl vinyl ether with bisphenol A [36]:



Cationic UV cure coatings have been reported using vinyl ether oligomers, prepared from toluene diisocyanate/polyethylene glycol prepolymers terminated with 4-hydroxybutylvinyl ether together with ethylene glycol divinyl ether as reactive diluent, a diaryliodonium tetrakis(pentafluorophenyl)borate salt as initiator and isopropylthioxanthone as photosensitizer [40].

Tensile strength of films from a vinyl ether–terminated poly(dimethyl)siloxane/TDI prepolymer were higher than with propylene glycol and the cure rate was more rapid. 1-Propenyl ether compounds are reported to cure rapidly, cationically, using triarylsulfonium hexafluoroantimonate salts [24].

29.4. EFFECTS OF PIGMENTATION

Since many pigments absorb and/or scatter UV radiation, they generally inhibit UV curing to some degree [41]. Scattering leads to reflection back out of the film, and absorption also reduces UV availability to the photoinitiator. The effect becomes more serious as film thickness increases, since the pigment plus the photoinitiator reduce the amount of UV that can reach the lower layers of the film. With a strongly absorbing pigment such as carbon black, the films that can be UV cured are limited to 1 to 2 μm in thickness. Hence, printing inks pigmented with carbon black can be UV cured, but not black coatings.

The most widely used pigment in all other types of coatings is rutile TiO_2. However, rutile TiO_2 absorbs some violet light and essentially all but the very nearest UV, even at quite thin film thickness. Rutile white coatings with good hiding can be cured using a blend of 25% BAPO and 75% HMMP (Section 29.2.1) [14]. To permit flow, low levels of pigmentation are used (PVC of 6), requiring film thicknesses of 50 to 100 μm for hiding. Anatase TiO_2 does not absorb as strongly in the near UV, so that thicker films can be UV cured than with rutile, but hiding by anatase is not as efficient.

Equations have been developed that permit calculation of the fraction of UV of each wavelength that will be absorbed by photoinitiator in the presence of pigments that absorb and scatter UV [42]. The equations permit calculation of the total fraction of radiation absorbed as a function of wavelength, and perhaps more important, permit calculation of absorption in the bottom layer of films of different film thicknesses. The database needed and the calculations would be very extensive, so it appears more practical to make model calculations using the equations to illustrate the effect of variables and to guide formulators considering selection of pigments, photoinitiators, and their concentrations. Figure 29.2 illustrates the effect of concentration of photoinitiator on absorption of UV by photoinitiator in the bottom 0.1 μm of 15 μm films. The calculations were based on assumptions intended to illustrate the effect of 20 PVC of rutile TiO_2 in the film. The photosensitizer absorption was based on 2-chlorothioxanthone (CTX). With the assumptions used, the appropriate concentration of CTX for this system would be about 0.33%.

Curing is favored by using UV sources with higher contents of very near UV radiation and by using photoinitiators such as CTX with higher absorption coefficients in the very near UV wavelengths. As discussed previously, there is an optimum photoinitiator concentration that decreases as film thickness increases. Pigmented coatings are more sensitive than unpigmented coatings to this effect. The effect of reflection by the substrate can be critical in determining the film thickness that can be cured.

A further problem of pigmentation in curing arises from the large differential of absorption of UV at the surface and at the bottom of the films, which can result in wrinkling

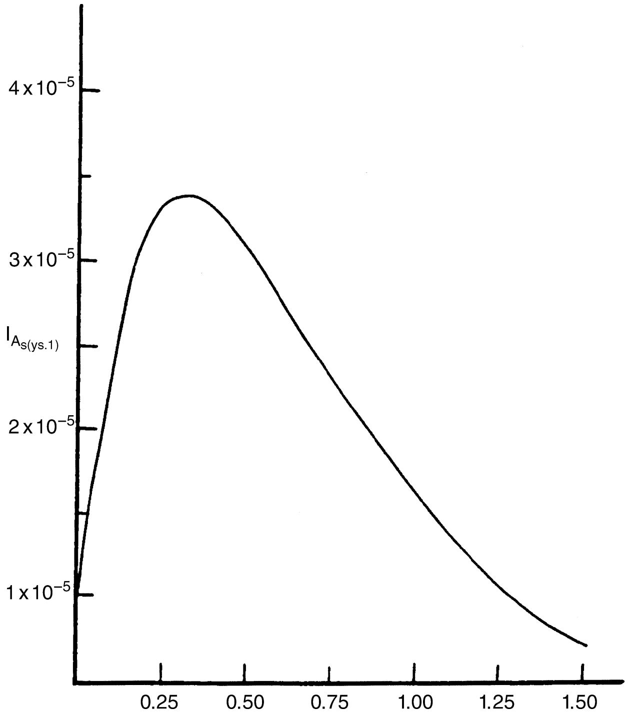


Figure 29.2. *Absorption by CTX of 375 nm radiation in the bottom 0.1 μm of 15 μm films with 20 PVC TiO_2 over an 85% reflectance substrate as a function of CTX concentration. (From Ref. [41], with permission.)*

(Section 24.6). If the surface layer of a film cures while the bottom layer is still fluid, then when the bottom layer cures it shrinks, causing the top layer to wrinkle. This effect is particularly likely to be seen with free radical cure done in an inert atmosphere or with cationic cure. In both cases, there is no inhibition of the surface cure by oxygen.

Pigmentation also affects flow properties. UV cure coatings are generally applied without solvent, which means that the volume of pigment in the wet coating is almost as high as the PVC of the final film. Without solvent, viscosity tends to be higher than desirable for good flow in the short time between application and cure. Even at 20 PVC, there is a significant increase in viscosity due to the presence of the pigment. By using sufficient monomer in place of oligomer, the viscosity can be reduced to application viscosity, but this reduces the curing speed. As one tries to make higher PVC coatings, the problem becomes more difficult. As PVC approaches CPVC, viscosity of a wet coating approaches infinity. The problem is compounded by the difficulty of stabilizing the pigment dispersion against flocculation with the relatively low MW vehicle (Section 21.1.3). Flow problems are just as serious for cationic systems as for free radical systems. However, pigment flow problems are expected to be alleviated in waterborne UV cure compositions (Section 29.2.5), which are applied as dispersions.

For many wood finish applications, transparent low gloss coatings are desired, but they are difficult to achieve with radiation cure coatings. Low gloss is attained in transparent lacquers for finishing furniture and paneling by adding low concentrations of small particle size SiO_2. When the lacquer is applied, the solvent evaporates, setting up convection currents in the drying lacquer film. The SiO_2 particles are carried up to the surface of the film by these convection currents. As the viscosity of the surface increases, the SiO_2 particles are trapped at the surface. The resulting high PVC at the surface gives low gloss. In UV cure coatings, there is no solvent to evaporate and therefore no mechanism to concentrate the pigment at the surface. If the level of pigmentation is increased to the extent necessary to provide low gloss, the viscosity is too high for application. As discussed in Section 29.2.5, low gloss transparent wood coatings are possible with waterborne UV cure.

Some progress has been made in reducing gloss by use of a dual UV cure method. A UV cure coating containing as much small particle size SiO_2 as viscosity permits and designed so that its cure is strongly oxygen inhibited is applied and cured in air. The lower layer of the coating cures preferentially. As the lower layer cures, it shrinks, exerting an unbalanced stress on the pigment particles in the upper parts of the film, forcing them toward the surface. An alternative explanation is that reactive monomer or oligomer undergoes net migration into the lower polymerizing region, thereby concentrating pigment in the upper nonpolymerizing region. Then the coating is UV cured again, this time under an inert atmosphere. Now, the surface layer cures, resulting in further shrinkage and further increasing PVC near the surface. In this way, medium gloss transparent coatings can be made. Several production lines have operated using this dual cure method.

29.5. ELECTRON BEAM CURE COATINGS

High-energy electron beams (EB) can be used to polymerize acrylate coatings. In EB cure compositions, the high energy electrons cause direct excitation of the coatings resins (P) as well as their ionization into radical cations ($P^{+}\cdot$) and secondary electrons (e^{-}).

$$P + EB \longrightarrow P^{*} + P^{+\cdot} \qquad P^{+\cdot} + e^{-} \longrightarrow P^{*} \longrightarrow I^{\cdot}$$

The major fate of the radical cations is recombination with the relatively low energy secondary electrons, which can yield additional excited state resins. The excited state resins (P^*) primarily undergo homolytic bond cleavage to free radicals that initiate polymerization of the acrylated resins.

The high energy electrons are generated by charging a tungsten filament at a high negative potential, 150 to 300 keV. The electrons are directed by magnets in a curtain through a metal "window" to the coatings to be cured. (The term *electron curtain* is also used.) The types of vehicles used are the same as those used in free radical–initiated UV curing. Since the polymerization reactions are oxygen inhibited and there is little differential in absorption between the top and the bottom of the film, it is essential to do EB curing in inert atmospheres.

Cationic polymerization of vinyl ethers [4,43], as well as highly reactive epoxides [44] can be induced by EB radiation in the presence of diaryliodonium and triarylsulfonium salts. The readily reducible onium salts have been implicated in the generation of cationic initiators by oxidation of free radical species as well as by capture of secondary electrons. Scavenging of secondary electrons by onium salts tends to lengthen the lifetime of cations and to improve the prospects for cationic polymerization [43].

The principal advantages of EB curing over UV curing are that no photoinitiator is needed and that pigments do not interfere with the curing. These advantages are often offset by the higher capital cost of the electron beam or curtain generating equipment, the need to use inert atmospheres, and the need for shielding to protect workers from the electron beam. The advantage of being able to cure pigmented systems is real but is of limited importance in coatings, since the flow problem is not alleviated by EB curing.

29.6. DUAL UV/THERMAL CURE AND SELECTED APPLICATIONS

UV curing is generally limited to flat sheets or moving webs or cylindrical objects, which can be rotated in front of the radiation source, to achieve uniform cure. However, dual UV/thermal cure compositions have been developed for multi-shaped substrates, such as an auto body, to provide thermal cure in areas, called *shadow areas*, that are not exposed directly to the radiation. An investigation of various approaches to UV curing on automobiles has been described [45]. A dual UV/thermal cure coating, exposed with a combination of two fluorescent lamps (one with maximum intensity at 313 nm, the other at 351 nm) and a xenon flash lamp, followed by thermal curing for 30 minutes at 70°C, gave excellent film properties. The rapid UV cure minimizes sagging, and the subsequent thermal cure provides cure in the shadow areas. A related UV/thermal dual cure study of auto clear coats utilized a free radical photoinitiator/acrylated resin composition blended with an alkyd–MF resin composition and reported good gloss and mar resistance of the cured coating [46].

Dual UV/thermal cure compositions have been reported, based on thermal redox generation of radicals, so that the same functionality, such as acrylate groups, can be used for both UV and thermal cure [47]. Examples include through cure of black coatings. Dual UV/thermal cure waterborne coatings have also been reported. Compositions containing carbamate-functional acrylated PUDs together with MF resins can be UV cured followed by thermal cross-linking of the carbamate groups with the MF resins [48].

Researchers are actively seeking *photolatent catalysts* that generate acids or tertiary amines when exposed to UV [49]. Such catalysts are useful in dual UV/thermal cure compositions. For example, a photolatent catalyst that releases strong acid can promote acid catalyzed thermal cure, such as with MF resins, avoiding package stability problems. In combination with conventional photoinitiators, the UV exposure step not only effects UV curing, but also generates acid for the subsequent thermal step. Such acid precursors, known as *photoacid generators* (PAGs), are commonly precursors of sulfonic acids such as oxime sulfonates [50]. PAGs are used widely in the electronics industry for photoimaging. Photolatent catalysts that release amines can extend the pot life of 2K polyurethanes to a full working day, of substantial value in auto refinish shops and other applications [49].

UV cure printing inks, particularly lithographic inks, are widely used. The viscosity of lithographic inks is relatively high, on the order of 5 to 10 Pa•s, so there is not a flow problem. The films are thin, 2 μm or less, so interference of pigment with curing can be offset by use of highly absorbing photoinitiators and/or high photoinitiator concentrations. Since the films are not continuous, adhesion or curling difficulties resulting from shrinkage are not a major problem. The advantage of fast curing is large, as it allows the webs to be wound up quickly without offsetting on the back of the substrate. In printing of tin plate and aluminum for cans, there is the advantage that the four colors can be printed in line simply by having a UV lamp after each printing station; operating costs are lower than with heat cure inks. Ink jet printing is another rapidly growing market for UV inks [44].

Clear coatings for paper, plastic film, and foil are probably the largest volume market for radiation cured coatings [44]. The unpigmented coatings cure very fast at low temperatures. The important uses of UV curing for top coating wood furniture and filling of particle board are discussed in Chapter 31. Another large scale application that benefits from the fast curing at low temperature possible with UV cure coatings is top coating of vinyl flooring. It is especially applicable to flooring with patterns made by expanded foams, since the foam pattern is heat sensitive. Acrylated urethane oligomer coatings have the high abrasion resistance needed in a floor covering; acrylated polyester coatings have superior stain resistance.

Abrasion resistant clear coatings for plastics have been developed. The poor abrasion resistance of clear plastics is a distinct disadvantage in applications such as replacing glass in uses ranging from glazing to eyeglasses to automotive head lamps. Silicone-based coatings have been used for many years to improve the abrasion resistance (Section 4.4.1). These coatings require long thermal cure schedules and have high VOC levels. Radiation cure coatings based on trialkoxysilyl-functional acrylate monomers and colloidal silica cure in seconds and have low VOC emission [51]. They have excellent adhesion to polycarbonates and other plastics and have abrasion resistance equal or superior to solvent-based coatings [51,52].

An application for cationic UV cure epoxy coatings is for coil coating on tin plate for the exterior side of can ends. The superior adhesion of epoxy coatings makes them preferable to acrylate coatings for this application. In some cases, a UV cure coating is applied on one side of the strip and UV cured. Then a thermally cured epoxy coating is applied on the other side. When the strip is put through the oven to cure the thermally cured coating, the cross-linking of the UV cure coating is also advanced. More flexible films are obtained using epoxidized polybutadiene [53].

A large use of UV curing is for coating optical fibers for wave guides used in telecommunication cables. The process is carried out at high speeds in towers up to 25 m tall. The glass fiber is pulled from a heat softened blank of glass and then coated through a die coater, that is, a reservoir with holes on each end through which the glass is pulled. The UV lamps are aligned parallel to the fiber as it comes out of the coater; elliptical reflectors are placed both behind the UV source and on the opposite side of the fiber from the source. The fiber is at the focal point of the pair of reflectors. In this way, the coating is given very high dosages of UV, permitting cure speeds on the order of 20 m s^{-1} without an excessive bank of UV lamps. Acrylated urethane oligomers have been used since abrasion resistance is a critical requirement. Two UV cure coatings, a soft first coat with special optical properties and a harder outer coat, are applied and cured by the time the fast-moving coated fiber reaches the bottom of the tower [54].

A UV curable optical fiber coating transparent in deep UV has been developed to allow a Bragg grating to be engraved on the fiber directly by laser exposure through the coating. The vehicle selected was an acrylate-terminated dimethylsilicone resin, and the initiator was 2,4,6-trimethylbenzoyldiphenylphosphineoxide.

UV curing is also the basis for important photoimaging processes used in the printing and electronic industries [55,56]. In these applications, UV curable coatings on selected substrates are exposed through an image bearing transparency such as a film negative. Cross-linking occurs selectively under the transparent regions. The unexposed regions are subsequently removed, commonly by washing out with aqueous or organic solvent. The resulting image transfer into the coated substrate is a critical step in making printing plates as well as printed circuit boards and integrated microcircuits (e.g., computer chips).

29.7. ADVANTAGES AND LIMITATIONS

A survey of 130 people involved in radiation curing assessed the advantages, disadvantages, and prospects for the technology [44]. Eighty-nine percent of the respondents reported that reduced solvent emission is an important motivation for use of radiation cure. Generally, the formulations contain no solvent and VOC emissions are negligible.

Very short cure times are possible at ambient temperature with package stable coatings. In the case of clear acrylate compositions, curing times required are fractions of a second. Since the curing can be done at ambient temperatures, the coatings are applicable to heat sensitive substrates such as paper, some plastics, and wood. The energy requirement is minimal. Major losses in energy encountered in thermal curing systems are not experienced. The cure is done at or near to ambient temperature, so no energy is required to heat the object being coated except in the case of waterborne UV coatings. (The IR radiation from the UV lamps does cause a modest temperature increase.) In addition, heat loss from air flow through a baking oven, required to keep the solvent concentration below the lower explosive limit, is eliminated. The extent of this advantage is, of course, dependent on the cost of energy. The use of radiation curing in Europe and Japan has been greater than in the United States, at least in part because the cost of energy is higher in Europe and Japan than in the United States.

Capital cost for UV curing is low. This results primarily from the small size of the curing units as compared with ovens for baking. A UV cure coating needs only about 0.5 second exposure for curing. A line being run at a speed of 60 m min^{-1} need be exposed to UV over a distance of only 0.5 m. A UV curing unit with four lamps can do this in a total length of about 2 m. In contrast, a thermal cure oven has to be 100 or more meters long to provide time for curing at this speed. In addition, there has to be space for flash off of at least some of the solvent from conventional coatings before the coated object enters the oven and space for it to cool back down to handling temperature. The savings in building space can thus be large. Half of the end users in the survey report "improved physical properties/product performance" as a major motivation for using radiation cure [44].

There are, however, limitations and disadvantages to radiation curing. It is most applicable to flat sheets or webs for which the distance to the UV source or the window of the EB unit can be approximately constant. Cylindrical or nearly cylindrical objects can be rotated in front of the radiation source and fibers can be pulled through a circle of sources, but irregularly shaped objects are not easy to expose uniformly.

In the case of UV curing, pigmentation can limit the thickness of films that can be cured. In the extreme case of carbon black pigmented films, the limit is about 2 μm. Electron beam cure coatings do not have this limitation because there is no gradient of initiation from top to bottom of the film. Owing to the effects of pigmentation on flow, the level of pigmentation is limited in both UV cure and EB cure coatings, excepting waterborne formulations. Furthermore, low gloss coatings cannot be applied. These limitations can be overcome by using solvent containing coatings, but this eliminates many of the advantages.

Shrinkage during curing can lead to adhesion problems on metal and some plastic substrates (Section 6.2). When polymerization results from chain addition of free radicals to double bonds, there is a substantial decrease in volume, since the length of the carbon–carbon bonds formed is shorter than the intermolecular distance of monomer units. The degree of shrinkage is related directly to the number of double bonds reacted. In acrylic UV or EB cure coatings, the potential shrinkage is 5 to 10%. Since cure occurs in less than a second, there is not time for much of the volume shrinkage to take place before the free volume in the coating is so limited that movement becomes restricted. The stress from the restricted shrinkage applies a force to offset the adhesion forces holding the coating to a substrate so that less external force is required to remove the coating. Shrinkage can be minimized by using higher MW oligomers or higher ratios of oligomer to low MW reactive monomers, but these expedients increase viscosity and tend to increase cure time. Curing of epoxy systems by cationic photoinitiators leads to less shrinkage. The decrease in volume resulting from the formation of polymers from monomers is partially offset by an increase in volume from epoxy ring opening. Typical epoxy UV cure compositions shrink less than 3%. Adhesion of cationic cure coatings can be further enhanced by surface treatment of the substrate [57]. Some of the problems with UV curing can be reduced by using waterborne UV coatings as discussed in Section 29.2.5.

Porous substrates such as paper and wood give good adhesion, since the mechanical effect of penetrating into the surface of the substrate holds the coating on the substrate. However, there can be a curling problem with thin substrates as a result of the tension from shrinkage on one side of the substrate.

The photoinitiator in free radical initiated coatings is only partly consumed in curing, so a substantial fraction remains in the films. The photoinitiator can accelerate photodegradation of films exposed outdoors. Conventional UV stabilizers and antioxidants tend to reduce UV cure rates, which limits their use. These constraints limit the use of UV cure coatings in the range of exterior applications but do not exclude it. Studies on automotive clear coats have shown that a UV curable formulation of specified acrylated resins, photoinitiators, UV absorber, and hindered amine light stabilizer (HALS) showed exterior durability after five years in Florida comparable to that of conventional thermal cure clear coats [58].

Cationic coatings have the advantage that they do not generate free radicals when films are exposed outdoors. Electron beam cure coatings have the distinct advantage that there is no photoinitiator in the system. However, even with EB curing, the coatings used must have excess unsaturation to cure on rapid schedules, and residual unsaturation can adversely affect exterior durability. Also, there are trapped free radicals that can react with oxygen after the cure and generate peroxides. Radiation-cure coatings tend to be more expensive than conventional coatings, so that commercial applications are primarily those where UVs cure permit unique advantages.

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30

Product Coatings for Metal Substrates

In 2002, U.S. shipments of product coatings for OEM (original equipment manufacture) application had a value of \$5.26 billion [1]. This was approximately 33% of the value of all U.S. shipments of coatings. In this and the following chapter on coatings for nonmetallic substrates, we discuss some of the major OEM product coating end uses to illustrate the factors involved in selecting coatings for particular applications. A large fraction of industrial coatings is used on metals. Multitudes of products are coated; space permits discussion of only a few. We have selected four of the larger end uses: automotive, appliance, container, and coil coatings.

30.1. OEM AUTOMOTIVE COATINGS

OEM automotive coatings for cars and trucks are the largest single market for industrial coatings. The global market for automotive coatings in 2001 was reported to be \$6.6 billion; the U.S. market accounted for \$2.5 billion [2]. Coatings for repair and refinishing of cars are discussed in Section 33.3. The discussion here is further limited to coatings applied to the exterior bodies of automobiles. Coatings for plastics in cars are discussed in Section 31.2.2. Many other coatings are used on car interiors, wheels, trunk linings, air filters, and so on. The coating operation is a major part of auto and truck assembly, occupying about half the space and using more than half the capital investment in the entire assembly plant.

There are two major reasons for coating an automobile: appearance and corrosion protection. Initial appearance can be a critical factor in the sale of a car; the coating is the first thing a potential buyer sees. The purchaser can be attracted by the good appearance of the coating; furthermore, if the coating is poor, the purchaser may assume that the

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manufacturer is careless not only in applying the coating, but also in other aspects of manufacturing the automobile. Maintaining the excellent appearance of the coating over many years of service is also critical. If the coating does not continue to look good, not only may the owner of the car be unhappy but others may decide not to buy that make of car because they have seen that the coating does not stand up well. High-gloss coatings are used, and gloss retention is a critical requirement. Corrosion protection is another critical performance requirement. The use of salt on icy highways provides an environment that can lead to rapid corrosion of steel. In the 1970s and 1980s, coatings were developed that together with improved steel, provide protection against corrosion for the lifetime of the car.

The steel used in car bodies may be cold-rolled steel; it may have been electrogalvanized or hot-dip galvanized; or it may be a special alloy that includes zinc. Before coating the car, body parts are fabricated and assembled, including the doors, hood, and trunk lid. After careful cleaning to remove dirt and oil, the body is chemically conversion coated (pretreated) as detailed in Section 6.4.1. For steel, the conversion coating process deposits a mesh 1 to 5 μm thick, of zinc phosphate and zinc–iron phosphate crystals on the surface. Modern conversion coatings are complex formulas, often containing manganese in addition to zinc. Different conversion coatings may be needed for zinc coated steel and alloys. The car body is then carefully cleaned and rinsed; the last rinse water contains a dilute solution of chromic acid having the primary purpose of preventing the onset of rusting during the short time before painting begins.

30.1.1. Electrodeposition Coatings and Primer–Surfacers

Virtually all of the steel vehicles in the world are primed with cationic E-coat as discussed in Section 27.2. E-coat primers provide excellent adhesion to metal and resist displacement by water. The strong driving force of the electrophoretic application is thought to aid penetration into the phosphate crystal mesh on the metal surface. The amine groups on the binder resin provide strong interaction with the phosphate coating and the metal surface. The binders are designed to be nonsaponifiable; even if the coating is scraped through, undercutting will be very slow, and the coating will continue to protect the metal next to the gouge against corrosion. The E-coat covers all metal surfaces, including recessed areas, such as the interior of rocker panels below the doors that cannot be coated by spray application. The process provides a relatively uniform film thickness on all metal surfaces of about 25 μm of dry film.

Although E-coat primers provide excellent corrosion protection, there are three problems involved in their use. (1) They lack good UV resistance. If the top coat allows UV to reach the E-coat, degradation occurs at the E-coat surface, destroying intercoat adhesion and leading to delamination. Subsequent coats must prevent UV from reaching the E-coat surface. (2) The film thickness can be so uniform that surface irregularities in the metal and conversion coating are copied in the surface of the primer film. (3) It can be difficult to achieve the required adhesion of top coat to the E-coat surface. E-coat primers have been formulated that provide greater smoothness (the term *filling* is often applied) by reducing the pigment content of the primer. The viscosity of the uncured primer film is lower, and when the primed car body is baked, more leveling can occur than if the PVC were higher. Although this aids in obtaining surface smoothness, adhesion of top coat to the smooth, glossy E-coat surface is more difficult, making achieving chip resistance more difficult.

There have been many efforts to develop E-coats that can be coated directly with top coats, but most auto assembly plants use an intermediate coating variously called a primer surfacer, a tie coat, or just a primer. In some cases, there is an additional antichip coating in areas such as the rocker panels and nose of the hood.

Three classes of primer–surfacers are currently used. Worldwide, in 2004, these coatings were 73.9% solventborne, 19.5% waterborne, and 6.6% powder [3].

An example of a binder in a chip resistant solventborne primer–surfacer is a one package urethane polyester coating, utilizing a blocked isocyanate [4]. In some cases, a two package (2K) polyurethane primer–surfacer is used. The primer–surfacer has a lower cross-link density than the E-coat primer, providing greater opportunity for the solvent in the top coat to penetrate into this surface than into the surface of the E-coat primer. The primer–surfacer is formulated with a higher PVC, so that surface roughness provides a greater opportunity for top coat adhesion. Also, a highly pigmented primer–surfacer can be relatively easily sanded to flatten defects such as dirt. The primer film is usually thick enough to avoid sanding through to bare metal, but if this happens, the spot is repaired with catalyzed coatings containing passivating pigment such as strontium chromate. An example of a waterborne chip resistant primer is a urethane acrylic, based on blocked isocyanates and water-reducible acrylic resins [5]. The mechanical properties involved in stone chip resistance and approaches to testing are discussed in Ref. [6].

Powder primer–surfacers are being used over E-coat on some cars to reduce VOC emissions. They also provide improved chip resistance. Adhesion to the E-coat surface is presumably obtained by the high baking temperature, 150°C, used with the powder primer–surfacer. The greatest interest has been in epoxy-functional acrylics made with glycidyl methacrylate (GMA) (Section 13.1.2) as a co-monomer and cross-linked with dicarboxylic acids such as dodecanedioic acid [$HOOC(CH_2)_{10}COOH$] [7] or a carboxylic acid–functional resin [8]. An epoxy-functional acrylic for automotive primer–surfacer is said to require an $\bar{M}_n$ below 2500, a calculated T_g above 80°C, and a monomer composition such that melt viscosity is less than 40 Pa•s at 150°C [9]. Such a resin can be made with 15 to 35% GMA and 5 to 15% butyl methacrylate (BMA), with the balance being methyl methacrylate (MMA) and styrene.

A current trend is toward use of color key primers; the colors are picked for use under a group of top coats with related colors. Use of several different color primers is a significant expense but can improve the appearance when top coats have thin areas with less than 100% hiding. Color key primers also make stone chip damage less noticeable since chipping to the primer results in little or no color change. A further advantage is that colored primers can be sprayed under the hood, in the trunk, and on the inside of doors. Then a relatively thin layer of the more expensive top coat gives a satisfactory appearance. The primer must have good exterior durability to compensate for thin spots in the top coat or excessive loss of UV absorbers from the top coat on baking. Otherwise, UV radiation will degrade the surface of the primer, causing loss of adhesion of top coat to primer and, ultimately, to delamination. UV absorbers and HALS stabilizers (Section 5.2.) can be added to the primer–surfacer to improve its UV resistance. A UV absorber in the base coat and top coat that strongly absorbs UV in the wavelength range 290 to 310 nm also helps protect the primer from degradation. Partial migration of UVA and HALS among the coats is to be expected.

30.1.2. Top Coats

The primary purpose of top coats is appearance. Top coats are high gloss and must maintain their appearance for long periods. While the primary factors in maintaining appearance are resistance of the resin binder to photoxidation and hydrolysis, durability of the pigment in the film is also a critical factor (Chapter 5). There are many other requirements, including resistance to scratching, to acid precipitation (rain, fog, and dew), to bird droppings, to sudden thunder showers on a car that has been sitting in the hot sun, to the impact of pieces of gravel striking the car, to gasoline spillage, and so on. Until the early 1980s almost all top coats were *monocoats*, a single coating composition applied in several coats. Monocoats have been largely supplanted by *base coat–clear coat systems*; a base coat containing the color pigments covered by a transparent coating. Base coat–clear coat systems provide better gloss and gloss retention than monocoats.

In both monocoat and base coat–clear coat systems, a majority of top coats are metallic or other polychromatic colors. As discussed in Sections 19.4 and 20.2.5, metallic coatings give an attractive appearance, due to the change in color with the angle of viewing. When viewed at an angle near the perpendicular, the color is light, and when viewed at larger angles, the color is darker. The extent of this phenomenon is called the degree of *color flop*, or just *flop*. High color flop depends on three factors: minimal light scattering by the coating matrix between the aluminum flakes; a smooth, high gloss surface; and orientation of the aluminum flakes parallel to the surface. Other special effect top coats are pigmented with interference pigments such as pearlescent and cholesteric pigments.

Minimal light scattering by the coating matrix requires that pigment selection and dispersion provide transparent films when prepared in the absence of the effect pigment. Most dispersions are made with media mills. Nano color pigments for automotive metallic coatings are prepared by grinding suspensions of the conventional color pigments in butyl acetate with a commercial dispersing agent using very small balls in the mill. The mill base is then used to make tinting pastes with excellent transparency for color matching metallic colors [10].

Also, all resins and additives in the coating must be compatible so that there is no haziness in the unpigmented film. The final surface should be as smooth as possible. Surface unevenness can be affected by many factors. Surface roughness can result from roughness of the initial metal substrate and phosphate layer [11]. Rough primer–surfacers can result from dry spray on difficult to paint areas such as the verticals on or below the deck lid. Leveling of orange peel after spraying can be difficult to avoid in vertical areas, where relatively dry spray is used to avoid sagging. Door jambs can be particularly difficult and are the part most noticed when you get into a car. Overspray can result in poor leveling.

Orientation of aluminum flakes parallel to the surface has been achieved in everyday production for decades, but it has never been entirely clear why orientation is as good as it is [12,13]. Most workers have concluded that an important factor is shrinkage of the film after application; shrinkage is accompanied by increasing viscosity of the film most rapidly near the surface as the solvent evaporates, leading to a viscosity gradient. This viscosity gradient causes the upper edge of an aluminum platelet to be immobilized before the lower edge, and the platelet swivels toward parallel orientation as the film shrinks. In general, the lower the solids of the coating as it arrives at the substrate, the better the alignment will be. Some workers think that spray droplets spread out when they strike the surface, and the resulting flow forces tend to align the flake particles parallel to the surface. It has also been suggested that the spray droplets must penetrate the surface of the wet film and crash on the substrate [13]. The rapid drop in viscosity as a high-solids clear coat goes into the oven can cause flow, resulting in some loss of orientation. These and other factors may influence orientation. Changes in atomization, air flow, solvent evaporation rates, and gun to surface distance during spraying can cause substantial variations in flake alignment [14]. Transfer efficiency is greatly improved by electrostatic spraying; however, it is more difficult to obtain good surface smoothness and metal orientation using electrostatic spray. It has been suggested that there may be some alignment of the metal flakes parallel to the lines of force in the electrostatic field that are perpendicular to the substrate. Use of automatic high-speed rotary bell spray guns further complicates the problem of obtaining a uniform appearance.

Most monocoats are formulated with thermosetting acrylic and melamine–formaldehyde (MF) resins. To achieve high gloss, pigmentation levels are low. In solid colors, PVCs of 8 to 9% are used; in the case of metallic colors, PVCs are much lower—on the order of 2 to 4%. Owing to the low pigment content, relatively thick films (on the order of 50 μm) are required for hiding. Since the coatings are spray applied, some areas have significantly over 50 μm of dry coating: for example, around the A post, between the windshield and the front door openings. Higher PVCs are possible with base coats because there is no requirement for gloss. Relatively thin (12 to 20 μm) base coat films can provide adequate hiding [15].

Until recently, the highest solids at which it has been possible to formulate high performance solventborne monocoats is about 45 NVV. This has also been near the upper limit of solids that provides outstanding exterior durability. If the molecular weight (MW) of the acrylic resin is reduced further to increase the solids above 45 NVV, the average number of functional groups per molecule and MW get so low that the fraction of molecules with single functional groups becomes too large to permit good properties with thermosetting acrylic resins synthesized by free radical polymerization (Section 8.2.1).

Clear coats can be sprayed at somewhat higher solids than monocoats. As discussed in Section 24.3, as resin solids increase, the problems of controlling sagging increase. Automotive coatings are particularly vulnerable to sagging, since the film thickness applied is large and variable. As solids have been increased, it has become necessary to add thixotropic agents to increase the viscosity at low shear rates to minimize sagging [16,17]. Conventional thixotropic agents make a coating hazy due to light scattering, thereby reducing gloss. Therefore, viscosity modifiers have been designed with refractive indexes similar to those of the acrylic binder. Those most widely used are acrylic microgels, which are highly swollen gel particles that are lightly cross-linked so that they can swell, but not dissolve, in the liquid coating (Section 24.3). The microgels make the coating thixotropic (i.e., the viscosity decreases with the high shear going through the spray gun, stays low long enough for leveling, but then increases, reducing sagging). The mechanism of their action is not fully understood, but swelling of the particles and flocculation are thought to play a role [15,16].

Application of a clear coat over a pigmented base coat gives higher gloss. Historically, clear coats were not used in automotive finishes because of the cost of an extra coating step and because the exterior durability of available clear coatings was inadequate. However, with development of better binders and light stabilizers, especially combinations of HALS and UV absorbers (Section 5.2), clear coats now have long-term exterior durability. Total combined film thickness is only slightly greater than that of a single coat system. The base coat contains roughly twice the PVC of a monocoat. Thus, a base coat with a dry film about 12 to 20 μm thick, depending on the color, has about the same hiding as a 50 μm monocoat. The clear coat thickness should be about 40 to 50 μm, but considerable variation is experienced in production. Thin (less than 30 to 35 μm) areas appear satisfactory but have inferior durability. Properly formulated and applied base coat–clear coat systems have high gloss and long-term gloss retention. The advantage is particularly marked for metallic coatings. The same overall VOC emission can be achieved using a lower solids base coat and a higher solids clear coat. The lower solids in the base coat permits better orientation of the aluminum in the coating and hence superior color flop. The higher level of pigmentation leads to a somewhat rougher surface of the base coat than of a single coat, but this is covered by the clear coating. Waterborne base coats generally give superior metal orientation, since they are applied at 20 to 25 NVV.

Although it would be possible to bake the car body after application of the base coat, then apply the clear coat, and bake the car again, it is more economical to apply the clear over a wet base coat and bake the overall system just once. Part of the solvent must evaporate from the base coat film before clear coat is sprayed over it; otherwise, the force of the spray of the clear coat would distort the base coat. On the other hand, if too much solvent has evaporated, intercoat adhesion may be adversely affected. The solvent must be permitted to flash off until distortion will not occur, and then the top coat is applied. The flash-off time required is about 2 minutes but varies with spray booth ventilation conditions as well as coating formulations. In some systems, to permit application of the clear coat in 2 minutes, it is necessary to incorporate a small amount of wax, zinc stearate, or cellulose acetobutyrate in the base coat formulation [18]. The additive apparently orients at the surface and minimizes distortion of the layer. Care must be exercised, since excess additive could interfere with intercoat adhesion.

Worldwide, in 2004, 57.7% of base coats were solventborne and 42.3% were waterborne. In the United States about 35% were waterborne; in Germany almost 90% were waterborne [3].

Solventborne base coat binders are often thermosetting acrylic resins with MF cross-linkers. It has been reported that hydroxy-functional urethane modified polyesters are also useful in base coats [18].

Published papers on waterborne base coats mention MF cross-linkers with water-reducible acrylics, water-reducible polyester–polyurethanes, and acrylic latexes [19–21]. Use of acrylic latexes appears to be gaining favor as experience is gained in designing the complex combinations of rheological characteristics needed for application and flake orientation [12,20]. Waterborne base coats require a dehydration bake in which most of the water and some of the solvent is driven off before application of the top coat. This process must be carefully controlled. If too much water remains in the film, it will blow out during the clear coat bake resulting in popping. If the base coat is overbaked, it may become porous and adsorb clear coat solvent, affecting flow of the clear coat and again, leading to popping.

The lower film thickness of the base coat and the flash-off time required before applying the clear top coat reduce the popping problem (Sections 24.7 and 26.1) that tends to occur with waterborne single coats. Some plants apply two thin base coats, which further minimizes the problems of popping and sagging. Control of sagging during application requires that the waterborne base coat be shear thinning, which also reduces surface distortion during subsequent application of the clear coat. The low solids (15 to 20 NVV) of waterborne base coats facilitates aluminum orientation. Opaque colors can be applied at 25 to 35 NVV. Waterborne base coats are formulated for application at relative humidity (RH) of about 60%, since it is less expensive to increase RH than to decrease it. Acrylic–polyurethane dispersions (PUDs) are in wide use for formulating base coats. For example, base coats are formulated with an acrylic–urethane PUD and an MF resin [22] (Section 12.7.2).

Water-dispersible carboxymethylcellulose acetobutyrate has been shown to provide reduced dry-to-touch times, improved metal orientation, reduced sagging due to faster viscosity build up, and improved leveling in waterborne base coats [23,24]. Addition of alkyl esters of 2,4,7,9-tetramethyl-5-decyne-4,7-diol to a waterborne base coat gives film excellent flow and leveling without orange peel. There is virtually no foaming [25]. A highly cross-linked copolymer of MMA, BA, ethylene glycol dimethacrylate, and acrylamide dispersed in water is used as an additive to waterborne base coats. The acrylic dispersion minimizes strike in by solvent from solventborne clear coat, which results in nonuniformity; it also provides excellent aluminum orientation [26].

Worldwide, in 2004, clear coats were 97.9% high-solids solvent-borne (of which 82.7% were 1K coatings and 15.2% were 2K), 1.2% waterborne, and 0.9% powder [3].

Many types of clear coats are being used and others evaluated. In addition to transparency and high gloss, major considerations include acceptable VOC, resistance to environmental etching, mar resistance, and cost. Most clear coats are acrylic resins with various cross-linkers. The acrylic resin is the major factor controlling VOC content. Considerable research has been aimed at blending low MW polyester and polyurethane polyol resins with acrylic resins to increase solids without reducing the MW of acrylic resins below the level that provides adequate film properties.

Soon after introduction of base coat–clear coats, a serious problem was encountered. After a few days or weeks in some locations, shallow, unsightly pits developed in the clear coat. The suspected cause was acid hydrolysis of cross-links in the top coat, so the coatings were said to have poor *acid etch resistance*. Since other factors are now known to contribute to the problem (Section 5.5), the terminology now used is *environmental etch resistance* [27]. Outdoor tests of environmental etch resistance, performed near Jacksonville, Florida, give useful but still not very reproducible results. No other exposure site has been found that gives better reproducibility. A laboratory test has been developed with cyclic exposure to acidic water, darkness, UV exposure, and humidity exposure [28].

To have good environmental etch resistance, a coating must have good hydrolytic stability under acidic conditions. The activated ether groups in hydroxy-functional acrylic–MF cross-linked films are subject to hydrolysis (Section 11.3). Environmental etch resistance of MF cross-linked coatings can be improved by increasing T_g, which minimizes penetration of water into the film. Since urethanes are more resistant to hydrolysis under acidic conditions, isocyanate cross-linked acrylics generally have superior environmental etch resistance. Many urethane clear coats have been two package (2K) coatings (Section 12.4); however, weighing against the use of 2K coatings is the need for dual spray systems, concern about toxicity, and cost. Another approach is to use hydroxy-functional urethanes. For example, a low MW hydroxy-functional urethane derived from the reaction of a triisocyanate and a diol such as neopentyl glycol has been reported to give good clear coat properties when cross-linked with MF resin [29]. Moisture-curable trialkoxysilylacrylic resins provide good etch resistance [30,31]. Clear coats based on a combination of MF resin and trialkoxysilyl cross-linking tend to have better environmental etch resistance than those based on MF cross-linking alone. Epoxy-functional acrylics cross-linked with dicarboxylic acids or anhydrides also provide good environmental etch resistance. Since reduced solubility of water in films increases environmental etch resistance, highly fluorinated resins (Section 17.1.4) improve environmental etch resistance but are expensive.

Another approach to improved environmental etch resistance is to use MF resin to cross-link carbamate-functional resins (Section 11.3.4) [32]. Such clear coats have been shown to have high mar and acid resistance, exterior durability, and hydrolytic resistance.

Higher solids are also possible. For example, a coating made with the reaction product of hydroxypropyl carbamate with an isocyanate prepolymer derived from IPDI, together with an MF resin and dodecylbenzenesulfonic acid catalyst, has 85 wt% weight solids.

In another study, a carbamate-functional siloxane resin, carbamate-functional acrylic resin, and MF resin was used in formulating clear coats. The carbamate-functional siloxane is prepared by reacting a hydroxy-functional siloxane with 1-methoxy-2-propylcarbamate (see Section 16.1.1.1). The acrylic resin is made by reacting a hydroxypropyl acrylate/butyl methacrylate copolymer with 1-methoxy-2-propylcarbamate. A dispersion of colloidal silica in a solution of the carbamate-functional siloxane is added. The resin composition with nano-pigmentation gives a clear coat with outstanding gloss retention after weathering and mar/scratch resistance testing [33].

Mar resistance is discussed in Section 4.4.2; Ref. [34] provides a review of mechanical properties required for mar resistance. Marring can result from automatic car washes, keys, dry wiping, brushing against tree branches or shrubs, and so on. Mar resistance requires a hard film that is highly elastic; this combination requires compromises. Films with low coefficients of friction improve mar resistance.

Various cross-linking reactions are being worked on. Hydroxy-functional acrylic polymers can be cross-linked with MF resins (Section 11.3), polyisocyanates (Section 12.4), or combinations of the two. Epoxy-functional acrylic resins can be cross-linked with dicarboxylic acids (Section 13.3.2). Trialkoxysilyl-functional acrylic resins can be cross-linked by reaction with atmospheric water [35]. In baking automotive clear coats, methoxysilyl groups of trimethoxysilyl-functional acrylic resins hydrolyze at room temperature to silanol groups, which co-react during baking to cross-link the coating. The scratch resistance before and after weathering is superior to MF cross-linked coatings. Such coatings are reported to be widely used [36].

Use of auxiliary cross-linkers such as blocked polyisocyanates and/or MF resins further enhances the properties obtained with silyl-functional acrylics [31]. 3,5-Dimethylpyrazole- or 1,2,4-triazole-blocked polyisocyanates are preferred, since they permit curing at somewhat lower temperature and do not have the yellowing problem of methyl ethyl ketone–blocked isocyanates (Section 12.5).

MF cross-linked coatings generally provide excellent mar resistance, but as noted previously, generally have inadequate environmental etch resistance. Urethane cross-linked coatings have good environmental etch resistance, but poor mar resistance. Also as noted previously, cross-linking with a combination of urethane and MF and cross-linking silyl-functional acrylics with auxiliary cross-linkers can provide both mar and environmental etch resistance. Mar resistance can be further improved by incorporating some fluoroalkyl acrylate in the acrylic resins to decrease the coefficient of friction. Carboxylic acid cross-linked epoxy-functional acrylics suffer from inferior mar resistance.

Acrylic resins prepared by controlled free radical polymerization (CFRP) are being used in automotive clear coats. The solids of the SuperSolids clear coats are reported to be 65% with the possibility of future coatings with up to 90%. At the same time the scratch and mar resistance are substantially higher. Du Pont has been awarded the EPA clean air achievement award for their work [37]. In contrast to conventional free radical polymerization, CFRP permits preparation of block copolymers so that all molecules of the polymer have at least two functional groups at low MWs. Also, the MW distribution is narrower, which permits higher solids at the same number average MW. (See Section 2.2.1.1 for discussion of CFRP.)

Use of 2K waterborne urethane coatings is growing (Section 12.7.3). In a review of the status of 2K waterborne urethane clear coats, the advantages of using unmodified polyisocyanates and in line mixing of the two components are emphasized [38].

Compared to the effects of conventional pigments, the use of nano-pigments, especially nano-fillers, is said to result in improved scratch, abrasion, heat, radiation, and swelling resistance, decrease in water permeability, and increase in hardness, weatherability, modulus, and strain to failure while maintaining toughness. These properties reflect the high surface area of nano-pigments so that there is an increase in adsorption of resin on the pigment surfaces, hence a larger fraction of immobilized resin. In some cases, the films have two T_gs. When the particle size of the pigments is smaller than the wavelength of light, coatings pigmented with nano-pigments are transparent. Nano-sized ceramic spherical pigments are used in clear coats to reduce marring; the coatings are sometimes called *ceramic paints*.

Nano-sized zinc zirconium silicate has been patented for use as a UV absorber in automotive clear coats. The small particle size does not reduce transparency of the clear coat. Other advantages are insolubility and nonvolatility [39].

A very desirable research goal is development of UV curable automotive clear coats. They would have the advantages of low bake temperature and very low VOC emissions. The rapid low temperature cure can overcome the problem of sagging encountered with very high solids coatings. UV cure coatings on flat panels can give film properties suitable for automotive clear coats. A study of the effect of various photoinitiators, UV absorbers, and hindered amine light stabilizers (HALS) on the curing and exterior durability of UV-cure automotive clear coats over a white base coat and a blue metallic base coat has been published. A clear coat formulated with a specified combination of acrylated resins, photoinitiators, and UV stabilizers, including a HALS derivative, applied over a blue metallic base coat, showed exterior durability after 5 years in Florida comparable to conventional thermal cure clear coats, a surprising technical achievement [40].

However, the UV sources available for flat sheet curing cannot provide uniform cure on a three dimensional object such as an automobile. An investigation of various approaches to UV curing on automobiles has been described [41]. A dual UV/thermal cure coating exposed with a combination of two fluorescent lamps (one with maximum intensity output at 313 nm and the other at 351 nm) and a xenon flash lamp, followed by thermal curing for 30 minutes at 70°C is reported to give excellent film properties. The rapid UV cure minimizes sagging, and the subsequent thermal cure provides cure in the shadow areas.

Waterborne dual UV/thermal cure clear coats are based on a waterborne coating made from a resin prepared by reacting a HEA–HDI allophanate, IPDI isocyanurate, 1,6-hexanediol, thioglycolic acid, and TMP urethane with the residual isocyanate groups blocked with 1,2,4-triazole and neutralized with TEA [41]. A dual cure coating is also formulated with a PUD, an acrylic latex, and adipic dihydrazide. The PUD is made from IPDI, HEA, monomethyl ether of a polyethylene glycol, a sulfonate functional polyester diol, and ethoxylated TMP triacrylate, dispersed in water, and chain extended with hydrazine. The latex is a copolymer of MMA, MAA, EA, and diacetoneacrylamide. See Section 17.6 for discussion of cross-linking via diacetoneacrylamide [42].

Very low emissions could also be achieved using powder coatings for exterior automotive coatings (Chapter 28). Powder automobile top coats have been in a development stage since the late 1960s. In Japan in the early 1980s, powder coatings were used as nonmetallic monocoats. Major limitations are the need for a separate spray facility for each color (or very expensive cleanup between color changes) and the very poor color flop of metallic powder coatings. These limitations do not apply to clear coatings. Major development effort is being applied to powder clear coats, and they are used in at least two European car assembly plants. Fine particle size powder is required to achieve the smooth films needed for clear coats. For example, a powder coating made with an epoxy-functional acrylic resin with average particle size of 10 μm with a narrow distribution of particle size formulated with dodecanedioic acid having a particle size of about 3 μm, gave good surface smoothness [7]. The small particle size of the dodecanedioic acid is required for the extruder mix to achieve the desired properties. Special application equipment is required for application over nonconductive surfaces and to handle the small particle size [43].

Aqueous dispersions of powder clear coats have also been adopted in one auto plant. An aqueous powder coating is prepared by dispersing powder obtained by spray drying a combination of a water-reducible hydroxy- and carboxy-functional acrylic resin, a PUD made with IPDI having terminal NCO groups blocked with a combination of malonic ester and methyl ethyl ketoxime, and tris(alkoxycarbonylamino)triazine [44].

Generally, plastic components are coated separately and then installed on the car body. There would be substantial advantages to a "universal coating" that could be applied to flexible and rigid plastics and steel in one operation. (The design criteria for such a coating are discussed in Ref. [45].) However, formidable problems must be overcome to make universal coatings practical. As discussed in Chapter 31, plastic parts usually require different coatings than metal parts.

30.1.3. Factory Repair Procedures

During assembly of a car, it is common for the coating to be damaged or to have blemishes caused by dirt, resulting in need for repair. The wide range of defects that occur during manufacture and use of automobiles are discussed in an excellent pair of papers [46]. Reducing the frequency and cost of repairs is a major goal in auto production. Some factories have achieved "first-run OK" rates of 90%, but others fall well short of this level. Repairs are made at several stages in the process: after application of the primer–surfacer to the car body, after the base coat and clear coat have been applied, after assembly, and after shipment to the dealer. Once the glass, upholstery, tires, and the like have been installed, the car can no longer be baked at the temperatures for which regular production coatings are designed. Either the entire car can be baked to about 80°C or the area repaired can be heated somewhat above 80°C with infrared lamps.

When cars were coated with acrylic lacquer, repair was relatively simple, since the thermoplastic systems stay soluble in the solvent in the repair lacquer. However, thermosetting enamels are more difficult to repair. Achieving adhesion to the surface of the cross-linked coating is more difficult. Minor blemishes in the clear coat can be corrected by light sanding and buffing; spot repair of small defects going deeper into the paint is sometimes possible. Larger damage, however, may require refinishing of the entire panel to which the damage occurred or even repainting the entire car body. In panel refinishing, the top coat is removed, any bare metal is primed, and special repair base coat and clear coats are applied to the entire panel. Since the coating cannot be baked at a high temperature, additional strong acid catalyst must be added to coatings, which contain MF cross-linkers, to allow curing at lower temperature. The excess catalyst remains in the film and can lead to more rapid hydrolysis. Durability of such repairs is good, but not as good as the original coating. Urethane 2K repair coatings are being used increasingly, since they cure at relatively low temperatures without loss in long term durability. It is unlikely that corrosion resistance of repaired areas is equal to that of unrepaired areas, because the E-coat is often sanded through during the repair process. As with OEM auto finishes, dual UV/thermal cure compositions, which have the potential of minimizing sagging and ensuring cure in shadow areas, are being studied for repair clear coats (Section 29.6).

30.2. APPLIANCE COATINGS

Major markets for OEM appliance coatings are for washing machines, dryers, refrigerators, air conditioners, and ranges. In some cases, single coats are used, but a major part of the market is for primer–top coat systems. For applications that require corrosion protection, such as washing machines and air conditioners, cationic E-coat primers (Section 27.2) are used on the highest quality products. Nonelectrodeposition primers are frequently applied by flow coating (Section 23.3). To minimize VOC, water-reducible epoxy ester–based primers are appropriate.

Cationic E-coat epoxy coatings are used for some applications as single coats. Although epoxy coatings chalk badly on exterior exposure, the drum of a dryer or the interior of an air conditioner does not get exposed outdoors, but a high degree of corrosion protection and impact resistance are needed. The uniform coverage of edges attainable with E-coat permits use of 12 μm E-coats to replace 50 μm solution epoxy coatings on air conditioners, with a substantial reduction in manpower required for application while maintaining the necessary performance [47]. White E-coats have been applied to appliances. Anionic acrylic E-coats can be used on aluminum, but for steel, as discussed in Section 27.1, discoloration results from iron salt formation. Single cationic E-coats based on acrylic resins (Section 27.2) avoid this problem on steel.

Thermosetting acrylic coatings are generally used over primers. For single coat compositions, polyesters are more commonly used because they tend to exhibit better flexibility and adhesion to treated steel or aluminum than do acrylics. The most commonly used cross-linkers are amino resins. For washers and dishwashers, benzoguanamine–formaldehyde resins (Section 11.4.1) are used because they impart greater resistance to alkaline detergents. For other applications, conventional MF resins are used because of lower cost. In end uses for which performance requirements are not severe, such as hot water heaters, lower cost semioxidizing alkyd/MF based coatings may be most appropriate.

Use of powder coatings as top coats for appliance applications has been growing rapidly and is reported to be the largest single market for thermosetting powder coatings [48] (Chapter 28). The long runs of single colors make powder coatings a natural choice for appliances. A limitation is the greater difficulty of achieving good leveling with powder coatings then with liquid coatings. Whereas some orange peel can be desirable to conceal metal irregularities, powder coatings may have too much orange peel. However, in some cases, particularly in Europe, consumers are accustomed to the orange peel typical of porcelain enamels, and the finish from powder coatings is readily accepted. Low VOC emissions, low fire risk (with proper precautions in handling powders), low energy requirements, and reuse of overspray powder are strong economic and environmental reasons for using powders. Hydroxy-functional polyester or acrylic resins are used as binders with a blocked isocyanate or tetramethoxymethylglycoluril (Section 11.4.3) as cross-linker. Alternatively, carboxylic acid–functional resins are used together with triglycidyl isocyanurate (Section 13.1.2) or tetra(hydroxyethyl)adipamide (Section 17.5) as cross-linker.

Another approach to reducing VOC emissions at the appliance manufacturer's factory is to use coil coated metal (Section 30.4). The solvent emissions occur at the coil coating factory, where they can be burned to provide part of the fuel for curing the coatings. A potential problem with coil coated metal is that the edges are bare. The appliance must be designed so that cut edges are turned under and protected by a sealant. In some cases, it is possible to weld through the coating in areas that are not visible.

30.3. CONTAINER COATINGS

Container coatings were historically called *metal decorating coatings*, since a major portion of the business was in coating flat sheets, followed by lithographic printing and a finishing varnish (clear top coat) to protect the ink. There were many uses for such sheets: metal boxes, trays, wastepaper baskets, bottle caps and crowns, and most important, cans. Plastics have replaced coated metal in most of these applications other than bottle caps, crowns, and cans. The field is now usually referred to as *container* or *can coatings*. In the United States alone, about 135 billion cans are produced annually, of which about 100 billion are beverage cans.

Most cans are food or beverage containers, and one of the key requirements is that there be no possibility of introducing toxic compounds into the foods or beverages. In the United States, all can linings must be acceptable to the Food and Drug Administration (FDA) and in the case of meat products, the Department of Agriculture. Contrary to what many people seem to believe, the FDA does not approve coatings; it lists acceptable ingredients. Rules are published in the Code of Federal Regulations (CFR), Title 21, Part 175. The most important is 21CFR175.300, which deals with resinous and polymeric coatings. In most cases if all of the components of a new coating have already been used in can coatings, a new coating will be acceptable. In some cases it is necessary to prove that no material is extracted into any food or beverage that will be packed in the can. However, new raw materials must pass extensive tests. Toxicity considerations affect predominantly interior can coatings, but in some cases there are also restrictions for possible contamination from exterior can coatings. When metal sheets coated on both sides are stacked, the exterior coating on one sheet is in direct contact with the interior coating on the next sheet in the stack. In this configuration, migration of low MW components between coatings is possible.

In the European Union, food contact legislation for coatings is formally different from country to country. But European food contact legislation applicable to plastics is used more and more for can coatings, especially with respect to specific migration limits for chemical starting compounds.

The effect of coatings on the flavor of the food or beverage packed in the container is critical. Although flavor requirements are particularly important for interior coatings, care must also be exercised with coatings for exterior application. Flavor changes can result from extraction of some contaminant from the coating; absorption of flavor agents from the packed food into the coating, reducing the flavor of the food; or failure to isolate the food or beverage from the metal of the can. Flavor can be affected by minute amounts of substances. To assure that all residual solvent and other volatile flavor detractors are driven out of the coatings, high baking temperatures are used. The only way to evaluate the effects of coatings on flavor is by making test packs of the food or beverage in the container and tasting the food or beverage. As a result, major suppliers of can coatings maintain flavor panels of people trained to taste and, particularly, to use consistent words to describe flavors.

For beer cans, a major aspect of the flavor problem is to prevent contact between the beer and the can because metals catalyze flavor changes in beer. For this reason, the final interior coating is spray applied after formation of the can to avoid potential problems from breaks in the can lining resulting from stresses during can forming operations. Linings are spray applied to the interior of soft drink cans not only to protect flavor, but also to protect the can; the acid present in most soft drinks could eat through the metal without a coating barrier. An interesting sidelight on history is that in the early days of packing pineapple products and grapefruit juice in cans, coatings for lining these cans that would resist their high acidity were not available. They were packed in cans with heavy-tin-weight linings to protect the steel bodies. Tin affects the flavor of the pineapple products and grapefruit juice and acts as a bleaching agent, allowing light color fruits and juices to retain their light color. Even though organic coatings that could be used with these products are now available, most are still packed in heavily tinned cans. Apparently, consumers are used to and prefer canned pineapple and grapefruit products that have a tinny flavor.

There are two major classes of cans: three-piece and two-piece cans. In a three-piece can, one piece is the body and the other two are the ends. Metal sheets are coated, or continuous strips of metal are coil coated. Blanks for the can bodies are stamped out of the coated metal, formed, and sealed into the cylindrical body. The body is formed, usually into a cylinder, and sealed by soldering, by welding, or with an organic adhesive. Soldering is now restricted to nonfood cans because of concern about lead toxicity. The side seam is sprayed with a fast drying coating called a *side striper* to cover exposed metal resulting from soldering or welding. Solventborne side stripers predominate; some waterborne stripers, and for containers for aggressive products, powder coatings, are used. The coatings are applied while the metal is still hot, assisting in curing of the coating. The ends are made separately; they are stamped out of coated sheets or coil coated metal, formed, and equipped with a formed-in-place rubber gasket. One end is put on by the can maker; the other end is put on after the can has been filled.

Coatings on metal sheets are generally applied by direct roll coating (Section 23.4). In some cases, transfer rollers with sections cut out are used so that the coating is applied only in selected areas. For example, the edges that will be soldered or welded at the sides of the body of the can are commonly not coated. On coming out of the coater, the sheets are fed onto wickets attached to a conveyor. This permits the sheets to go through the baking oven in an almost vertical position, reducing the necessary length of the oven. Baking schedules vary with the application. Interior food can coatings may be cured in less than a minute at 200 to 210°C, and exterior white and varnish coatings may receive only 10 minutes at 150°C. Inks are applied by offset lithography; in which the ink is transferred from a lithographic plate to a rubber blanket and is offset to the sheet.

There are two processes for making two-piece cans. Drawn and wall-ironed (DWI or D&I) cans are formed by drawing a cup from a flat blank and then ironing the walls to thinner thickness and greater depth. In draw–redraw (DRD) cans, a coated blank is formed into a shallow cup and then drawn one or two more times to achieve the desired height and configuration and shape of the bottom of the can. The other piece of a two-piece can is an end, similar to the ends of a three-piece can.

Examples of DRD cans are shallow cans for tuna fish and taller cans for vegetables and pet foods. Flat sheets are coated, and then the can is drawn and formed. In some cases, such as shoe polish and auto wax cans, printed sheets are formed into two-piece cans. The design must be distortion printed; that is, the print must be designed so that it looks correct *after* the distortion that results from forming. In general terms it costs less to coat and print flat sheets before forming than to coat and print a formed can. The ability of the coating to withstand this degree of formation depends on the depth of draw. It is not just a matter of how deep the can is, but also how wide. Forming a large diameter can involves less distortion than forming a narrow can; a deep can involves more distortion than a shallow can. Bottle caps and crowns are made from coated and distortion printed sheets and then are punched out and formed.

Beverage cans and some food cans are DWI cans; uncoated metal is drawn and formed before coatings and inks are applied to the exterior, and a lining is sprayed into the interior of the can. The exterior coating is applied by rotating the can against the transfer roll of a small coater, and inks are transferred from a litho plate to a soft rubber roller that in turn transfers the inks to the can surface. Baking is done in short time cycles at high temperature. Some lines produce over 2000 cans per minute. It is estimated that the coating reaches a peak temperature of about 205°C for only about 1 second. Only partial cross-linking occurs in the short time. The cross-linking is completed when the can is baked again after the interior lining is applied. Interior coatings are applied by spray. A small spray gun is inserted automatically into a spinning can; the gun sprays and then is pulled out of the can. To assure removal of essentially all solvent, the final part of the curing is done with air directed into the can bodies. Typically, the cure schedule is about 2 minutes at 200°C. Final forming of the top of the can to fit the end is done after the coating and printing are completed.

There are three major types of metal used in cans: tin plate, steel, and aluminum. The choice of metal depends on the end use. Beverage cans are two-piece aluminum cans. Pressure from the carbonation of either soft drinks or beer keeps the thin walled aluminum cans sufficiently rigid. In Asia and Europe some tinplate cans are used. Most food cans are three-piece cans made from tin-plated steel. In the case of food cans, which do not have significant interior pressure, aluminum does not compete with steel because thicker walls of aluminum would be required to achieve adequate rigidity. However, many shallow fish cans are being made with aluminum. There has been some discussion of using aluminum for food packing by putting a small piece of dry ice into the pack before sealing. Vaporization of the CO_2 provides the pressure necessary for rigidity. However, people associate slightly bulging food cans with spoilage, so consumer acceptance has been slow. A large fraction of pet food cans are made from treated steel—called *black plate*—since it is less expensive and the highly reflective tin coating is not needed.

30.3.1. Interior Can Linings

The composition of interior can coatings depends on the food or beverage to be packed in the can. In most cases, if the food is to be cooked, it is cooked in the can. A common cooking cycle is 60 minutes at 121°C. Most beer is pasteurized in the can at a lower temperature. In both cases, the interior and exterior coatings must maintain their adhesion and integrity through the cooking or pasteurizing process. A paper has been published reporting studies of tests for dry and wet adhesion of several coatings on various tin plate substrates. It was found that electrochemical impedance spectroscopy (EIS) was the most reliable test procedure. Organosol (Section 17.1.2) and epoxy–phenolic (Section 13.3.1) coatings showed the best dry and wet adhesion, both before and after sterilization [49].

Most vegetables and fruits are packed in cans with an interior coating called an *R enamel*. Historically, R enamel was a phenolic varnish. Now, it is more common for R enamel to be a phenolic resin modified with some drying oil derivatives during its synthesis or an epoxy–phenolic coating—a resole phenolic (Section 13.6.1), with a BPA epoxy and phosphoric acid catalyst. To achieve adequate flexibility, high MW epoxy 1007 or 1009 resins (Section 13.1.1) were formerly used. New resole phenolics have been developed that can be used with lower MW 1001 or 1004 BPA resins, thus decreasing VOC emissions [50]. For packing vegetables that give off hydrogen sulfide during cooking, such as corn, fine particle size ZnO pigment is dispersed in the coating, which is called a *C enamel*. The ZnO reacts with H_2S to form white ZnS. This prevents or conceals formation of unsightly black tin sulfide by reaction of tin oxides with H_2S.

Waterborne coatings have also been developed to reduce VOC emissions. Epoxy–phenolic emulsions with nonionic surfactants have been used but tend to have marginal properties. Waterborne coatings based on amine salts of a carboxylic acid–functional epoxy phenolic are said to have properties superior or equal to those of solventborne coatings [51].

Cans for fish and other oily foods are generally lined with an epoxy-phenolic or resole phenolic resin (Section 13.6.1). To obtain sufficient formability to permit drawing of two-piece fish cans, cross-link density is reduced by using a mixture of *p*-cresol and phenol in making the resole phenolic resin. Poly(vinyl butyral) is commonly incorporated in the formulation to promote adhesion and act as a plasticizer. The extent of cross-linking is adjusted for flexibility, together with resistance to swelling and softening by oils from the fish (and in some cases, additional oil in which the fish is packed), during processing and storage. Thin film thickness is used; this helps permit forming without film rupture. Aluminum flake pigment is sometimes incorporated in the coating to minimize permeability. In linings for meats such as ham, one of the key requirements is that the coating permit the meat to slide out of the can easily after the top is removed. This requires incorporation of a release agent, such as petroleum wax, in the can lining.

An increasing fraction of food cans are DRD or DWI two-piece cans. The draw–redraw process requires that coatings have a greater degree of ductility than the coatings used for interiors of three-piece food cans. Most commonly, vinyl organosol (Section 17.1.2) coatings lightly cross-linked with phenolic resins or MF resins have been used, since the vinyl chloride copolymer binder shows ductility below T_g [52] (Section 4.2). In some European countries, there is concern about possible toxic reaction products from HCl scavengers and toxic emissions from factories recycling vinyl chloride copolymer–coated cans [53]. This has led to work on other more distensible coatings. For example, epoxy resins have been designed that will take considerably deeper draws than those required for conventional BPA epoxy coatings [54].

Large volumes of coatings are used for lining beverage cans. Historically, most spray applied interior coatings were solventborne vinyl chloride copolymers or high MW epoxy/amino resin/phenolic coatings. The volume solids of these coatings at application viscosity were very low, 12 to 15% NVV. The high cost of solvent and the high level of VOC emissions forced a change. Waterborne coatings based on acrylic–epoxy graft copolymers are now widely used in lining both beer and soft drink cans [55,56]. Styrene/ethyl acrylate/acrylic acid side chains are grafted onto a BPA epoxy resin. The resin is "solubilized" with dimethylaminoethanol (DMAE) in glycol ether solvent and reduced with water (Section 13.4). To lower the cost of some soft drink can linings, it has been possible to use a special latex binder blended with small amounts of the graft copolymer and epoxy phosphate as adhesion promoters.

Concern has been expressed about use of BPA epoxy resins in interior coatings, since BPA is an estrogen mimic. Procedures for more accurate analysis of BPA extractables have been published [57]. Studies of extractables from beverage can linings have shown no detectable BPA using analysis methods sensitive to 5 ppb. Average migration from food can linings was 37 ppb, a level that is estimated to lead to a maximum potential dietary exposure of approximately 2.2 ppb, which is below the levels considered to be of concern [58].

30.3.2. Exterior Can Coatings

Most food cans are not coated on the outside; rather, paper labels are used. The appearance of coated and printed cans is more attractive than that of paper labels. Some food and all beverage cans are coated and/or printed. Printed metal cans are not affected by water such as from ice chests or condensation when cans are brought out of a refrigerator into humid air.

The general procedure used on the exterior of sheets for the bodies of three-piece cans is to apply a base coat, often called an *enamel*, print on the base coat up to four colors by offset lithography, and finally, top coat with a finishing varnish. The most common color for base coats is white, but a variety of colors are used for specific products. Color stability and lack of color change on baking and can processing (sterilization) are critical requirements. To minimize VOC emissions, waterborne acrylic coatings cross-linked with MF resins are widely used vehicles. The lithographic printing inks are either baking or UV cure inks. The vehicles for the baking inks are long oil alkyd resins with some MF resin cross-linker, while the vehicles for the UV cure inks are blends of acrylated epoxidized soy (or linseed) oil with acrylated epoxy resin and acrylate reactive diluents (Section 29.2.4).

The finishing varnishes are also acrylic–MF or sometimes polyester–MF binder compositions. To decrease friction in forming machines and conveyors, the finishing varnish commonly contains a small amount of petroleum wax or fluorinated surfactant to reduce surface tension so that the cans will have a low coefficient of friction. Two inks are applied, the sheets are baked, the other two inks are applied, the finishing varnish is applied, and the sheets are baked again. This is called *wet-ink varnishing*, since the varnish is coated on the printed surface before the last two inks are cured. With UV cure inks, each ink is partially cured by passing under a UV lamp before the next ink is applied. Commonly, finishing varnishes are not used over UV cure inks.

For 2-piece cans, white waterborne acrylic base coats are used. The film thickness varies from 8 to 15 μm; even at 15 μm, hiding is less than 100%, but the coating is definitely white. An increasing proportion of two-piece cans are simply printed with inks 2 to 3 μm in thickness with no base coat. Appearance of these cans is inferior, but they cost less than cans that are coated with a base coat before printing. A transparent yellow–brown base coat is used on some cans to give a bronze or gold color to the relatively shiny metal surface.

UV cure coatings are also used on some beverage cans (Chapter 29). Exterior finishing varnishes are acrylated resin coatings cross-linked by photogeneration of free radicals. Coatings for the exterior side of can ends are epoxy resins cross-linked by photogeneration of acid. The UV cure end coating is applied to the side of the sheets that will be on the outside of the cans and passed under the UV lamps, giving a partially cured film; the other side, which will be on the inside of the can, is coated with an FDA-listed epoxy–phenolic thermal cure coating. When the epoxy–phenolic is cured in an oven, the cure of the UV cure epoxy coating is advanced to completion by the photogenerated acid still present in the films. This thermal complement to the UV cure also enhances adhesion of the coating.

30.4. COIL COATING

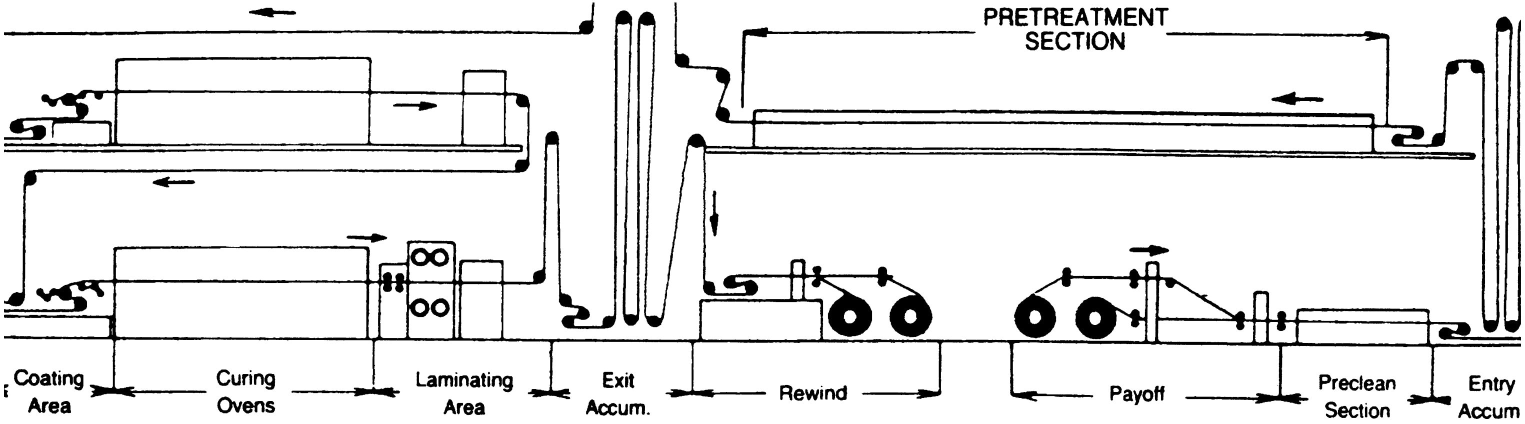
Steel and aluminum are manufactured in long, continuous strips that are rolled into coils. In many cases, the coils are cut, formed, and fabricated before they are coated, as in production of automobiles, for example. In other cases, it is possible to coat metal coils and later fabricate the final product from the precoated metal. When precoated metal can be used, there can be substantial advantages (Section 30.4.1), and coil coating has grown into a major industrial coating process [59] whose growth continues.

Coil coating started in 1935 as a process for coating venetian blind slats. The strips of metal were about 5 cm wide, and the line was run at a rate of about 10 m min^{-1}. Modern coil lines can coat metal up to 1.8 m wide at rates as high as 275 m min^{-1}. Most lines run at a rate of around 100 to 200 m min^{-1}. A schematic drawing of a coil line is shown in Figure 30.1.

The metal is shipped from the steel or aluminum mill in coils weighing up to 25,000 kg that are 0.6 to 1.8 m wide and 600 to 1800 m long. In some lines, as shown in Figure 30.1, the first step is precleaning; brushes remove any physical contaminants. The strip then goes to the entry accumulators. The rollers of the accumulators move apart to accumulate a significant length of coil, so that when one coil is about to run out, the next coil can be stitched (welded) on while the accumulator rolls move together, supplying strip to the line without interruption of the process. After the stitching is done, the new coil is fed to the coating line. As the process continues, the accumulator rolls gradually separate to store strip for the next change of coils.

Next, the strip is carried through the metal treatment area. Detergent washing and rinsing are followed by application of various conversion coatings, including phosphates, complex oxides and chromates, water rinse, and finally, chromic acid or other rust-inhibiting rinse. Because of concerns about toxicity of chromates, proprietary chromate-free conversion coatings are being adopted. All the cleaning and conversion coating procedures must be designed to work at high speeds. Since the metal is moving at 100 to 200 m min^{-1} or more, the total time for cleaning and treatment is on the order of a minute or less. Next, the strip is carried through a dry-off oven and finally, to coaters and a baking oven. A laminator is also shown in Figure 30.1, although laminating of film in line with coating is not common. It is more usual to have two coating stations, each followed by a baking oven. Often, a primer and a top coat are applied on one side of the strip and another coat on the back side. It is fairly common to coat, cure, and then print one or more colors.

Most coatings are applied by reverse roll coating, but sometimes direct roll coating is used for thinner films (Section 23.4). Reverse roll coating is used for thicker films for which close control of thickness is critical and for which the flow advantages that result from the wiping action, in contrast to the film splitting action in direct roll coating, is important. To achieve even film thickness across a strip 2 m wide, the rolls have to be



Pre Finish Metals 72-in. coil coating line will begin at "payoff," at right, and will follow directions indicated by arrows, finishing at "rewind."

Line #6 Specifications

Strip widths 24.0" to 72.0"
Strip thickness 0.018" min. to 0.135" max.
Speeds up to 700 f.p.m.
Maximum coil size 50,000 #
Coil I.D. 20" or 24"
Coil O.D. up to 78"
Capable of laminating top and bottom side

Capable of applying primer and finish coat to both sides in one pass
Capable of paint finish embossing 0.007" to 0.016"
Capable of gravure and flexographic printing
Shipping and receiving facilities capable of handling more than 35 railroad cars and 90 trucks per day
Housed in a 266,000 sq. ft. building on a 52 acre site

Figure 30.1. *Coil-coating line. (From Ref. [59], with permission.)*

crowned, that is, designed so that their diameter is greater in the middle than on the edges, since the pressure involved tends to bow the rolls to a small degree. To avoid damage to the rollers, the line is programmed so that very shortly before a stitched section joining two coils passes through the coating nip between the rollers, the rollers are automatically separated slightly and then almost immediately returned to normal operating pressure.

Coil coating of embossed metal tends to hide the embossing. To retain the pattern, after coating, the stock moves under a high-velocity air knife, which removes excess coating from the embossed areas. As a result, the coil is reported to have a uniform thickness of coating on the entire surface, which maintains the embossed design [60].

At the high line speeds, the dwell time in the ovens is less than a minute, even with long ovens. In some cases, the dwell time is as low as 10 seconds, but more commonly is in the range 12 to 45 seconds. After a short initial period, hot air is directed over the surface of the coatings at high velocity. The air temperature can be as high as 400°C. The temperature reached by the coating on the metal is the critical temperature for curing the coating. This temperature cannot be measured directly, but is closely related to the metal temperature, which can be measured. The temperature considered most important is the *peak metal temperature* (PMT); this can be as high as 270°C. After the coating is baked, the strip passes through the exit accumulator to the rewind. The exit accumulator stores coated strip during removal of a coated coil. In some lines the strip passes over chilling rolls, or through water quenching, to reduce the temperature before the strip is rewound into a coil. The pressure in the center of the rewound roll is very high; consequently, the T_g of the coating on the metal must be very high, to avoid blocking. For most applications, however, the cross-link density must not be so high that the film loses elasticity, which is needed to allow subsequent fabrication of the steel into its final form.

Near infrared curing of coil coatings has been started on at least one coater. Cure is reported to be complete in 1 to 4 seconds compared to 12 to 45 seconds on a conventional line.

The exhaust air from the hoods over the coaters, and particularly from the oven, contains solvents. On most lines, the exhaust air streams are used as part of the air used to burn the gas to heat the ovens or are fed through an oxidizer. In this way, part of the residual heat from the oven exhaust is recycled and the solvent is burned. Burning the solvent essentially eliminates VOC emissions, and the fuel value of the solvent is recovered. As a result, there has been less incentive to change to waterborne or high-solids coatings in coil coating applications than in other applications. There are still pressures to reduce solvent content because the fuel value of solvents is low compared to the cost of the solvents and because some lines are not equipped to burn solvent. New regulations controlling emission of hazardous air pollutants (HAPs) that will go into effect in 2006 require that stack emissions not exceed 0.38 lb of HAP per solid gallon of coating applied. Most coil coaters can now meet this requirement, but some will have to upgrade their lines. This addition to the VOC requirements will give a further advantage for coil coating over many other application methods.

Coatings on aluminum are frequently single coats; but on steel, primer–top coat systems are most widely used. Binders for primers were traditionally based on BPA epoxy resins; epoxy esters and epoxy–MF resins are examples. However, polyurethane, polyester, and waterborne latex primers are being used increasingly.

Many types of coating binders are used for top coats. Oxidizing alkyds with MF resin are the lowest cost and are sometimes used on the reverse side of the coated strip as a *backer*; polyesters are supplanting alkyds in this application. Backer coatings may be pigmented or unpigmented, and they contain a small amount of incompatible wax. The purpose of the backer is to avoid metal marking of the top surface coating by rubbing against a bare metal reverse side of the coil. Alkyd–MF coatings are also used as top surface coatings for which corrosion resistance requirements and/or exterior durability requirements are modest. Polyester–MF binders are widely used, especially as single coats; exterior durability and corrosion protection are generally superior to those obtained with alkyd coatings. Over the years, incremental improvements in the design of polyester resins and in formulations have led to polyesters with substantially improved outdoor durability. Polyester–blocked isocyanate coatings have been used to a degree for applications for which abrasion resistance and flexibility are particularly important. Close temperature control in the ovens is important with urethane coatings, since urethanes may discolor and decompose relatively rapidly at the baking temperatures involved in coil coating. Thermosetting acrylic–MF coatings are used, generally over primers.

For greater exterior durability, one can use silicone-modified polyesters and silicone-modified acrylic resins (Section 16.1.2). For example, one might use 30% silicone-modified polyester resin with a small amount of MF resin as a supplemental cross-linker as the binder for color top coats for high performance residential or industrial siding. In the same quality line, the white top coat might well be just a polyester–MF coating. Although the white might start to chalk slightly after many years of outdoor exposure, this would not affect the appearance adversely. However, even a small amount of chalking of a color, coating makes an easily seen change of color, due to the change in surface reflection. Such changes are particularly serious in exterior siding, since the exposure varies depending on the location on the building. The resulting nonuniform chalking of the color coating is very evident. For the highest exterior durability, polyvinylidene fluoride resin coatings are used (Section 17.1.4). In some cases, such coatings show only slight indication of change after exposure outdoors for more than 25 years.

Organosol and plastisol coatings are used for some coil coating. The relatively low viscosity organosols are applied at about 25 μm, and the higher viscosity plastisols are used for film thicknesses of 100 μm or more. As discussed in Section 17.1.2, the vehicle in these coatings is a dispersion of vinyl chloride copolymer in plasticizer and solvent. Such coatings provide reasonable exterior durability with excellent fabrication properties. They have the advantage that they need not be cross-linked and hence can be run with as little as a 15 second dwell time in the oven. Solution vinyl resins are used for coil coating metal for can ends for beverage containers.

Increasing use is being made of latex vehicles for coil coating. They have the advantage of high MW, so mechanical properties can be achieved without need for much, if any, cross-linking. High-gloss coatings cannot be made, and there can be greater problems of leveling than with solventborne coatings. Leveling problems are minimized by using reverse roll coating and by using associative thickeners to control viscosity. Associative thickeners minimize latex particle flocculation relative to conventional water-soluble polymeric thickeners such as hydroxyethyl cellulose (Sections 24.2 and 32.3).

An extensive study of the corrosion resistance of 12 coil coated sheets at three South American sea shore locations has been reported. Location 1 was marine-polar, with low temperature, high humidity, very low SO_2 and Cl^- exposure, and little sun. Location 2 was marine with moderate temperature, high humidity, moderate SO_2 and Cl^- exposure, with high sun exposure. Location 3 was marine-desert with high temperature and humidity, very high SO_2 and Cl^- exposure, and high sun exposure. At location 1, the best performance was shown by an alkyd–MF coating on galvanized steel. At location 2, the best performance at incision marks was a polyester primer with chromium pigment on Galvalume, on the unruptured surface the best performance was with three samples: an epoxy–acrylic primer with a silicone-modified polyester top coat on galvanized metal, a polyester primer with a silicone-modified polyester top coat on Galvalume, and a polyester primer and polyester top coat on Galvalume. At location 3, the best performance was a polyester primer and polyester top coat on Galvalume. At all three locations, the poorest performance was an epoxy primer with a polyester top coat. No details were given of the binders in the various coatings [61].

UV cure coatings are potentially of great interest in coil coating because of rapid cure and limited emissions. Active research is under way, but actual production is limited so far. Cationic UV cure epoxy coil coatings on tin plate are used for the exterior side of can ends. The superior adhesion of epoxy coatings makes them preferable to acrylate coatings for this application. In some cases a UV cure coating is applied on one side of the strip and UV cured. Then a thermally cured epoxy coating is applied on the other side. When the strip is put through the oven to cure the thermally cured coating, the cross-linking of the UV cure coating is also advanced.

Powder coatings are also being applied to coil stock. One approach, which is in limited commercial use, is to electrostatically spray the strip with automatic spray guns [62]. A disadvantage of this process is that line speeds are slow. Another process being introduced is to run the coil strip through a “cloud” of electrically charged powder particles; the strip then passes into an induction heating oven for fusing and curing [63]. Since there is no contact of rollers with the coil, embossed or perforated metal can be coated. It is projected that line speeds can be higher than for conventional coil coating.

30.4.1. Advantages and Limitations of Coil Coating

Important advantages of coil coating have promoted the growth of the business to a major component of industrial coatings. For long production runs, the cost is low compared to that of coating preformed metal. The rate of application of coating is faster and the labor cost is lower. Coating utilization is essentially 100%. Oven designs are such that energy use in curing is much more efficient. In general, floor space requirement is much less, so capital cost for buildings is lower. Since solvent is restricted to the immediate area of a roll coater, fire hazards and toxicity hazards are reduced over those of spray application. Since in most cases, solvent is incinerated, VOC and HAP emissions are generally very low. Film thickness of the applied coatings is more uniform than is generally obtained in coating preformed products. Since the coatings are applied on uniform thickness metal, curing of all parts of the coating tends to be more uniform than in curing coatings on fabricated products. For many applications, the performance of coil coatings is superior. This difference is particularly evident when comparing high quality precoated exterior siding to house paint. A large part of this difference results from the superior performance of baked coatings to that of air dry coatings. The manufacturer using precoated metal gains some substantial advantages. The VOC and HAP emissions and fire hazards associated with coatings application are eliminated, and insurance costs drop. There is no waste disposal problem with sludge from spray booths. There may be a substantial saving in floor space.

There are limitations to coil coating. The capital cost of a line is very high; therefore, lost production time in shutdowns is expensive. It is economical only for fairly long runs of the same color and quality of coating. The cost of changing color is high because the coater must be shut down for cleanup. However, many modern lines have multiple coating heads, which substantially reduce downtime due to color changes. In a line of coated metal with several colors, the inventory cost can be high, since an inventory of several colors must be kept. If a stylist changes colors, the obsolete inventory cost can be high or, said another way, the flexibility of changing colors is more limited than when the assembled product is coated.

Color matching is a challenge to a coil coating supplier. Generally, very close color matches are needed. Hiding is less than complete, and the color of the metal or primer affects the color of the coating. Color can also be affected by the high temperature baking schedule. It is not possible to duplicate in the laboratory a curing schedule of 30 seconds with high-velocity 400°C air. A color matcher must learn to compare color differences that can be expected in the laboratory with what will happen on a particular coil coating line and then do the color matching, taking the difference into consideration.

The coated metal must be able to withstand fabrication into the final product without film rupture. This may require acceptance of somewhat softer, more flexible films than could be specified if the product were coated after fabrication. When the coated metal is die cut to make the eventual product, bare edges of metal are exposed. Welding of coated metal can be a problem. Coatings that do not interfere with the welding process are available; however, the appearance of the coated surface is destroyed around the welded area. In some applications, bare edges are not a problem and the product is not welded. In other cases, it is critical for the designer of the finished product to ensure that the cut edges do not show and are not in locations where they will be subject to corrosion, and that any welding will be done in areas that will not show.

Examples of large applications for coil-coated metal are siding for residential use, original siding for mobile homes, venetian blinds, rain gutters and downspouts, fluorescent light reflectors, appliance cabinets, can ends, and can bodies for fruits and vegetables. Newer examples include antimicrobial coil coatings for making stock for air conditioning duct work, metal kitchen counters, refrigerator boxes, walk-in coolers, and the like. The antimicrobial agent is called AgION, a silver-ion-on-zeolite product. Legislation is increasingly requiring many roofing materials to have high reflectance and high emittance, White and light colored coil coated metal has high reflectance, thus reducing heat absorption. Furthermore, infrared reflective pigments (Section 20.2) enable formulation of "cool building" coatings in a broad range of colors. However, some radiation is absorbed, so there is still heating. This heat is lost by thermal emittance into the atmosphere and into the building [64].

Preprimed weldable coil stock is used to a limited extent in some automobile plants to replace E-coat primer on fabricated cars. There is also the possibility of E-coating the car bodies assembled with precoat stock, presumably with a conductive coil-coated primer.

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31

Product Coatings for Nonmetallic Substrates

Many products made from wood and plastics are coated in factories; examples are wood furniture and paneling, hardboard paneling and siding, plastic auto body parts, and computer cases. Do-it-yourselfers paint wood products at home, but the products they use are generally different and are discussed in Chapter 32. Other nonmetallic substrates are also coated in factories (e.g., paper, textiles, and films). Because of space limitations, we will focus on wood, plastics, and glass.

31.1. COATINGS FOR WOOD

The world market for resins for *industrial wood coatings* in 2004 (Table 31.1), as reported in a Bayer study, had a total value of 1.9 million euros [1]. The world market for formulated coatings for industrial wood finishing in 2004 was 2.2 million metric tons. The percentage of each type is shown in Table 31.2. The U.S. market for wood finishes dropped from 303 million liters in 1995 to 202 million liters in 2003. The primary cause was the marked increase in furniture imports from Asia. This is consistent with the large remaining market for nitrocellulose lacquers, much of which is used in the Chinese furniture industry [2].

31.1.1. Coatings for Wood Furniture

There are many styles of furniture, and furniture coatings are affected by styling. Furniture styling and manufacture are different in North America than in Europe; most of our discussion deals with the U.S. market. A large fraction of wood furniture made in or imported into the United States is styled to resemble antique furniture. Styling is generally

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Organic Coatings: Science and Technology, Third Edition, by Zeno W. Wicks, Jr., Frank N. Jones, S. Peter Pappas, and Douglas A. Wicks

TABLE 31.1. Worldwide Market for Resins and Intermediates for Industrial Wood Coatings, 2004

Resin Type	Percent
Nitrocellulose	7
Alkyds	6
Polyols	18
Polyisocyanates	19
UV cure (urethane acrylates)	15
Acrylic	10
Unsaturated polyesters	10
Polyurethane dispersions	15

Source: Ref. [1].

initiated in the high end of the market: expensive wood furniture that involves a great deal of hand labor and artistry in its manufacture. A representative finishing process is described in some detail since a major part of furniture is finished to resemble high style furniture but uses manufacturing and finishing techniques that permit lower costs.

Fine quality furniture is made from a combination of woods. The tops and sides are made from five-ply *plywood*, the legs and rails are made from solid wood, and carved-wood decorative pieces are commonly attached to the furniture. The center ply of the plywood can be wood, but other cores, such as *chipboard*, are used. Chipboard is made by pressing wood chips and an adhesive binder into sheets and curing the sheets. Chipboard is a desirable core material because it is more dimensionally stable than wood. A ply of wood *veneer* is laid up with glue on each side of the core. Another layer of veneer is laid up on each side, cross-grain to the first layer. The top, or face, veneer, the side seen on the furniture, is usually from a hardwood selected for the beauty of its grain pattern.

Grain patterns are affected by the kind of tree from which the wood is obtained and by the way the veneer is cut from a log. The top of a table is generally too large for the face veneer to be made from only one piece; it is laid up from several pieces. They are carefully selected and put together to give a particularly beautiful pattern. Adhesive is needed not only between the layers in the plywood, but also to connect the edges of the individual pieces of veneer in the top face. Each tabletop is unique because the grain patterns in the separate pieces of veneer are different. In many cases, elaborate patterns are laid up. Many kinds of wood are used: pecan, walnut, and oak are among the most commonly used. All these hardwoods have open pore structures and prominent grain patterns. In some styles, mahogany, which has straighter grains and shallower pores, has been

TABLE 31.2. Worldwide Market for Industrial Wood Coatings, 2004

Coating Type	Percent
Nitrocellulose lacquers	31
Polyurethanes	41
UV curing	3
Acrylic	12
Unsaturated polyester	6
Waterborne	7

Source: Ref. [1].

popular. Woods that have little pore structure, such as maple and birch, have a more limited market than those with bold patterns.

In U.S. furniture manufacturing, the various components are cut for a run of the same style and sets of furniture. The furniture is assembled before it is finished. The various components are of different colors; if the final color of the furniture is to be lighter than any part of any of the component pieces, the wood is *bleached* with a solution of 30% hydrogen peroxide; the bleaching solution is activated with sodium or potassium hydroxide. Bleaching is now seldom done in the United States.

In earlier times the next step was to spray a dilute solution of hide glue on the surface. Now, low solids poly(vinyl alcohol) size solutions are used. The process is still called *glue sizing*. After the size has dried, the wood fibrils that stick up from the surface are stiffened so that the surface can be smoothed by sanding to minimize concentration of stain at the fibrils, which would give an unattractive appearance. With some woods, sanding without glue sizing gives satisfactory results.

Next, the wood is colored with a solution of acid dyestuffs in solvent or with dispersions of transparent pigments. The *stain* is selected and applied to give the overall base color to the furniture, Spraying stain requires skill to obtain even coloration.

A *wash coat* is a low solids [less than 12 wt% (NVW)] low viscosity lacquer. A thin layer is applied to minimize displacement of the stain, to stiffen wood fibers for sanding, and to prepare the surface for the next step, filling.

The purpose of *filling* is to color the pores of the wood to emphasize the grain pattern and to fill the pores to near the same level as the rest of the wood. The pores must be filled with the colored filler without leaving filler on the surfaces between the pores. Usually, the color of the filler is a dark brown and the stains are lighter yellowish or reddish browns, but for special effects, one can use white filler with black stain or other color combinations. The vehicle is linseed oil and/or a linseed long oil alkyd with a hard resin such as limed rosin, and driers with aliphatic hydrocarbon solvents. The color pigments used for dark colors are natural earth pigments with a high loading of inert pigments at a PVC over 50%. The entire piece of furniture is sprayed with a liberal coating of filler, the filler is "padded" into the pores by rubbing vigorously with a pad of cloth, and then excess filler is wiped off. If the wood has been properly wash coated and the filler is wiped evenly when the degree of solvent flash off is right, the pores of the wood are filled. Adequate drying of the filler is critical because residual solvents can result in shrinkage, graying, and loss of adhesion of succeeding coats.

A *sanding sealer* is then applied. Its purpose is to prepare the surface for application of top coat. The sealer must be easy to sand smooth without "gumming" the sandpaper. A formulation for a typical sanding sealer includes nitrocellulose; a hard resin, such as a maleated rosin esterified with a polyol; and a plasticizer such as blown soy oil (Section 14.3.1). Sanding sealers contain 3 to 7% of zinc stearate, based on the lacquer solids, to aid sanding. After diluting with lacquer thinner to spray viscosity (about 20% volume solids), the sealer is applied and after drying is sanded smooth. UV cure sealers with very low VOC are being used by some manufacturers, especially under waterborne coatings.

Wood is not naturally as uniform in color as the overall staining makes it. By spraying different shades of stains to selected areas, the color can be varied and the grain highlighted. Shading is a skilled art; in recent years *shading stains* have been replaced in large measure by *padding stains*. Padding stains are made with similar dyes but have some binder and somewhat slower evaporating solvents; they are applied by hand with a rag moistened with the stain, and less application skill is required.

The furniture is then sprayed with a *top coat*. Nitrocellulose is used as the primary binder in high-style furniture lacquers for three major reasons. First, the appearance of furniture finished with nitrocellulose lacquers is outstanding; the lacquers provide an appearance of depth, fullness, and clarity of the grain pattern that has not been matched by any other coating. Second, lacquers dry quickly, so they can be rubbed a short time after application and then packed and loaded into a truck for shipment without *printing*. The term *printing* in this context means surface imperfections resulting from wrapping material denting the surface of a coating that is too soft. Third, lacquers are thermoplastic and permanently soluble, so they are easily repaired in case of damage during shipment. The mechanical properties of the final film are better with higher molecular weight (MW) nitrocellulose, but solids are reduced. A hard resin such as an esterified maleated rosin is blended with the nitrocellulose. Plasticizers, usually including a short oil coconut alkyd (Section 15.4), provide the required flexibility. The balance of nitrocellulose, plasticizer, and hard resin is critical. If the coating is too soft, it will be difficult to rub; if it is too hard, the lacquer will be subject to cracking as the wood expands and contracts with changes in moisture content and/or exposure to rapid temperature changes. If the lacquer is applied over a pale colored wood, UV absorber (Section 5.2.1) is added to reduce yellowing of the wood. Citric acid is also commonly added to chelate iron salts that produce reddish colors with phenolic compounds naturally present in wood.

After the initial coat of top coat is applied, the next step is *distressing*. Distressing uses a variety of techniques to give an antique appearance to furniture. Stylists are not trying to make fake antiques; rather, the furniture is styled to have an antique appearance. In the old days, quill pens with black india ink were used, resulting in drops of ink falling on tabletops. Now little drops of black pigment glazing stain are applied. Sometimes, a colonial forefather was a little tipsy when he sat down to write and put the feather end of the quill pen into the inkwell and then set it down on the tabletop. Sometimes, colonials walked on their tables with hobnailed boots or banged the tabletop with their pewter beer mugs. It is startling to walk by the finishing line in a fine furniture factory and see someone swinging a chain at the tops of those carefully prepared pieces of furniture. Another common thing to see is a little black pigmented stain rubbed into inside corners. Over the years in antique furniture, dirt accumulated in corners, so the new furniture is made permanently dirty in these areas. Proper distressing requires artistic skill.

Finally, another coat of top coat is applied and the lacquer is dried, usually in a force dry oven at 40 to 60°C. Then the lacquer surface is *rubbed*, first by sanding with fine sandpaper and a lubricant and then rubbing with cloth and rubbing compound. The result is a soft appearing low gloss finish.

While the solubility of nitrocellulose lacquer finishes is an advantage in that it permits easy repair, it can also be a disadvantage. If solvents such as nail polish thinners are spilled on a lacquer surface, the finish will be marred. A way of solving this problem and still obtaining the beauty of a nitrocellulose finish is to add a small amount of polyisocyanate cross-linker to the lacquer just before application. The isocyanate cross-links with the hydroxyl groups on the nitrocellulose. If this step is to be done, all solvents must be urethane grade, that is, contain no more than traces of alcohols and water, and the nitrocellulose must be wet with plasticizer rather than with isopropyl alcohol.

Wood furniture produced by this process is beautiful but expensive. A much larger part of the market is for furniture designed to look as much as possible like this high-style furniture but which can be manufactured and finished at lower cost. There are many approaches with varying degrees of cost savings; an intermediate cost approach is described next.

Instead of using plywood tops and sides made with expensive hardwood veneers that must be finished painstakingly, one can use printed tops and sides with solid wood legs and frames. *Particle board*, that is, pressed wood chips and particles with a resin binder, is first filled with a UV cure filler. Note that this is a very different filler than referred to above for filling the pores in wood. *Particle board* has a rough surface, and before use in furniture tops, it must be coated with a filler and sanded smooth to give an even surface for the application of a base coat and printing. This was originally done with highly pigmented solventborne coatings applied at about 30 vol% solids. However, the low solids requires two or three coats to give sufficient film thickness to permit sanding to a smooth surface without cutting down into the substrate. With UV cure, the volume loss is only a few percent, so an adequate layer can be applied in one coat. This together with the fast cure means that UV cure fillers are less expensive to apply. The pigments used are clays and silica that absorb or scatter only minor amounts of UV. Aluminum trihydroxide absorbs still less UV and may be a particularly effective inert pigment [3]. The inert pigment minimizes the problem of oxygen inhibition. The high level of pigmentation leads to poor leveling, but it does not matter, since the surface is sanded. Furthermore, the pigmentation results in less resin being at the surface, so air inhibition is less of a problem. Originally, the fillers were styrene–polyester systems, but the higher speed of acrylics has led to their adoption despite their higher cost. The filler is applied to the particle board with a roll coater that has a brush roller.

The filled and sanded panel is next coated with a *base coat*, a highly pigmented nitrocellulose lacquer whose color becomes the overall underlying color of the piece of furniture, corresponding to the color of the stain in high-style furniture. The stain used on the solid wood parts approximately matches the color of the base coat. The base coat is then ready for offset gravure printing. The gravure printing cylinders are made from photographs taken of carefully selected hardwood top veneer plywood that was stained, filled, shaded, and distressed by highly skilled finishers. One cylinder prints the darkest tones of the original finished wood, a second prints the medium depth tones, and the third prints the lightest tones. The printing ink colors for the three cylinders are selected to approximate the colors of the three depths of color on the original. The inks are pigment dispersions in plasticizer, so they adhere well to the base coat and to subsequent lacquer coats. A light coat of lacquer is applied to protect the print.

The frame and legs of the furniture are assembled and finished up to the stage of applying top coat, followed by assembly of the printed tops and sides onto the furniture. Then the entire piece of furniture is coated with semigloss nitrocellulose lacquer top coat. Semigloss lacquer, not gloss lacquer, is used to give a finish with a *hand-rubbed effect* without extensive hand rubbing. The semigloss is obtained by pigmenting with a low level of fine particle size SiO_2, such that the PVC of the final film averages 2 to 4%. When the solvent evaporates after application, convection currents resulting from solvent loss carry the pigment to the surface of the film, where it is "trapped" in the viscous surface layer. As a result, the PVC of the top layer of the film is high enough that low gloss can be obtained, while the overall PVC is low enough that only a minor degree of light scattering occurs.

A disadvantage of furniture finishing systems discussed so far is that they require use of low solids coatings with very high VOC emissions. The low solids requires multiple coats, or at least more passes with a spray gun, so the application cost is high. Hot spray (Section 23.2.4) is frequently used. A temperature of 65°C permits increasing solids from 20–24 NVW to 28–34 NVW. This results in a significant reduction in VOC emissions, but still far short of probable future requirements.

In 1995 the U.S. EPA revised their wood furniture coatings regulation after extensive discussions with the industry. It was agreed that regulations should be expressed as pounds of VOC per pound of coating solids on the wood surfaces. The overall limits were set at 2.3 lb of VOC, including a maximum of 1.0 lb of HAP per pound of solids. In new plants or finishing lines, HAP emissions are limited to 0.8 lb per pound of solids. For specific coatings the following maxima were set: waterborne top coats, 0.8 lb; higher-solids solvent-borne sealers, 1.9 lb; top coats, 1.8 lb; and acid-cured alkyd amino sealers, 2.3 lb.

Limits of 275 $g\,L^{-1}$ of VOC for coatings for wood furniture took effect in California in 1994. As VOC regulations become more stringent, it seems probable that a larger fraction of furniture tops will be high pressure laminates with wood grain prints. Laminates have been used for many years on commercial and institutional furniture; now their use in household furniture is increasing.

There have been efforts for many years to replace nitrocellulose lacquers to achieve higher solids. Alkyd–urea–formaldehyde (UF) top coats, frequently called *conversion varnishes* or *catalyzed finishes*, have been used for many years. Tall oil alkyds with a butylated–UF resin are typical. Just before use, one adds about 5% of *p*-toluenesulfonic acid catalyst, based on UF resin solids. A flatting pigment dispersion and a small amount of poly(dimethylsiloxane) to minimize orange peel (Section 24.2) are usually added. The top coated furniture is force dried at 65 to 70°C for 20 to 25 minutes. The NVW is typically about 38%, about twice that of lacquers. Hot spray can further increase the solids, but pot life must be watched carefully, and as the solids increase, low gloss becomes more difficult to achieve. With conversion coatings the appearance of depth is not as good as that obtained with a nitrocellulose lacquer, but is still presentable. The coating is solvent resistant and more heat and gouge resistant than are lacquer coatings. Repair is more difficult but is needed less frequently. Conversion varnishes are most widely used on furniture for commercial use and for kitchen cabinets.

High-solids coatings based on isocyanate chemistry are a more recent developments. Aldimine–isocyanate two package (2K) 90% solids gloss clear coats (Section 12.4) have been formulated that have a pot life of about 3 hours and a dry time of about 1/2 hour [4]. Moisture-curable urethane coatings are used in coating wood in applications where high abrasion resistance is needed. Isocyanate prepolymer mixtures such as propoxylated ethylenediamine/TDI and 2,2,4-trimethylpentane-1,3-diol/TDI prepolymers are used as a vehicle for moisture-curable wood coatings [5]. A moisture-curable wood finish based on a TMP/1,4-butanediol/IPDI prepolymer with 3-glycidyloxypropyltrimethoxysilane is reported to cure by hydrolysis of the alkoxysilane groups and subsequent reactions not only with other alkoxysilane groups but also between the silanol groups and isocyanate groups [6].

Considerable effort has been expended on waterborne finishes for wood furniture. Application of a waterborne coating directly on wood leads to excessive grain raising, which may limit their use to applications where there is already a solventborne sealer on the wood. Substantial reductions of solvent use are possible by emulsifying nitrocellulose (NC) lacquers into water [7]. Lacquers with VOC of 300 to 420 $g\,L^{-1}$, excluding water, can be made compared with VOC on the order of 750 $g\,L^{-1}$ for conventional NC lacquers. Solids of the NC solution internal phase can be maximized by using only true solvents, esters and ketones. Short oil alkyds using ester solvents (other than the small amount of xylene needed for azeotroping in producing the alkyd) are selected as plasticizers. Water wet NC is used rather than conventional isopropyl alcohol wet NC. A surfactant is incorporated in the lacquer as an emulsifying agent; sodium alkylphosphate surfactants are recommended. The advantage of easy strippability for repair is retained. However, a long dry time and slow development of print resistance have limited their use. Combined nitrocellulose/acrylic latex–based lacquers have been recommended. Furniture sealer and top coat formulations with VOC in the range 240 to 400 g L^{-1} have been described [8]. Film physical and appearance properties are reported to be superior to those of acrylic latex counterparts.

Thermosetting latex top coats are also used. For two package coatings, a variety of cross-linkers for hydroxy-functional and carboxylic acid–functional latexes can be used. Hydroxy-functional latexes are readily prepared by using hydroxyethyl (meth)acrylate as a co-monomer. The resulting latexes can be formulated with urea–formaldehyde (UF) or melamine–formaldehyde (MF) resins as cross-linkers. UF resins tend to evolve high levels of formaldehyde from hydrolysis; MF resins evolve lesser amounts of formaldehyde. MF resins are soluble in BA/HEMA/MAA latex polymers so that they act as plasticizers to promote interdiffusion. As temperature increases, the interdiffusion rate increases faster than the rate of cross-linking, until many of the potential reactions have occurred, but at some point the XLD reaches a point at which that interdiffusion ceases. The rate of cross-linking can be increased by the addition of a catalyst such as pTSA. Although this permits shorter cure times, the pot life of the coating decreases and the residual acid in the final film can lead to reduced stability of the films to hydrolysis since the catalyst also catalyzes hydrolysis.

Water-reducible acrylic resin–based coatings (Section 8.3) have been used. At a sufficiently high MW, they can be used as thermoplastic coatings. Thermosetting resins can be cross-linked with polyaziridine cross-linkers (Section 17.7). There is concern about the toxic hazard of aziridine cross-linkers in spray application. Methylated urea–formaldehyde resins can be used as cross-linkers under force dry conditions. Acetoacetoxy-functional water-reducible acrylic resins made with acetoacetoxyethyl methacrylate as a co-monomer are cross-linked with diamines [9] (Section 17.6).

Two package waterborne polyurethane top coats (see Section 12.7.3 for a discussion of various types) are being used increasingly, since they provide low VOC emissions with a minimum of HAP solvents. The films have excellent abrasion resistance. The cost is relatively high, and special application equipment is required [10]. A statistical study of the effect of several variables on the performance of hydroxy-functional acrylic latexes cross-linked with a nonionic hydrophilically modified polyisocyanate finishes for wood kitchen cabinets has been published [11]. It was found that a high hydroxy content of the latex (hydroxyl number 52), small particle size of the latex, core-shell preparation of the latex, and low T_g (obtained by increasing level of coalescing solvent) enhanced performance. Pigmented waterborne 2K coatings formulated with an acrylic latex and HDI isocyanurate that has been hydrophilically modified by reacting with a sterically hindered amino sulfonic acid salt is reported to disperse easily and give superior stain resistance compared with other 2K waterborne urethane coatings and 2K solventborne urethane coatings [1].

Solvent-free, waterborne 2K epoxy–amine furniture coatings were compared to solventborne coatings in a study sponsored by the U.S. EPA [12]. Many of the film properties were comparable, but appearance would limit the types of application for which this waterborne coating would be satisfactory.

In Europe and to a more limited degree, in the United States, UV cure acrylic top coats are used. A large part of European furniture is manufactured in flat sheets and assembled after coating. Furthermore, the finish on much European furniture is glossy. UV curing is ideal for such an application. The fast cure at low temperature is appropriate for wood. Early coatings were based on styrene–polyester resins, but acrylic coatings were later adopted because they cure more rapidly and emission of styrene is avoided (Section 29.2.4). They are applied before assembly of the furniture by roll coating on tops already finished up to the top coat. The coatings are gloss or high semigloss, are solvent resistant, and have excellent mechanical properties. They have the advantage of little or no VOC emission. Their use in the United States has been limited, where most furniture uses low semigloss coatings and is finished after assembly. Furthermore, as discussed previously, most U.S. furniture has a low gloss top coat, which is difficult with solvent-free UV cure coatings. Waterborne UV cure coatings have recently been developed that permit formulation of low gloss coatings (Section 29.2.5).

31.1.2. Panel, Siding, and Flooring Finishes

Large quantities of coatings are applied to plywood and hardboard sheets to make precoated interior paneling and exterior siding. A small part of the market is for finishing expensive, high quality hardwood plywood used for paneling executive offices. This paneling is finished in essentially the same way as that used for the highest end of the wood furniture market. A variety of other products constitutes the bulk of the market.

One class of commodity wall paneling is made using three-ply plywood whose top veneer is a relatively featureless, low cost luan. The panel is dried to remove surface water, grooved to make a plank effect, and then sanded. A dark colored lacquer is applied to the grooves by pinpoint automatic spray guns and the panel is dried. A lacquer sealer colored with dyes is applied. The panel is sanded again and then printed with two or three prints to give the appearance of walnut, rosewood, or some other attractive wood with prominent grain patterns. Finally, a low gloss top coat is applied. The coatings have generally been nitrocellulose lacquers. Although this business was developed in the United States, most production has shifted overseas, initially to South Korea and more recently to the Philippines. The predominant source of the wood is the Philippines, so finished product rather than raw material can be shipped; also, air pollution regulations in South Korea and the Philippines are less stringent.

A related but quite different application is for “door skins.” In the manufacture of interior doors, a common approach is to assemble the door and then laminate a top veneer (the *skin*) to the particle board surface. The skins are veneer, laid up and adhered to kraft paper. The veneer is commonly birch or luan, sometimes printed with a hardwood grain pattern. Commonly, the coating on door skins is gloss or high semigloss. Whereas low gloss is preferred on wall paneling to avoid glare from reflection of lights, higher gloss is preferred on doors because it is easier to clean. Since the surface area of doors is relatively small, glare is not a serious problem. This combination of factors has led to the widespread use of UV cure coatings for door skins.

A variety of UV compositions has been studied for wood coatings. For example, $C_6F_{13}(CH_2)_2OCOCH{=}CH_2$ as a monomer in an epoxy–acrylate oligomer as a UV cure coating for wood paneling provides high hydro- and oleo-phobicity, improved chemical resistance, and better scratch resistance then those of coatings without the fluorine monomer [13].

Part of the interior paneling market is precoated hardboard. Hardboard is made by mixing wood fibers and shreds, then curing in hydraulic presses. The lignin in the wood acts as a binder to hold the wood fibers together; sometimes the lignin is supplemented with phenolic resins. Depending on the pressure applied, the density of hardboard can be varied. Furthermore, patterns can be embossed into the surface of the hardboard. A variety of hardboards are made. Using smooth-surface hardboard, one can apply a base coat, prints, and a semigloss top coat to make 4 by 8 foot panels that look like any kind of wood. Smooth surface hardboard is often coated by curtain coating (Section 23.5), since this gives level films.

Tongue and groove paneling can be simulated by routing out grooves and painting them a dark brown color. The paneling is finished by roll coating a base coat that does not flow into the grooves appreciably, followed by printing and top coating. A pattern of ticks (short line dents scattered over the surface, as in hardwoods) can be embossed. When the board is finished, it not only has the grain of the wood but also has the little dips of a tick pattern as well as the grooves to give the effect of planked paneling.

One can simulate wood with holes, such as pecky cypress. The hardboard is embossed with the hole pattern copied from real pecky cypress paneling. The *hole coat*, generally a dark brown, is applied using roller brushes to assure that the coating covers surfaces inside the holes completely. Then a base coat is applied by *precision coating*. A precision coater is a roll coater in which the application roll is a gravure printing roll covered uniformly with cells so that the upper surface of the panel is coated but no coating is applied in the holes. Generally, the color is a relatively light brown to provide a contrasting background color. Then grain pattern prints are applied, followed by a transparent semigloss top coat. One is not restricted to replicating pecky cypress or wormy chestnut; brick, stone, travertine marble, and other materials can be simulated. Other interior hardboard paneling is designed primarily for bathrooms. The coatings are high gloss pigmented coatings. Sometimes, joints are embossed in to make the panels look like tiles. Sometimes, prints such as marble are used with a clear gloss top coat.

Since, in contrast to plywood, hardboard can withstand high temperatures, baking coatings, with all their advantages in performance properties, are used. Since unlike wood, hardboard does not undergo grain raising, water-reducible acrylic–MF finishes are used. Although the average film thickness of a base coat is relatively high, popping is not a major problem, since the coating thicknesses applied by roll coating and curtain coating are more uniform than when coatings are applied by spray (Sections 23.4 and 23.5).

High-density hardboard is also used for exterior siding. The largest volume of siding is factory primed with a primer designed to have at least 6 months of exterior durability before exterior house paint is applied (Section 32.1). Acrylic–MF binders are used in the primers, generally waterborne to reduce VOC. Challenges in formulating these primers are to be sure that the coating cross-links sufficiently that the coated boards coming out of the oven can be stacked without blocking and also that the paint to be applied to them in the field will have good adhesion. The combination requires careful control of cross-link density. The primers are low gloss because high loading with inert pigment reduces cost and enhances adhesion of paint to the surface. The largest volume is used in siding for tract houses. The primed siding is erected onto the house, but painting is postponed until the house is sold so that the buyer can pick the paint color. An extensive study of exterior durability of different hardboards with different combinations of coatings has been published [14]. The best results were obtained when preprimed board was field coated with an alkyd primer and acrylic latex top coats. Petrolatum and other oily substances are present in some hardboards. If the paint applied on the siding is porous, over time some substances can migrate to the upper surface of the paint, leading to discoloration or sticky areas that will pick up dirt to give a blotchy appearance. The problem can be minimized by using only paints with PVC $<$ CPVC.

Fully prefinished exterior siding is manufactured on a smaller scale than preprimed siding. The primed board is top coated in the factory with a baking acrylic enamel or, for greater exterior durability, a silicone-modified acrylic resin–based coating (Section 16.1.2). The durability is superior to field applied paint, but flexibility in color selection for tract homes is sacrificed. Fully prefinished siding is more commonly used on commercial buildings.

Kitchen cabinet waterborne coatings are formulated with hydroxy- and carboxy-functional acrylic latexes with a urea–formaldehyde cross-linker. While some coalescing solvent is needed, VOC emissions are much lower than with solventborne coatings. The variables in formulating such coatings are discussed in Ref. [15].

Waterborne UV cure clear coats for application to wood articles such as window frames having good exterior durability have been developed. A polyurethane dispersion (PUD) terminated with acrylate groups made with aliphatic isocyanates is used with low MW acrylate coreactants [1]. Waterborne UV cure acrylate-functional PUD give coatings with satisfactory adhesion [17].

Nano-aluminum oxide (average diameter 13 nm) markedly improves the scratch resistance of UV cure wood flooring coatings, The Al_2O_3 is dispersed in the UV curing coating, which also includes 3-trimethoxysilylpropyl methacrylate as a coupling agent between the pigment and binder [18].

Moisture-curable urethane coatings are used for applications such as floor coatings, for which abrasion resistance and hydrolytic stability are important. They are called urethane coatings even though these cross-links are urea rather than urethane groups. Since urea groups also form intermolecular hydrogen bonds, presumably they can affect resistance to mechanical stress in a manner similar to urethane groups (Section 12.6). Another wood flooring coating is based on a urethane–acrylic PUD and pentaerythritol tris(β-(*N*-aziridinylpropionate) [16]. Waterborne wood floor finishes prepared using drying oil–modified PUDs show a combination of abrasion resistance and resistance to heel marking. 2K waterborne urethane coatings in which the urethane cross-linker is a hydrophilically-modified allophanate polyisocyanate are useful in wood finishing.

Uralkyds have been widely used for finishing wood flooring and other wood products because of their abrasion resistance and ease of application. However, they have a VOC of over 500 $g\ L^{-1}$. New regulations in southern California and the northeastern states require 275 $g\ L^{-1}$. This VOC can only be attained with waterborne resins. (See Section 15.7 and Ref. [19] for a discussion of such coatings.)

31.2. COATING OF PLASTICS

Plastics have become a major substrate for coatings. Design of the coatings is complicated by the variety of polymers used in plastics and the range of approaches that are possible for decorating the surfaces. Reference [20] has several useful chapters in which various approaches are discussed; coatings for plastics are reviewed in Ref. [21]. For molded plastics there are two alternatives: (1) *in-mold coating*, in which the inside of a mold is coated, the plastic material is put into the mold, and the outer surface is the coating when the part is taken out of the mold; or (2) *post-mold coating*, in which the molded part is coated.

31.2.1. In-mold Coating

Polar thermosetting plastics can be in-mold coated; a variety of coating materials is used for in-mold coating, depending on the plastic. To assure good adhesion to the plastic, it is desirable to use compositions related to the composition of the plastic: for example, the use of *gel coats* with glass-reinforced plastic parts. Gel coats are pigmented styrene–unsaturated polyester resins (Section 17.3) that are cured along with the resin in the molding compound so that the coating is chemically bound to the main body of the plastic. The molding resin is usually a styrene solution of a phthalic anhydride, maleic anhydride, propylene glycol polyester. For some products, similar polyesters are used in the gel coats. More expensive isophthalic, maleic anhydride, neopentyl glycol resins are used in gel coats when superior hydrolytic and exterior durability are needed. In-mold coating with gel coats is used in making glass reinforced styrene–polyester molded products such as boats and shower stalls.

With polyurethane RIM (reactive injection molding) parts, in-mold coatings with free hydroxyl groups permit reaction with isocyanate groups in the molding compound. Rigid urethane steering wheels are made by coating the inside of the mold with the appropriate color enamel. Rigid urethane foam parts to replace wood carvings for furniture are in-mold coated. The inside of the mold is sprayed with a lacquer which is color-matched to the base coat of the furniture. In the past many in-mold coatings were solventborne coatings, frequently low solids lacquers. These high VOC coatings are being replaced with higher solids coatings, waterborne coatings, and powder coatings.

Coating of interior automotive plastic components has for many years been done by post-mold coating. Waterborne in-mold coating is now beginning to be introduced. It is reported that the new technology achieves rapid part throughput, high transfer efficiency, greater gloss control, and superior mar and chemical resistance [22].

For some plastic automobile parts that are to be assembled onto the steel body of the car and painted with the same top coat as the rest of the body, the interior of the mold can be coated with a primer to provide adhesion to the plastic and intercoat adhesion with the top coat. Sometimes, such a primer is made with conductive pigments, such as acetylene carbon black, so that electrostatic spray will be effective over the plastic parts.

A further alternative approach is to use coated films as a laminate for in-mold application of coatings [23]. The coating is reverse roll coated on a smooth, heat resistant, high gloss polyester film. A size coat is applied to the surface of the coating, and then a film of plastic of the same polymer (or a compatible polymer) as the plastic part to be coated is laminated. The resulting coated film is vacuum formed into a mold, coated side out, followed by a sheet of the plastic. The part is removed from the mold and the polyester film is stripped off, leaving the coating on the surface of the plastic substrate. Multiple layers of coating can be applied. For example, for finishing plastic parts for use with base coat–clear coat systems, the polyester film would be coated first with the clear coat, followed by the base coat, and then laminated to the plastic film.

31.2.2. Post-mold Coating

Coatings are also applied to plastic articles after they are fabricated. Many of the coatings used for metals can be adapted for certain plastics, and many of the selection criteria are the same as for metals. However, there are important differences. Adhesion (discussed in Section 6.5) is usually the central problem in coating plastics. The coatings must be more flexible than those for metal. This follows from the easier deformability of many plastics and all elastomers; the coatings must be at least as easily deformed as the substrate. As a rough guideline, elongation-at-break (Section 4.2) of the coating should be greater than that of the plastic substrate.

To obtain good adhesion, the surface of the plastic must be clean. Machining oils, sanding dust, finger prints, and so on, must be removed. Many plastic parts have residual mold release agents on the surface. If a mold release must be used in making the plastic article, it is desirable to use a water-soluble soap such as zinc stearate as a mold release, since it is relatively easy to remove. Wax mold release agents are more difficult to remove, and silicone or fluorocarbon mold releases should not be used for plastic parts that are to be painted. Surface contaminants and mold release are removed by spray washing in three stages. First, a detergent wash is used followed by a water rinse, and finally, by a deionized water rinse. At the end of the washer, droplets of water are removed by compressed air jets, and the part goes into a drying oven before coating.

After the surface is clean and dry, the surface tension varies widely, depending on the type of plastic. In general, thermosetting plastics and thermoplastics with polar structural groups, such as nylons, have relatively high surface tensions, although lower than those of metals. Often, they can be coated without further surface treatment. However, the surface tension of some less polar plastics, particularly polyolefins, is lower than that of most coatings, and the polarity of the surfaces is very low. Primers are required that have very low surface tensions and that can penetrate the surface of the plastic. Alternatively, the surface of the plastic can be treated to increase its surface tension and provide polar groups that can hydrogen bond with components of the coating to promote adhesion (Section 6.5).

A very challenging problem in coating plastics is the finishing of plastic bumpers, grills, and other exterior plastic components of automobiles. Papers of a symposium on painted plastic components published in *JCT Research* provide an excellent summary of the present status of the work [24]. The components are molded from a polypropylene–ethylene/propylene/butadiene rubber blend (called TPO in the United States and PP-EPDM in Europe and Asia). Due to the low surface tension of the crystalline polypropylene surface, coatings will not adhere well, so a surface treatment is required.

Adhesion can be achieved by applying a thin coat of a chlorinated polyolefin (CPO) primer. CPOs are prepared by grafting maleic anhydride to an isotactic polypropylene and chlorinating the resulting graft copolymer. A wide variety of CPOs is available with different MW, maleic content, and degree of chlorination. Most primers have been solventborne, incorporating acetylene black to make the coating conductive to permit electrostatic spraying of a base coat on the primed part.

One of the papers in the symposium gives an excellent presentation of efforts to understand the mechanism by which the CPO primers promote adhesion [25]. The chlorinated polymer is thought to migrate into the surface of the polyolefin, resulting in a surface to which a broader range of coatings can adhere. A large number of variables can affect the performance. Injection molded plastics tend to provide better adhesion than compression molded plastics. The structure of the CPO, MW, degree of chlorination, maleic content, and film thickness are important variables. The solvent used can make a major effect on the extent of penetration; hydrocarbons give greater penetration than do polar solvents. Baking generally promotes penetration. Care must be exercised to assure that the solvent is all evaporated before the base coat is applied, to prevent it blowing out through the film when the top coats are baked. Although solvents can improve adhesion, care must be exercised in the selection of solvents for plastics such as TPO (thermoplastic polyolefin blended with rubber) so that the crystallinity of the plastic is not disturbed, since that would affect the cohesive strength of the plastic [26]. The TPO primer films must be on the order of 3 to 5 μm thick; the primer is thermoplastic, and thicker films may lead to cohesive failure. The need for thin films dictates that the primer must be applied in high

VOC formulations. The crystallinity and cohesive strength of TPO is also affected by the baking temperature used for curing the coatings [27]. It is also reported that a solution of chlorinated polyolefin can be added to the top coat to obtain adhesion to TPO without the need for a separate primer [28]. (See Section 6.6 for a discussion of testing methods.)

Adhesion of top coat to the primer is sometimes inadequate. Addition of ethylene/vinyl acetate copolymer to the primer is reported to improve intercoat adhesion [29]. Another approach is to graft acrylic side chains by esterifying some of the maleic groups with HEA and then making a graft copolymer with acrylate monomers. 2K urethane base coats are formulated with the resin and are reported to resist delamination without the use of a separate primer [30].

Automobile base coat and a clear coat are applied over the primed TPO. For example, an acrylic–MF base coat with a trimethoxysilyl-functional acrylic clear coat can be applied. A UV absorber and HALS compound are included in a 2K urethane clear coat to assure exterior durability. However, durability is not as good as that obtained with the same system over steel. It has been found that the UVA and hindered amine light stabilizer (HALS) can migrate through the coatings and down into a TPO plastic, resulting in poorer durability. To minimize this problem, the use of UVAs and HALS with hydroxyl groups that will react with an isocyanate in the clear coat to bind the stabilizers to the polymer chains leads to much higher retention of stabilizers in the clear coat and improved durability [31].

In baking automotive clear coats for plastics, methoxysilyl groups of the trimethoxysilyl-functional acrylic resins hydrolyze at room temperature to silanol groups, which react during baking to cross-link the coating. The scratch resistance before and after weathering is superior to that of MF cross-linked coatings [32].

A waterborne coating for poly(phenylene oxide) plastic interior auto parts made with a urethane–acrylic hybrid PUD and two acrylic latexes has been disclosed [33,34]. A waterborne primer, formulated with graft copolymers of acrylic monomers on polypropylene, enhances adhesion to polypropylene (or blends of polypropylene/ethylene–propylene) rubber, as well as to acrylic top coats [35].

Instead of applying a special primer, the surfaces can be oxidized to yield polar groups; there are several approaches to oxidation treatment [36]. Oxidizing agents such as chromic acid/sulfuric acid baths are effective and have been used for many years. However, disposal of chromate containing wastes is now tightly controlled. To avoid Cr(VI), sodium hypochlorite with a detergent has been recommended for treating the surface of polyolefin polymers to improve adhesion [33]. Alternatively, a surface can be oxidized by directing an oxidizing flame from propane or butane onto the surface. Care is required to ensure that all surfaces are adequately treated. Flame treatment is widely used in Europe for the surface treatment of plastic parts for automobiles. Yet another approach to oxidation of the surface is by *corona discharge*. The plastic parts are passed through a cloud of ionized air generated, as described in Section 6.5, by electrodes with many wire ends at high voltage. The ions oxidize the surface of the polyolefin. For irregular shaped parts, the corona discharge can be carried out in a vacuum chamber; this method is frequently called *plasma discharge*. Still another approach is to spray a solution of benzophenone on the surface of a polyolefin and then expose the part to UV radiation. This leads to the generation of free radicals that initiate autoxidation of the surface. This process is particularly effective with rubber-modified polyolefins. A drawback of these four approaches is that they do not make the surface conductive enough for efficient electrostatic spraying. In such cases, TPO primers with conductive pigments are preferred.

From the standpoint of adhesion, it is preferable for the plastic part to have a somewhat roughened surface. Plastics that are highly filled with pigments have rougher surfaces to which it is easier to adhere. Alternatively, the surface of the mold can be designed to impart some roughness to the molded pieces. Adhesion can be promoted by baking at temperatures above the T_g of the plastic. However, in many cases, heating above T_g distorts the molded part. This is one of the advantages of in-mold coating: Adhesion is promoted by the heat involved in molding the plastic, avoiding the problem of heat distortion when baking post-coated plastic moldings.

Adhesion can also be promoted by using solvents in the coating that are soluble in the plastic. This reduces the T_g of the plastic at the surface, permitting penetration of binder from the primer into the surface of the substrate. However, very volatile strong solvents must be avoided on high T_g thermoplastics such as polystyrene and poly(methyl methacrylate); such solvents cause *crazing*, that is, the development of a network of microcracks in the surface of the plastic. A possible explanation for crazing is that the solvent penetrates into the plastic; then, if it is very volatile, it evaporates rapidly from the surface while there is still solvent left just below the surface. When the solvent diffuses out from below the surface, there is a reduction in volume, leading to stresses sufficient to crack the surface layer of the plastic. Another potential problem with using penetrating solvents is the possibility of solvent popping caused by the release of solvents from the plastic after cross-linking of the coating is well advanced. In a study of factors that affect popping on sheet molding compound parts (molded fiberglass reinforced polyester plastics), it was found that the problem can be minimized by using primers with the lowest possible solvent permeability [37]. Permeability can be reduced by using highly cross-linked or partially crystalline binders in the primer.

Moisture-curable urethane coatings have been used on plastic flooring. For example, a coating with high abrasion resistance, particularly for urethane elastomer flooring, is formulated with a moisture-curable urethane made from polytetramethylene glycol, 1,4-butanediol, H_{12}MDI, and MDI [38]. Just before application, DBTDL and DABCO solutions are added as catalysts.

Electrostatic spraying of plastics is difficult, since the plastics are usually insulators and therefore cannot be adequately grounded to give the charge differential needed to attract charged spray droplets to the surface. Surface resistivity of plastics and time for charges on their surfaces to dissipate can be measured and correlated with the feasibility of electrostatic spraying [39]. The charge dissipation time is affected not only by the composition of the plastic, but also by the humidity in the spray booth. Conductive tie coats or primers can be applied to the plastic; the effect of a range of conductive primers on the charge dissipation time has been studied [26]. It has also been shown that the effect of surface charges on the plastic substrate in the electrostatic spraying can be reduced by placing a continuous grounded metal backing in contact with the plastic substrate [40]. When the object being sprayed has both plastic and metal components, there can be nonuniform deposition of coatings even when a conductive primer has been applied to the plastic, since the metal can distort the electrostatic field near the plastic–metal interfaces.

The lower curing temperatures possible with two package polyurethane coatings make them particularly attractive for many applications, to minimize the possibility of heat distortion of the plastic product [41]. The higher abrasion resistance and flexibility available with urethane coatings are frequently also advantageous. While acrylic resins can be cross-linked with polyisocyanates, higher solids are possible with hydroxy-functional polyesters. For example, a polyester resin prepared from adipic acid, isophthalic acid, neopentyl glycol, and trimethylolpropane in a mole ratio of 1 : 1 : 2.53 : 0.19 with an $\bar{M}_n$ of 730 and an $\bar{f}_n$ of 2.09 hydroxyl groups per molecule was cross-linked with various trifunctional aliphatic isocyanates at a 1.1 : 1 NCO/OH ratio [41]. The coating provided a good balance of properties on a variety of plastics, including good impact resistance at -29°C.

Another approach to coating plastics subject to heat distortion is radiation curing (Chapter 29). The temperatures involved in radiation curing are generally not substantially above ambient and can be further reduced by filtering out IR radiation. For example, UV-cure gloss top coats are applied to plastic flooring. The low temperature curing is particularly important in coating flooring such as vinyl tile. Plastic flooring often has an embossed foam decorative layer as the upper surface; elevated temperatures could collapse the foam.

Dual UV/thermal cure primer-sealer coatings for unsaturated polyester–styrene glass fiber sheet molding compound (SMC) automotive components have been developed to solve the serious popping problem that occurs when solventborne coatings are applied and baked. As the coated part is baked, gas from pores in the plastic and solvent from the coating lead to popping. The problem has been solved by applying a primer–sealer to the SMC components based on a 2K urethane coating with acrylate functionalities. The coatings are exposed in a UV chamber to a maximum temperature of 65°C and then baked at 121°C for 20 minutes. In the UV chamber, the components are hung on a conveyor with UV lamps at several angles so as to minimize shadow areas [42]. Adhesion is facilitated by the much lower shrinkage than in traditional UV curing since the fraction of unsaturation is low due to the relatively high MW resin.

Use of some solvent in UV cure coatings permits using less low viscosity monomeric acrylates, thereby reducing shrinkage during cure and minimizing the adhesion problem. Proprietary UV cure base coats and clear coats for flexible plastic automotive components reduce the time for application and cure to 7.5 minutes, compared to 35 minutes for thermal cure coatings [43].

In many applications, the function of the coating is decorative, such as for color; but there are many examples of functional coatings for plastics. The UV cure top coat applied to plastic flooring mentioned earlier has the functions of increasing wear life, stain resistance, and gloss retention. Coatings are applied to polyethylene tanks to reduce permeability. Magnetic coatings are applied to tapes and sheets to make recording tapes.

Transparent plastics can serve as replacements for glass for applications ranging from window glazing to eyeglasses, but they are less abrasion resistant than glass (Section 4.4.1). Surface coatings to improve abrasion resistance have been developed based on alkoxysilanes and colloidal silica [44]. The coatings provide excellent abrasion resistance to plastics such as polycarbonate, but have relatively high VOC levels and long curing times. Radiation cure coatings have been developed with low VOC that cure in a few seconds (Section 29.6).

31.3. COATINGS FOR GLASS

In general, it is difficult to achieve adhesion to untreated glass such that the adhesion resists soaking in water or strong bases. Such adhesion is possible with the use of reactive silanes as discussed in Sections 6.4.3 and 16.2 [45]. For example, an aqueous polyurethane dispersion (PUD) having blocked NCO groups together with a hydroxy-functional PUD and silane additives is used for coating glass bottles. The coating is baked at 190°C for 20 minutes and resists loss of adhesion when the coated bottle is soaked in water or in a solution of NaOH [46]. Because NaOH solutions are used to clean recycled bottles, this resistance is critical.

A commercially important application for coatings on glass is coating optical fibers for wave guides used in telecommunication cables (Section 29.6).

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Architectural Coatings

In 2002, U.S. shipments of architectural coatings had a value of \$7.211 billion [1]. This was about 45% of the value of all U.S. coatings shipments. Architectural coatings are also called *trade sales paints*. There are two overlapping markets for these paints: contractors and *do-it-yourselfers*, who paint their own homes and furniture. The contractor is particularly concerned with the cost of application, which is greater than the cost of the paint. For example, contractors want paints that cover in one coat and touch up readily. The do-it-yourselfer is more likely to be concerned about ease of cleanup, odor, and the range of colors available. Concern with the cost of paint itself varies significantly within both groups. In the United States, paint is sold through several distribution systems: large merchandisers, hardware and lumber stores, paint stores owned or franchised by paint companies, and independent dealers. Some paint is sold directly to large contractors by paint manufacturers. There are three, sometimes overlapping classes of paint companies: large companies that do extensive national advertising to promote trade name paints; smaller regional companies that sell only locally, primarily to local contractors but commonly with regional stores for sales to contractors and individuals; and companies that sell private-label paints to large merchandisers or hardware chains, primarily for do-it-yourself use. Some paint companies design their paints to be most suitable for the climate and style trends in specific regions of the United States.

Large companies generally make several lines of the major product types: for example, good, better, and best. The good grade is designed for the person whose principal criterion for selecting paint is price per unit volume. Such paint is usually adequate for the application with fair coverage. But buying the cheapest paint is usually a false economy. The best paint is usually designed to give the longest life and to have as good coverage as can be designed into that class of paint; it may also be easier to apply and have better appearance. The "better" paint is a compromise between the two.

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Although some colored paints are produced at the factory, the majority are manufactured as tintable paints that are custom-tinted at the point of sale. The manufacturing company supplies an extensive line of color chips or standards, with liquid tinting colorants and formulations to use with paints called *bases*, in order to match the color chips. This makes it possible for the paint store to provide thousands of colors with only a limited inventory.

A multitude of products is made for the architectural market. We restrict discussion to the three largest classes of paints: *exterior house paint*, *interior flat wall paint*, and *gloss enamels*. Space limitations do not allow inclusion of smaller but still significant product lines, such as stains, varnishes (Sections 14.3.2 and 15.7), floor paints, and many specialty products.

32.1. EXTERIOR HOUSE PAINT

An extensive discussion about finishing wood with many types of coatings is provided in Ref. [2]. This section is limited to exterior house paint, that is, paint applied to exterior wall surfaces. Paint for trim around windows, doors, and on shutters is generally semigloss paint or gloss enamel, discussed in Section 32.3. The great majority of exterior house paint sold in the United States is latex paint. The exterior durability of latex paints is superior to that of air dry solventborne house paints. Latexes are made by emulsion polymerization (Chapter 9) and undergo film formation by coalescence (Section 2.3.3). Solventborne house paints are used if outside painting must be done when the temperature is below 1 to 7°C (the minimum application temperature is given on the label), since latex paints do not coalesce properly at such low temperatures. Latex paints do not adhere well to a chalky surface, that is, a surface with a layer of poorly adherent pigment and eroded old paint; careful washing to remove chalk is required. As of 1999, EPA national maximum VOC emission for exterior flat paint was 250 $\mathrm{g\,L^{-1}}$ [3]. (See Section 18.9.2 for further information about EPA and California Air Resources Board regulations.)

Latex paints perform better than oil or alkyd paints on wood siding. When oil and alkyd paints were widely used on wood house siding, paint failures by blistering were common. Water can get into siding from the back side. Since films from oil and alkyd paints have low water vapor permeability, when water reaches the back side of a film and starts volatilizing in the heat from the sun, blisters are formed. Latex paints are not cross-linked and have T_g values below summer temperatures and therefore have relatively high moisture vapor permeabilities. When water gets to the back of a latex paint film, the water vapor can pass through the film; blistering is unusual.

Latex paints are more resistant than oil or alkyd paints to grain cracking. Wood expands and contracts as its moisture content increases and decreases. A coating applied with an acrylic latex binder maintains its extensibility after many years of exterior exposure and can expand and contract with the wood. Highly unsaturated oil and alkyd coating films continue to cross-link with exterior aging, becoming less extensible and more likely to crack as the wood expands and contracts. Oil and alkyd paints also commonly fail by chalking after exposure. High quality latex paints are less likely to fail by chalking or, at least, have longer lifetimes before chalking occurs to a serious extent.

Leveling of latex paints is generally not as good as that of solventborne paints. This is not viewed as too serious a problem in exterior house paints, but it is with gloss paints, as discussed in Section 32.3. This disadvantage is offset in exterior house paints by the accompanying superior sag resistance of latex paints compared to solventborne paints.

Since they remain thermoplastic with aging, latex paints are more prone to retain dirt on their surface than are oil or alkyd paints. Dirt pickup is undesirable anywhere, but is a particular problem in places where lignite and soft coal are used for heating and cooking, where white latex paint turns an unsightly blotchy gray after only a few months exposure. As discussed in Section 2.3.3, film formation of latex paints occurs by coalescence of the polymer particles. Coalescence requires that the temperature during film formation be above the T_g of the particles. If the paint is to be applied at low temperature, the T_g must be correspondingly lower. However, this means that when the temperature is high during the summer, the film is soft and susceptible to dirt pickup, even when the dirt content in the air is not excessive. Dirt pickup decreases as T_g is increased from 0° to 10°C and styrene–acrylic latex paints show less dirt pickup than straight acrylic latex paints [4]. However, they tend to chalk in sunny exposures of the southern latitudes of North America, and thus have not been employed extensively in the United States. Lower-gloss paints generally have lower dirt pickup than that of higher-gloss paints.

The condition of the wood surface to be painted can be a significant factor in the performance of paint. Contamination with dirt and oil can interfere with adhesion. When bare wood is exposed outdoors, the surface degrades quickly. Painting degraded surfaces can result in what looks like adhesive failure but is actually cohesive failure of the wood. It is reported that even a three to four week exposure of freshly cut wood to weather can affect adhesion adversely [2]. Many woods discolor when exposed to UV; this is particularly noticeable in outdoor exposure but happens more slowly indoors. Two coat finishes have been developed that markedly decrease the discoloration of wood. The first coat next to the wood contains a nitroxy HALS (Section 5.2.3), and the second coat contains a combination of bis-, tris, and tris-*para*-substituted/tris-resorcinol-triazines as UV screeners (Section 5.2.1) [5].

It is recommended that before painting new wood, joints and cracks be caulked and that the wood be treated first with a paintable water-repellent preservative and then primed with an alkyd or latex primer. On many kinds of wood, a latex paint can be used for both the primer and top coat. However, woods such as redwood, cedar, and some pines contain water-soluble materials that extract into a latex paint, leading to reddish-brown stains. The extractives are naturally occurring phenolic compounds. Special *stain-blocking* latex primers are made for use over redwood and cedar. Formerly, these primers were formulated with a somewhat soluble lead pigment, which formed insoluble salts with the phenolic compounds. To avoid lead compounds, other ways to insolubilize the phenolics have been found. One approach is to include in the formulation a cationic ion-exchange latex. Many houses are sided with preprimed hardboard siding (see Section 31.1.2 for a discussion of painting this siding).

As mentioned earlier, another potential problem in applying latex house paints can be poor adhesion to chalky surfaces. The surface of chalky paint is covered with a layer of loosely held pigment and paint particles. When latex paint is applied over such a surface, the continuous phase of the paint penetrates among the particles down to the substrate, but latex particles are large compared to the interstices among the chalk particles and do not penetrate significantly. When the water evaporates and coalescence occurs, the paint film penetrates the chalk particles only partially, with limited binding of the chalk particles together and to the substrate. As a result, adhesion can be poor. Latex chalk sealers made with very small particle size latexes are available.

Alternatively, one can use an oil- or alkyd-based primer. With oil or alkyd paints, the continuous phase penetrates among the chalk particles; the binder from the paint surrounds the chalk particles and penetrates through them down to the substrate surface, minimizing the adhesion problem. Adhesion of latex paints can be improved by careful cleaning of the surface to be painted to remove all chalk. For large areas such as entire wall sections of a house, power washing is effective for removing chalk as well as dirt and loose paint. Another formulating method is to replace about 15% of the latex polymer binder with long oil alkyd resin or synthetic drying oil. The alkyd or oil is emulsified into the latex paint. After application, as the water evaporates, some of the alkyd or oil can penetrate between the chalk particles, providing improved adhesion. For the paint to have a good storage life, the alkyd or oil should be hydrolytically stable. The drying oil or alkyd reduces the exterior durability of the paint compared to pure latex paints, especially in resistance to chalking, fading, and mildew growth. The problem of adhesion over chalky surfaces is becoming less common as the incidence of chalky weathered surfaces declines, owing to the decreasing use of oil-based paints and "cement paints."

Table 32.1 gives a formulation recommended by a latex manufacturer for a high quality exterior white house paint [6]. This formulation is not given to recommend it or these raw materials over others; rather, it provides a framework for discussing the reasons for the

TABLE 32.1. Exterior White House Paint

Material	Weight (lb)	Volume (gal)	PVC
Water	65.42	10.25	
Triton CF-10	1.00	0.11	
Colloid 643	2.00	0.28	
Tamol 731A	14.18	1.50	
Potassium tripolyphosphate	1.00	0.05	
Ti-Pure R-706	225.00	6.70	19.18
Minex 4	150.00	6.85	19.60
Attagel 50	5.00	0.25	0.72
Natrosol 250 MHR (2.5%)	125.00	15.00	
Kathon LX (1.5%)	1.70	0.20	
Rozone 2000	6.00	0.66	
Disperse at high speed for 13 to 20 minutes, then let down with Rhoplex Multilobe 200	320.00	36.00	
Ropaque Ultra	45.00	5.25	7.85
Colloid 643	2.00	0.28	
Texanol	11.10	1.40	
Triton CF-10	0.50	0.07	
Propylene glycol	16.35	1.90	
Acrysol RM-2020 NPR	11.00	1.25	
Natrosol 250 MHR (2.5%)	14.40	1.25	
Water	85.55	10.25	
	1122.20	100.00	

Properties

PVC (%) (TiO_2 19.18; Minex, 19.60; Attagel, 0.72; Ropaque, 7.85), 47.4
Volume solids (%), 34.8
Stormer viscosity, equilibrated (KU), 96
ICI viscosity, equilibrated (m Pa·s), 16
VOC (g L^{-1}, excluding water), 100 g L^{-1}

many components of a latex paint and for the indicated order of addition during making of the paint. Note that the formulation is given in terms of both volume and weight of the ingredients. In general, the weight figures are used for production purposes, although fluid metering devices are sometimes utilized. The volume figure indicates the volume contribution to the wet paint.

Triton CF-10 is a low foam nonionic surfactant to aid in wetting the pigment. (See Section 9.1.1 for a discussion of surfactants.) Colloids 643 is an antifoam agent (Section 24.8). The minimum level of antifoam necessary for controlling foam should be used; excess antifoam can result in crawling when paint is applied and can interfere with color acceptance (Section 32.2). Selection of antifoams is empirical; the manufacturers of proprietary antifoams offer test kits with samples of various products. The formulator tries the samples to find which is most effective with the particular formulation. Tamol 731A is a sodium salt of a carboxylated polyelectrolyte used as a pigment dispersant. Potassium tripolyphosphate (KTPP) is also a pigment dispersant.

Ti-Pure R-706 is a rutile TiO_2 pigment, surface treated for ease of dispersion in waterborne coatings. The PVC of TiO_2 in the formulation is 19.18%. The Ropaque Ultra added later in the formulation provides additional light scattering. In this formulation, dry powder TiO_2 is called for. In many cases, large manufacturers of latex paints use TiO_2 in liquid form (slurries), that is, dispersions of TiO_2 in water supplied by the pigment manufacturer for more economical material handling (Section 20.1.1).

Minex 4 (nepheline, an alkaline aluminum silicate) is an inert, pigment having lower cost than an equal PVC of TiO_2. Its refractive index is sufficiently similar to that of the binder in the paint that it contributes little directly to hiding. The fine particle size allows it to serve as a *spacer* pigment to increase the hiding efficiency of the TiO_2. Use of spacing pigments is discussed further in Section 32.2. Attagel 50 is an attapulgite clay to provide thixotropy to control settling and syneresis.

A variety of types of inert pigments can be used. Particle size, cost per unit volume, and color are major selection criteria. Calcium carbonate is inexpensive and is sometimes used as an inert pigment in exterior latex paints, but there is a potential problem. Latex paint films have quite high water permeability; water and carbon dioxide, which are in equilibrium with carbonic acid, can permeate the film. Calcium carbonate dissolves in carbonic acid to give a calcium bicarbonate solution that can diffuse out of the film. On the surface, the water evaporates, leaving a deposit of calcium bicarbonate in areas protected from rainfall, such as porch ceilings and under eaves, which then reverts to insoluble calcium carbonate. The white deposit, called *frosting*, on the surface of the film is undesirable, especially with colored paints. Thus, calcium carbonate should not be employed in latex paints that may be tinted to a dark color. Furthermore, calcium carbonate–pigmented paints are subject to degradation by acid rain; not only can frosting result, but also film properties deteriorate and the films become more subject to mildew, due to porosity developed in the films by loss of calcium carbonate [7].

Natrosol 250 MHR is a hydroxyethylcellulose thickener. Kathon LX (chloromethyl/methylisothiazolone) is a biocide that serves as a preservative. Bactericides are needed to control bacterial growth in the can of paint. There are three adverse effects of bacterial growth: A putrid odor can develop; the metabolic processes release gases that can build up enough pressure to blow off the can lid; and since bacteria produce enzymes that can degrade cellulose derivatives such as HEC, the viscosity of the paint may drop.

Many other compounds are used as fungicides and bactericides [8]. Consumption of biocides for use in paints in 2002 is reported to be $60 million [9]. In many exterior paints, zinc oxide is used as one of the white pigments. It contributes somewhat to hiding, but its scattering efficiency is poor because the refractive index difference between it and the binder is relatively small. Zinc oxide is used primarily as a fungicide. It is also helpful in latex primers for tannin-stain blocking and for rust inhibition. Zinc oxide can cause large viscosity increases during storage of some latex paints. The effect of ZnO is system dependent; the variables and possible formulation approaches to minimize the instability problems are discussed in Ref. [10].

Testing of biocides is difficult because fungal and bacterial growth are dependent on ambient conditions and because many fungicides and bactericides are effective against only a limited number of organisms. ASTM D-2574-96 is a standard test method for resistance of latex paints in the container to attack by microorganisms. Diluted paints are more likely than undiluted paints to support bacterial growth; a test method based on inoculating diluted latex paint with several bacteria and fungi species has been reported to be reliable [11]. A rapid impedimetric test procedure has been reported [12]. A preliminary high throughput study of factors affecting the effectiveness of bactericides in latex paints has shown that the presence of phosphate groups accelerates microbial growth [13].

The best control of bacterial growth is to avoid contamination of the paint with bacteria. Housekeeping in a latex paint factory should be as good as it is in a food-processing facility. Furthermore, bactericides kill bacteria, but they do not deactivate enzymes that have been produced by bacteria. If the factory has places where bacteria can grow, enzymes can get into paint. The enzymes catalyze splitting of the HEC molecules and the viscosity drops, even though there is adequate protection against bacteria. Some thickeners are not subject to attack by bacteria.

Rozone 2000 (1,2-dichloro-2-*n*-octyl-4-isothazoline-3-one) is a mildewcide to minimize mildew growth on the applied paint film. Mildew is perhaps the most common cause of deterioration of the appearance of latex house paints. To be effective, an organic mildewcide must migrate to the surface of the film, where it is subject to leaching by water. When painting over mildewed paint, the old mildew should be killed with a mildewcide or with bleach before applying the new paint. If the biocides are adsorbed on the surfaces of zeolite, they are released more slowly from the film and thus the paint films maintain their antibacterial activity for longer times [14]. The search for more effective mildewcides is an active research area.

Latex cannot be added until after pigment dispersion is complete because some latexes would coagulate with the high shear exerted in the dispersion step. Therefore, after the pigment is dispersed, the high-speed impeller is slowed to avoid coagulation and excessive foaming.

Multilobe 200 is an acrylic latex in which groups of a few particles are polymerized together into non-spherical lobed particles [15]. At equal concentration, the viscosity of this latex is higher than the viscosity of comparable latexes with spherical particles, since the packing factor is smaller than for a spherical particle latex. Paints formulated with a lobed latex are shear thinning and give a higher high shear viscosity at the same low shear viscosity than do conventional latexes. The higher viscosity at shear rates experienced during application leads to thicker films with low levels of thickener and hence lower cost. Adhesion to chalky surfaces is said to be improved as compared to paints formulated with conventional latexes.

Latexes with part of the MMA replaced by styrene have lower cost, lower dirt pickup, and reasonably satisfactory exterior durability, although in sunnier latitudes they tend to chalk and fade more. Vinyl acetate–acrylate copolymers are even less expensive.

While their hydrolytic stability is inadequate for exterior use in climates with high humidities and rainfall, they are used outside in arid climates. Copolymers of vinyl versatate (a C_{10} branched carboxylic acid vinyl ester) (Section 9.3) have better exterior durability than that of vinyl acetate copolymers and are widely used in Europe as vehicles for exterior paint [16,17]. A VAc/BA/vinyl ester of a C_{12} branched acid copolymer latex in exterior paints is reported to have performance equal to that obtained with all acrylic latexes at a substantially lower cost [18].

Ropaque Ultra is a high T_g latex that contains nano-bubbles of water within the particles (Section 20.1.2) [19]. When the paint film dries, the water diffuses out of the particles, leaving nano-voids that scatter light, reducing the TiO_2 requirement. In calculating PVC, one includes the volume of these particles, since they do not coalesce with the latex binder particles during film formation.

Texanol is a coalescing agent; it is a mixture containing primarily the monoisobutyrate ester of 2,2,4-trimethylpentane-1,3-diol (TMB). It reduces T_g during film formation and then slowly evaporates. The high degree of steric hindrance of the ester group of Texanol provides hydrolytic stability.

Propylene glycol is in the formulation for two main reasons. First, it acts as antifreeze to stabilize the paint against coagulation during freezing and thawing. The expansion of water as it freezes exerts substantial pressure on the latex particles and can push them together with enough force to overcome the repulsion by the stabilizing layer, resulting in coagulation. The glycol lowers the freezing point; even if the temperature gets low enough to freeze the mixture, it freezes to slush, so that less pressure is exerted on the latex particles. The second function of propylene glycol is to control the rate of drying of the paint to permit *wet lapping* without disruption of the edge of the film. As water evaporates from a latex paint film, viscosity increases rapidly as a result of the increase in volume fraction of the internal phase. When paint is applied with a brush or roller, the edge of the wet paint film is painted over (lapped) so that no substrate is left unpainted or with only a thin layer of paint. With oil paint, there is no problem with wet lapping. With a latex paint, by the time lapping occurs, the viscosity of the applied paint may have increased enough so that the film is semisolid, but since only limited coalescence has occurred, the film is weak. The pressure of a brush or a roller can break up the film, resulting in irregular chunks of paint film along the lapped edge. This can be minimized by slowing the rate of evaporation of the continuous phase by incorporating slowly evaporating propylene glycol. In addition, propylene glycol aids coalescence, although it is less effective than other coalescents.

Acrysol RM-2020 is a nonionic associative thickener. It helps control viscosity of the paint as a function of shear rate, improving application characteristics. Associative thickeners permit formulation of latex paints that exhibit less shear thinning, so that viscosity at high shear rates can be higher; as a result, thicker wet films can be applied. Formulation with associative thickeners also reduces viscosity at low shear rates, so leveling is also improved without causing undue sagging or settling. (The thicker wet film in itself helps promote leveling, too, since the rate of leveling depends on wet film thickness, as discussed in Section 24.2.)

The viscosity of the external phase controls its rate of penetration into a porous substrate such as wood. If penetration is rapid, the viscosity of the paint above the porous surface increases rapidly, resulting in poorer leveling. The final water addition permits adjustment of the viscosity and solids content of the final paint. There is variation from batch to batch of the viscosity of any paint formulation.

The PVC of the paint is 47.4%; it is a relatively low gloss paint, as are most exterior latex paints. The gloss of this latex exterior house paints is quite low. The popularity of exterior satin finish paints has increased in recent years. Gloss is controlled by the PVC/CPVC ratio (Chapter 22). Exterior durability, as well as many other properties, is also affected by PVC. It is desirable to maximize CPVC, since the PVC of the paint at the same PVC/CPVC ratio increases with the CPVC. With a given latex, a major factor controlling the CPVC of latex paints is the particle size distribution of the pigments. Multiple inert pigments maximize the breadth of particle size distribution, which increases CPVC and permits higher pigment loading at the same PVC/CPVC, decreasing cost (Sections 22.1.1 and 22.1.3).

Commonly, the gloss of latex paints is lower than that of oil paints. The volume solids of the paint is 34.8%, substantially lower than that of exterior oil- or alkyd-based paints. As a result, coverage per unit volume of latex paints is lower than that of oil-based paints, but the cost per unit volume of latex paints is lower. The grams of VOC per liter of paint, excluding water, is 100, lower than that of alkyd- and oil-based house paints and well under current California air pollution regulations. However, these regulations are expected to tighten.

Note that despite the widely recognized shortcomings of the Stormer viscometer discussed in Section 3.3.6, in this case (and in most paint labs in the United States), it is the viscometer used. The viscosity of the unsheared paint is measured before shearing reduces the viscosity related to the thixotropy of the paint. The ICI viscosity is determined on a special cone and plate viscometer that measures viscosity at a high shear rate similar to that exerted by application of the paint by brush or roller. It is important to have the proper high shear viscosity because this is a major factor controlling film thickness.

Emulsions of methylsiloxane resins, an amino-functional polysiloxane emulsion, and a styrene–acrylic latex are used to formulate exterior house paints. Such coatings have been used on a large scale in Europe for many years but are just being introduced into the United States. They have outstanding exterior durability [20].

There is a considerable market for coatings that increase the exterior durability of wood but are not pigmented, or are lightly pigmented, as transparent stains. Results of a variety of treatments of coatings on fir and oak have been reported. The best results were obtained with waterborne transparent stain with an alkyd–acrylic dispersion binder pigmented with iron oxide. The performance was better than that of another system without the iron oxide in the stain and with a top coat containing a UV absorber (UVA) and hindered amine light stabilizer (HALS) [21].

A study of the performance of exterior latex paints on masonry has been published [6]. Key properties are water resistance, moisture permeability, exterior durability, dirt pickup resistance, color retention, low chalking, and good elasticity. A series of all acrylic and styrene–acrylic latexes were evaluated with a range of pigments. While styrene containing latexes in clear films had poorer exterior durability and color retention than all-acrylic latexes, this difference became minimal in pigmented paints. The overall best performance was shown using BA/MMA/EHA/MMA, and EHA/styrene latexes. EHA-containing latexes were noted for soiling resistance. EA/MMA showed poor performance. The inert pigments also affected performance; for example, SiO_2 increased chalking.

32.2. FLAT AND SEMIGLOSS PAINTS

The largest volume of architectural paint is interior flat wall paint; almost all is latex paint. Although flat wall paints are most common, low semigloss (“satin” or “eggshell”) wall paints are becoming more popular for their "soft" appearance. As of 1999, the EPA permitted level of VOC for interior flat paints was $250\,g\,L^{-1}$ [3]. However, lower VOCs will undoubtedly soon be required.

The major advantages of latex paints over the older oil-based paints are:

1. *Fast drying and less sagging*. If desired, two coats can be applied to the walls of a room during a day, the furniture moved back, and the room used that night. The rapid increase in low-shear viscosity in the early stages of film formation reduces vulnerability to sagging, even when relatively thick films are applied.

2. *Low odor*. The odor of mineral spirits and by-products from oxidation of drying oils in solventborne paints is unpleasant for days after walls are painted. Although the odors are less offensive, some odor from the slow evaporation of coalescing solvents from latex paints persists for up to a week. A reason for developing low VOC paints is to eliminate this odor problem.

3. *Ease of cleanup*. Spills, dripped spots, brushes, and rollers are easily cleaned with soapy water in the case of latex paints; solvent is required with oil paints. However, cleaning up must be done promptly because once latex has coalesced, cleaning it up is more difficult than with oil paints.

4. *Low VOC emissions*. Latex paints were widely adopted before 1967, when the first VOC regulations were adopted in the United States. Progress is being made in reducing the already low VOC, as discussed in Section 32.3. There is also the advantage with waterborne paints of substantially reduced fire hazard. Not only is solventborne paint flammable, but also rags wet with oil-based paints in a confined space can undergo *spontaneous combustion*, that is, ignite as a result of heat generated by autoxidation.

5. *Less yellowing and embrittlement*. White and light color acrylic and vinyl–acrylic latex paints retain their color better than do alkyd paints, which gradually turn yellow with age. Alkyds made with oils that contain very little linolenic acid, such as sunflower or safflower oils (Section 15.1.1), yellow more slowly than alkyds based on soybean oil or tall oil fatty acids, but they still yellow with time. Alkyd films also eventually become brittle, as autoxidative cross-linking continues far beyond the point of optimum film properties.

Wall and trim paints are generally stocked as white paint, and companion tintable paints are called *tint bases*. Liquid (or sometimes powdered) colorants are added to the tint base to make a color chosen by the customer from a large array of color cards. This requires that equal white tinting strength be maintained with the tint bases through quality control, or the colors obtained will differ. Furthermore, any new formulation must have the same white tinting strength as that of the formulation being replaced, or else the color cards and formulations in dealer stores will have to be replaced. In each quality line, two, or sometimes three or four, tinting bases are included. Often, the white paint itself in a can accept up to a few fluid ounces of colorant per gallon, to create very light or pastel colors. Bases to make deeper colors have lower levels of TiO_2, depending on how much colorant is to be added. Very deep bases may have no TiO_2 at all. Intermediate depths of shade could be matched using a lighter base, but the cost would be excessive because more tinting color would be needed to match the colors; hiding would be greater than needed. Tint bases are made with surfactants that help ensure compatibility between colorant and tint base. The tinting colorants are commonly "universal colorants" that can be used to tint either waterborne or solventborne paints.

Users are sometimes confused by the change in color of latex paint as it dries; the color of a dry film is darker than the color of the wet paint. In the wet paint, the interfaces between the water ($n = 1.33$), polymer particles ($n =$ approximately 1.5), TiO_2 ($n = 2.73$), and inert pigments ($n =$ approximately 1.6) scatter light to a greater degree than when the paint is dry. The dry paint has fewer interfaces as a result of coalescence of the latex particles, and there are smaller refractive index differences since the pigment particles are in a polymer matrix instead of water. Since light scattering decreases as water evaporates and the latex particles coalesce, the color gets darker; hiding also decreases as the paint dries.

Since exterior durability is not needed, lower cost vinyl acetate copolymer latexes (Section 9.3) are the principal binders for interior products. The T_g of VAc homopolymer is about 32°C, so that a softer comonomer such as butyl acrylate (BA) is needed to reduce T_g. Ethylene–VAc latexes have been introduced to replace VAc/BA latexes. Ethylene is not only a more effective co-monomer than BA for reducing the T_g of VAc polymers but appears to provide more effective plasticization as well. Paints made with VAc/ethylene latexes require less coalescing solvent, show better touch-up properties at low and room temperatures, and have better scrub resistance [22].

Table 32.2 is a supplier suggested formulation for an ultra low VOC interior eggshell paint [23]. The VOC for the paint is 6 g L^{-1}.

Natrosol Plus 330 MBR is a modified hydroxyethylcellulose associative thickener. Tamol 1124 is a dispersant that is the ammonium salt of a hydrophilic acid copolymer. AMP-95 is 2-amino-2-methyl-1-propanol. Strodex PK-90 is a dispersant that is said to promote color acceptance. Triton CF-10 is a low foam nonionic surfactant. Drewplus L-745 is an antifoam. Nuosept 95 is a biocide, a mixture of 5-substituted 1-aza-3,7-dioxabicyclo[3.3.0] octanes. Ti-Pure R-706 is a surface-treated rutile TiO_2 designed for use in waterborne coatings. Mattex is a surface-treated kaolin clay pigment. Attagel 50 is an attapulgite clay to

TABLE 32.2. Ultra Low VOC Interior Eggshell Paint

Component	Weight	Volume
Water	150.0	18.0
Natrosol Plus 220 MBR (3%)	50.0	6.0
Tamol 1124	6.0	0.6
AMP-95	2.0	0.2
Strodex PK-90	2.0	0.2
Triton CF-10	2.0	0.2
Drewplus L-145	1.5	0.2
Nuosept 95	1.5	0.2
Disperse the addition under agitation		
Ti-Pure R-706	230.0	6.9
Mattex	110.0	5.0
Attagel 50	5/0	0/3
Let down with		
Airflex EF811 (58.0%)	418.9	47.0
Water	83.0	10.0
Drewplus L-145	3.0	0.4
Acrysol RM-2020 NPR	20.0	2.3
Acrysol RM-8W	8.0	0.9
Benzoflex 9-88	6.0	0.6
Total	1098	99.1

control settling and syneresis. Airflex EF 811 is a VA/ethylene latex. Acrysol RM 2020 NPR and Acrysol RM-8W are hydrophobically modified ethoxylated polyurethanes (HEUR) associative thickeners. Benzoflex 9-88 (dipropylene glycol dibenzoate) is a coalescent.

For interior applications for which greater water resistance is needed, acrylic latexes or vinyl versatate copolymer latexes are used. A copolymer latex of BA, styrene, and 0.5% acrylamide shows superior scrub resistance [24]. Copolymer latexes of VAc and vinyl versatate are used in both interior and exterior paints. These copolymers have higher hydrolytic stability than conventional vinyl acetate copolymers. A combination of ethoxylated undecyl alcohol, a cellulose ether, and sodium vinyl sulfonate can be used as a surfactant/protective colloid in preparing the latexes. The effect of changes in chain length of the ethylene oxide units on the properties of latexes and paints has been reported. Increasing degree of ethoxylation gave smaller particle size latex particles and higher viscosity. In flat paints, optimum properties are obtained with 2 to 3% emulsifier concentration and 17 to 28 degree of ethoxylation. In gloss and semigloss paints, gloss improves with an increase of emulsifier content up to about 4%, where it levels off. The gloss improves as the degree of ethoxylation increases to 17. Above 4% concentration and 17 ethoxyl units, blocking increases dramatically. Similar results were obtained with VAc/ethylene latexes [25]. VAc/vinyl ester of a C_{12} branched acid latexes in interior flat wall paints have better scrub and stain resistance than VAc/BA latexes and styrene/acrylic latexes [26].

Acrylated castor oil has been used as a co-monomer, resulting in latexes that are formulated into semigloss paints with better block resistance while still permitting low temperature film formation. The latexes have the further advantage that coalescing solvents are not needed [27].

When painting ceilings, one is particularly anxious to get hiding in one coat, since painting over one's head and moving the ladder requires more effort than painting walls. The problem is particularly challenging because ceiling paints are commonly plain white, to reflect light diffusely. Since there are no color pigments in a white paint to absorb light, the hiding by white paints is poorer than any color paint made from it. The problem is compounded by the decrease in hiding when a latex paint film dries. The user thinks he or she has applied enough paint to hide marks on the ceiling, but comes back an hour or so later and finds that marks show through the dry paint. Special ceiling paints minimize this problem by formulating with PVC above CPVC. Dry paint films with PVC above CPVC have voids of air with $n = 1$ that add additional light scattering by the new interfaces between air and polymer as well as air and pigment. Formulations can be adjusted so that wet hiding and dry hiding are approximately equal. The films do not have as high mechanical strength as films of paint with PVC $<$ CPVC, and resistance to staining is poorer, but neither property is important for ceiling paints.

Owing to the high cost of TiO_2, coatings are not generally formulated with a PVC of TiO_2 more than 18% since incremental hiding at a higher PVC is not cost efficient. (This value is dependent on the actual TiO_2 content of the pigment and the stability of the dispersion.) Rather than using large quantities of TiO_2, lower cost inert pigments are used to occupy additional volume. Although there is some controversy, most workers accept that inert pigments with particle sizes smaller than that of the TiO_2, called *spacer inerts*, increase the efficiency of the TiO_2 [28]. A mathematical model has been developed that can be used to improve the spacing of TiO_2 by predicting the optimum inert pigment size distribution and concentration for a given formulation [29].

Aluminum silicate pigments are reported to permit replacing 50% of TiO_2 while maintaining good whiteness and hiding power. The effectiveness is reported to result not only from its action as a spacer, but hiding also results from the fact that the pigment is porous, so that it has better hiding power than most inert pigments [30].

Another approach to greater hiding at lower cost is to use a high T_g latex, such as polystyrene, as a pigment [31]. When the latex binder coalesces, the high T_g latex does not coalesce, but the particles remain separate, as with any other pigment. Including the dry volume of the high T_g latex particles as part of the pigment volume, paints can be formulated with a PVC greater than CPVC, resulting in air bubbles that increase hiding but without making the surface of the film porous. The paints provide equal hiding at lower TiO_2 content while retaining good enamel hold out and stain resistance. No convincing explanation of why an intact surface film forms in such paints has been published, but the method is said to be used on a large commercial scale.

Yet another approach to minimizing the TiO_2 requirement is to use as pigments special high T_g latexes, such as Ropaque Ultra [19], as shown in the formula for an exterior house paint given in Table 32.1 and explained in the text following the table.

A large fraction of latex flat wall paint is applied by roller. During roller application, latex paints *spatter*, some to a major degree. Paints with high extensional viscosity are likely to spatter severely [32] (Section 23.1.2). Extensional viscosity increases when high molecular weight (MW) water-soluble polymers with very flexible backbones are used as thickeners in a latex paint [33]. Spattering can be minimized by using low MW water-soluble thickeners with rigid segments in the polymer backbone, such as low MW HEC.

Whereas in many applications, the increase in external phase viscosity resulting from use of water-soluble polymeric thickeners is desirable, an application for which it is undesirable is on concrete block walls. Concrete block surfaces contain holes that are large compared to the pigment and latex particles, as well as pores that are small compared to them. When a solventborne paint is applied to concrete block, the coverage is low, since so much paint penetrates into the smaller holes. When regular latex paint is applied, the coverage is better. The lower viscosity of the external (continuous) phase relative to that of solventborne paint leads to more penetration of continuous phase into the small pores of the block so that the viscosity of the remaining paint increases rapidly and there is less penetration into the large holes. The coverage with latex paint can be improved further by omitting water-soluble thickener from the formulation. This further reduces the viscosity of the external phase, which can then penetrate more rapidly into the small pores and hence give even more rapid buildup of viscosity of the remaining paint. The effect is enhanced by the requirement that to have equal starting viscosity, the volume fraction of internal phase in the modified paint must be significantly higher than when water-soluble polymer is present. With increasing volume fraction internal phase, the viscosity increases more rapidly as the continuous phase is drained off in the small pores, so penetration into the large holes is reduced. A further advantage of latex paints, especially acrylic, styrene/acrylic, or styrene/butadiene latexes, relative to oil or alkyd paints is that they are not subject to saponification by the basicity of the concrete block and the mortar joints.

In a study of changes in composition and properties of latex paints applied to porous inorganic substrates, it was found that a significant amount of coalescing agent penetrated into the substrate, hence increasing the T_g of the film. There were also indications that binder penetrated. The authors recommend that it is particularly important to formulate paints with PVC close to CPVC for application to porous substrates [34].

When latex paint films form, surfactants sometimes bloom out of the film and collect on the surface. Usually, this is not noticeable; however, if water condenses on the paint surface, surfactant on the surface can dissolve. Then, when the water evaporates, surfactant concentrates in the last remaining water droplets, leaving brown spots of surfactant on the surface. The problem can be minimized by avoiding dark colored surfactants. However, surfactant can leave whitish spots on dark color paints. It has been shown that nonionic surfactants are more compatible with latex polymers and less likely to bloom than anionic surfactants [35]. Use of alkenyl-functional surfactants in latex preparation has been reported. The surfactant copolymerizes with the monomers during polymerization, giving latexes that are reported to have superior shear stability and freeze–thaw resistance. Paints prepared with the surfactant-bound latexes overcome the problems associated with the use of conventional surfactants such as surfactant blooming [36].

Although all latex paints have a low VOC compared to solventborne paints, there is still regulatory pressure to reduce or eliminate the VOC. To accomplish this, coalescing solvents and propylene glycol in the formula must be reduced to low levels or eliminated. Several approaches have been followed. Sequencing the composition of the monomer feed during polymerization so that the last part of the monomer feed has a higher fraction of monomers, giving a low T_g as in the power feed approach discussed in Section 9.1.3, would permit reduction of coalescing solvent. Addition of acrylic acid in the later part of the co-monomer feed has been suggested; water associates with a salt of the carboxylic acid, plasticizing the surface of the particles, promoting coalescence, and reducing the need for coalescing solvent. Another method is to use cross-linkable latexes with a lower T_g; cross-linking after film formation increases block and dirt resistance to offset the effect of the lower T_g (Section 9.4).

It is estimated that 120 million pounds of volatile coalescing agents are emitted in one year in the United States. A cross-linkable coalescing agent, the propylene glycol monoester of sunflower fatty acids, has been developed that essentially eliminates evaporation of the coalescent, thus reducing VOC. It is also reported to have less odor, increased scrub resistance, and produce higher gloss [37]. ADM received a 2005 presidential green award for the development.

An approach to eliminating the need for coalescing solvent is to use blends of high and low T_g latexes [38,39]. When a film of such a blend dries, the high T_g latex does not coalesce, but is dispersed in the continuous phase from the low T_g polymer. The hard particles act to reinforce the low T_g polymer film, increasing the storage modulus (E') of the film so that its block resistance is superior to that of a film from only the low T_g latex. The properties depend on the ratio of hard and soft latexes and on the particle sizes of the latexes. For example, excellent block resistance was obtained with a combination of 60% of a 37/61/2 styrene/BA/MAA latex with a particle size of 475 nm and $T_g = 9°C$ and 40% of a 70/28/2 styrene/BA/MAA latex with a particle size of 118 nm and $T_g = 62°C$. No coalescing agent was required for film formation at ambient temperature. The superior block resistance is said to result from the fact that close packing leads to a high concentration of the small-particle size latex at the surface of the film [39] (Section 32.3). Another approach to eliminating VOC is to make nano polymer/clay composite latexes. The latexes are made by polymerizing relatively low T_g acrylic monomers with clay dispersed in the water in which the emulsion polymerization is carried out. Films prepared from the latex have unusual toughness without compromising film formation. The latexes are used in zero VOC paints with low tack and dirt pickup [40] (Section 9.3).

Semigloss paints are made with lower pigment contents than flat paints. They are frequently used to paint doors and other woodwork. They are usually prepared using acrylic latexes to give better wash resistance, compared to other latex types.

Combined aqueous polyurethane dispersions (PUDs) and aqueous vinyl resins offer several potential advantages over each of the two separate types of polymers. (See Section 12.7.2 for a discussion of acrylated PUDs.) In general terms, polyurethane based polymers offer superior abrasion resistance, due to intermolecular hydrogen bonding. Vinyl resins have lower raw material costs and lower processing costs. PUDs have low minimum film formation (MFFT) temperatures in relation to dry film T_g due to the plasticizing effect of hydrogen bonding with water, reducing the T_g of the polymer particles. Used with high T_g acrylics, the MFFT is reduced without reducing hardness. For example, the open time of latex paints can be extended by adding a PUD with a T_g lower than that of the latex in the paint. A paint made with a latex composed of *n*-butyl acrylate (BA), 2-ethylhexyl acrylate (2-EHA), methyl methacrylate (MMA), and methacrylic acid (MAA), and modified with a PUD with a T_g of $-40°C$ has a longer open time, permitting re-brushing to ensure good hiding and lapping [41]. Coalescing solvents are required to permit film formation with latexes at low temperatures, whereas they are not required with PUDs.

Further improvement in properties can be obtained by polymerizing the acrylic monomers in a PUD or in a prepolymer precursor for a PUD. Semigloss wood coatings are formulated with a carboxy-functional PUD to which acrylic monometers, including *N*-(2-methacryloxyethyl)ethylene urea, are added and polymerized [42]. Latexes contain surfactants that can bloom to the surface of films, reducing gloss, whereas many PUDs can be made without surfactants.

32.3. GLOSS ENAMELS

The term *enamel* connotes a hard, glossy surface analogous to porcelain enamel. In the United States, gloss enamels are used both indoors and outdoors for trim around windows and doors, for shutters, for wood furniture, and on kitchen and bathroom walls. In some other countries, they are also used for walls. For gloss enamels, the merits and drawbacks of alkyd paints and latex paints are about evenly balanced, and latexes have partly, but not completely, displaced alkyds. Mounting pressure to reduce VOC may eventually tilt the balance toward latexes unless there is a technical breakthrough with alkyds. The 1999 EPA VOC emission standard for gloss paints is $380\ g\ L^{-1}$ and $450\ g\ L^{-1}$ for quick-dry enamels [3]. These levels are lower in California and certain eastern states.

32.3.1. Alkyd Gloss Enamels

As described in Chapter 15, alkyd enamels cross-link by autoxidation to form tough films that adhere well to a variety of surfaces and are block resistant and water resistant. An advantage of gloss alkyd enamels is that they have higher gloss than latex enamels. As discussed in Section 19.10.1, a polymer layer with very low pigment content forms at the upper surface of the coating during film formation from solution vehicle paints; this does not happen with latex paints.

The principal advantage of gloss alkyd paints is that they afford good hiding with one coat when used over a surface without sharp color contrasts. One-coat hiding is especially important to painting contractors, for whom the cost of application is higher than the cost of paint. Several factors account for the difference in hiding between alkyd and latex gloss paints. The NVV of a typical alkyd gloss paint can be 66% or even higher, whereas the NVV of a latex gloss paint is limited to about 33%. To obtain the same dry film thickness, one has to apply twice as thick a wet film of the latex paint.

Another factor that affects hiding is leveling. Assume that a uniform dry film thickness of, say, 50 μm of a paint provides just satisfactory hiding. If the paint levels poorly, there will be streaks of thinner film, say, 35 μm, and thicker film, say, 65 μm, and the hiding of the uneven film will be poor. Hiding is likely to be inferior to that of a uniform 35 μm dry film of the same paint. Since the 35 and 65 μm areas are immediately next to each other, the contrast emphasizes the poor hiding. Furthermore, not only is the hiding affected adversely by poor leveling, but also the contrast in colors resulting from the poor hiding in the valleys compared to the ridges emphasizes the poor leveling. Alkyd paints for brush application generally level better than latex paints because the solvent is slow evaporating mineral spirits. The difference in leveling is amplified when the paint is applied under warm, dry conditions. Yet another factor is that the volume fraction of internal phase in latex paints is higher than in alkyd paints since both the latex and pigment particles are dispersed phases. Therefore, even if the volatile material evaporates at equal rates, the viscosity of a latex paint increases faster.

As described in Section 24.2, Overdiep demonstrated that leveling of solventborne, brush-applied paints is promoted by surface tension differential–driven flow in the wet paint film [43]. When solvent evaporation begins, the fraction of solvent lost from the valleys of the brush marks is greater than that lost from the thicker ridges. Since the surface tension of the solvent is lower than that of the alkyd, the surface tension of the more concentrated alkyd solution in the valleys becomes higher than that in the ridges. The resulting differential in surface tension causes the paint to flow from the ridges into the valleys to minimize overall surface tension, thus promoting leveling. This driving force may be absent in the leveling of latex enamels (Section 32.3.2).

When selecting paints for repainting, it should be remembered that latex paints can be used over alkyds or latexes as long as the surface is properly prepared, but use of alkyds over latexes is risky. The solvent in alkyds may penetrate uncross-linked latex films and cause lifting.

The drawbacks of alkyd gloss enamels are largely the same as those of alkyd flat wall paints (Section 32.2). They include slow drying, odor, yellowing and embrittlement with age, and the need to use solvent for cleanup. In the future, perhaps the most important consideration will be VOC content. There is disagreement as to what level of VOC can be achieved with alkyd paints while retaining reasonable application and film properties. Many in the coatings field doubt that VOC can be reduced much below 250 g L^{-1} without a technical breakthrough. The problems of low-VOC alkyds include application characteristics, through dry, color change, and durability.

High-solids alkyds are discussed in Section 15.2. Solids can be increased to an extent by solvent selection, especially the use of hydrogen-bond acceptor solvents to reduce intermolecular hydrogen bonding. Although solids can be increased by reducing MW and by using narrower MW distributions, both of these approaches lead to inferior film properties and durability if carried very far.

A promising approach to increasing solids is the use of reactive diluents (Section 15.2). Such additives are low MW materials designed to reduce viscosity almost as efficiently as solvent, but also to co-react with the oxidizing alkyd during film formation. This permits reduction in VOC while maintaining film properties. An example is dicyclopentenyloxyethyl methacrylate. This reactive diluent has both an acrylate double bond and an activated allylic position. In the presence of driers, it can co-react with an alkyd such as a long oil linseed alkyd. Using this reactive diluent with specially designed alkyds is reported to permit formulation of gloss alkyd paints with a VOC of 155 g L^{-1}. The properties of the films are said to approach those of an alkyd paint with a VOC of 350 g L^{-1} [44]. Other types of reactive diluents are condensation products of mixtures of drying oil acid amides and acrylamide with (hexaalkoxymethyl)melamine [45] and oligomeric polyallyl ethers [46]. Although the use of reactive diluents is attractive, their cost and performance characteristics require further improvement. Use of polyallyl ethers has been questioned because of the potential for formation of toxic, volatile acrolein during cross-linking.

When paints containing oxidizing alkyds and driers are exposed to air, premature cross-linking will occur at the wet paint surface. This *skinning* is controlled by additives, as reviewed in Ref. [47]. The most effective was found to be methyl ethyl ketone oxime (MEKO). MEKO forms a complex with cobalt ions, $[Co(MEKO)_{1-8}]^{3+}$. The complex is in equilibrium with the components, so that while it is present it reduces the effectiveness of the cobalt. After the paint is applied, MEKO evaporates relatively rapidly, freeing the cobalt drier. The MEKO is added to the coating just before filling into containers. In some cases a further small amount of a solution of MEKO is added after the containers are filled and just before they are sealed, to prevent skinning during storage. Addition of 0.2% of MEKO prevents skinning for more than 250 days. It increases the dust-free time of an alkyd coating to 2 hours from 1 hour 45 minutes but the fully dried time is reduced from 4 hours 45 minutes to 4 hour. The initial effect results from the time for the MEKO to evaporate. The shorter drying time is thought to result from faster permeation of oxygen in the earlier stages after application while MEKO is inhibiting surface cure.

Two approaches to waterborne alkyds for trade sales paint have been investigated extensively. Efforts to develop gloss enamels based on water-reducible alkyd resins (Section 15.3) have not been very successful. A key obstacle has been the difficulty of making alkyds with sufficient hydrolytic stability for the required two-year shelf life. Water-reducible alkyds generally contain significant levels of solvent and may not reduce VOC much below 250 g L^{-1}. Emulsions of alkyds in water can also be used to prepare gloss enamels [48] (Section 26.3). They are used in Europe but have not been widely adopted in the United States. The VOC content can be lower, but the surfactants required for emulsification cause foaming on application and adversely affect film properties; and the shortcomings of odor and poor resistance to yellowing and embrittlement remain.

32.3.2. Latex Gloss Enamels

Development of latex gloss enamels has proven to be one of the most challenging problems of coatings technology. Key problems and potential solutions are discussed in this section. One problem is that of obtaining high gloss. As noted in Section 32.3.1, the clear polymer layer associated with the surface of alkyd enamels does not readily form as latex coalesces. The ratio of pigment to binder at the surface of a latex paint film can be reduced somewhat by using a finer particle size latex, but there is still a difference from alkyd paint films. Gloss is affected by flocculation of either pigment or latex. The choice of dispersing surfactants and thickeners, and their order of addition, can affect gloss. In one study it was shown that when a mixture of polyacrylic acid (PAA) and HEC was used as a thickener, gloss was higher if the HEC was added first than when PAA was added first [49]. Nonionic surfactants resulted in higher gloss than anionic surfactants. Other factors tending to reduce the gloss of latex paint films are the haze that results from incompatibility of surfactants (and possibly other components) and the blooming that results when surfactants migrate to the surface of the film. These problems can be minimized by making latexes with the lowest possible surfactant content and by selecting surfactants for pigment dispersion that are as compatible as possible.

Considerable work has been done using blends of compatible water-soluble resins with latexes to achieve high gloss. In floor wax applications, morpholine salts of styrene/acrylic acid copolymers have been used. When the film forms, the solution resin concentrates in the surface layer. When the film dries, the morpholine evaporates, leaving the free carboxylic acid groups. The film has sufficient water resistance for normal use, but it can be removed by mopping with ammonia water. This level of resistance is an advantage for floor wax but is not adequate for paint films. There have been some proprietary resins marketed that give better gloss with less loss of resistance properties.

In exterior and to a lesser degree, interior applications, the advantage of high initial gloss alkyd enamels is more than offset by the better gloss retention and resistance to cracking exhibited by latex gloss paints. Depending on location, alkyd enamels exposed outdoors lose so much gloss in a year or two that the coating may become nearly flat. Although a latex enamel starts out with a lower gloss, it retains most of its initial gloss for several years. In interior applications, the low odor, superior color retention, and greater resistance to cracking are important advantages of latex gloss paints.

The principal limitation of gloss latex paints is not their lower gloss; the major problem is achieving adequate hiding in one coat. The factors involved are discussed in Section 32.3.1. Not much can be done about the relatively low NVV of latex paints. The formulating challenge is to make latex enamels that can be easily applied in films thick enough for one-coat hiding. For maximum hiding, a latex enamel should be formulated to have a higher viscosity at high shear rate than that of an alkyd enamel. In practice, as is discussed later, the high shear rate viscosity of latex paints has traditionally been formulated to be lower than that of alkyd paints, further compounding the problem. Wet film thickness can be controlled to a degree by the extent to which the painter brushes out the paint. The painter tries to judge how much he or she should brush out by how well the wet paint is covering. In the case of alkyd paints, there is relatively little difference between the wet and dry hiding power of the paint. However, the wet hiding power of latex paints is greater than their dry hiding power. This increases the difficulty of judging how far to brush out a latex paint.

The need for good leveling is also described in Section 32.3.1. The driving forces for leveling of latex paints do not seem to have been considered in the literature. It is not obvious how surface tension differentials could develop during film formation of latex enamels. The surface tension of the water phase of latex paints is controlled primarily by the surfactants in the paint, which suggests that there probably is little change in surface tension as water evaporates. If this hypothesis is correct, the driving force for leveling of latex paints is the relatively small force of surface tension–driven leveling rather than the larger force of surface tension differential–driven leveling thought to operate with alkyd enamels. Another factor that may be important is dynamic surface tension. It has been shown that some surfactants reach equilibrium surface tension more rapidly than others [50]. The need for research is evident.

However, the major factor affecting the leveling and therefore the hiding of gloss latex paints is probably their rheological properties. As they have traditionally been formulated with water-soluble thickener polymers such as HEC, latex paints have exhibited a much greater degree of shear thinning than alkyd paints. This has led to latex paints having too low a viscosity at high shear rate, so the applied film thickness tends to be too thin, and too high a viscosity at low shear rate to permit adequate leveling. The problem is especially severe because the rate of recovery of viscosity after exposure to high shear rates is generally rapid with latex paints. The use of Stormer viscometers (Section 3.3.6) has been at least partly responsible for the prolonged time before the problem was well defined. This viscometer measures something related to viscosity in a midrange of shear rates but gives no information about viscosity in either of the critical regions—at high and low shear rates.

The reasons for this greater dependency of viscosity on shear rate in latex coatings have not been fully elucidated: at least two factors may be involved, flocculation of latex particles and/or pigment particles in the presence of HEC, and possible entanglement of chains of swollen high MW HEC [51]. Progress in minimizing the problem has been made by using *associative thickeners*, of which many kinds are available. (See Section 3.5.1 for discussion.) They all are moderately low MW hydrophilic polymers with two or more long chain nonpolar hydrocarbon groups spaced along the backbone. Use of such thickeners permits formulation of latex paints that exhibit less shear thinning, so that viscosity at high shear rates can be higher; as a result, thicker wet films can be applied [51,52]. Formulation with associative thickeners also reduces viscosity at low shear rates, so leveling is also improved. (The thicker wet film in itself helps promote leveling too, since the rate of leveling depends on wet film thickness, as discussed in Section 24.2.)

It has been shown that good formulations with associative thickeners not only level better but also give somewhat higher gloss [53]. Higher gloss, as well as better rheological properties, have been reported by use of a combination of associative thickeners [54], which may reduce flocculation of the TiO_2. Another factor in the improved gloss may be that associative thickeners are effective with small particle size latexes, which give the highest gloss [51]. It has also been shown that paints thickened with associative thickeners spatter less when applied by roller than do those thickened with HEC, and that most of the thickeners resist viscosity loss by bacterial action [51]. Sag control of latex paints is more difficult with associative thickeners but still easier than with alkyd paints; leveling and gloss are still not equal to those of most alkyd paints [53].

Another shortcoming of latex paints, particularly evident in gloss formulations, is the time required to develop final film properties. Part of the problem is that users are, in a sense, fooled by the drying properties of latex paints. They dry to touch more rapidly than do alkyd paints and can be handled sooner. However, they require longer to reach their ultimate properties. For example, even though latex paints dry more rapidly than alkyd paints, a longer time is necessary to develop the block resistance required to prevent windows and doors from sticking or to permit putting heavy objects on a newly painted shelf. The initial film formation of latex particles is rapid, but full coalescence is limited by the availability of free volume. Since the $T - T_g$ must be small, free volume is small. The situation is helped by using coalescing solvents. However, loss of these solvents is controlled by diffusion rate, which is also limited by $T - T_g$. It has been reported that latex particles having inner layers of relatively high T_g with a gradient to low T_g on the outer shell of the particles can provide film formation at low temperatures, yet achieve block resistance relatively quickly [55]. It has been recommended that a high T_g latex be used with larger amounts of carefully selected coalescing agents [56]. The dimethylether of dipropylene glycol is reported to be an effective coalescing agent with a relatively rapid rate of evaporation from films [57]. Whereas the initial loss of coalescing agent is controlled by volatility, losses in later stages are controlled by the rate of diffusion through the film, and the loss rate becomes very low. There is need for further progress, but as this problem is unlikely ever to be solved completely, there is a need to educate consumers better on the limitations of latex paints.

Progress has been made in developing gloss latex paints with adequate hiding by one coat, but further efforts lie ahead. The problem is made more difficult by the lack of adequate laboratory tests to measure gloss (Section 19.10.2) or absolute hiding (Section 19.3). The lack of adequate test procedures is particularly troublesome because many of the companies that supply raw materials to the paint industry, many of the people who establish specifications and regulations, and sadly, even people working as paint formulators are not aware that the laboratory tests are inadequate.

Another problem of some gloss latex paints is poor adhesion to old gloss paint surfaces when the new dry paint film gets wet. After wetting with water, some latex paint films can be peeled off the old paint surface in sheets. Such a film is said to exhibit poor *wet adhesion*. There is always a problem of achieving adequate adhesion when repainting old gloss paint surfaces, even with alkyd paints, but the problem with latex paints is more severe. It is essential to wash any grease off the surface and to roughen the surface by sanding, but even with such surface preparation, many latex paints do not show good wet adhesion. Wet adhesion improves with age, but it can remain seriously deficient for several weeks or even months. Latexes that minimize the problem of wet adhesion have been developed by several manufacturers. Incorporation of small amounts of hydrogen-bonding polarizable co-monomers such as methacrylamidoethyleneurea (Section 9.1) improves wet adhesion and wet scrub resistance.

Although VOC of latex paints is lower than that of alkyd paints, latex enamels are usually formulated with higher VOCs than other latex paints. Extra coalescing solvent is used to permit use of latexes with the relatively high T_g needed for block, scrub, and stain resistance. Their VOC is often only slightly less than the maximum (currently, $250\ \mathrm{g\ L^{-1}}$) allowed by the strictest regulations. There is mounting pressure to reduce VOC emissions further. One approach is to select the most efficient coalescing solvents to minimize the amount required. For example, the acetate of propylene glycol *n*-butyl ether has been recommended as an efficient coalescent [57]. 2-Ethylhexyl benzoate has been recommended as a replacement for Texanol as coalescent. It is reported that 25% less 2-ethylhexayl benzoate is required, thus reducing the VOCs; the odor is lower; and the evaporation rate is slower [58]. Another approach is to use blends of high and low T_g latexes [38]. The binder must be transparent, which requires that the difference in refractive index be small and that the particle size of the high T_g latex be small.

Core–shell copolymers of BA, MMA, and AA can be used to formulate gloss latex paints having high block resistance with no coalescent. The final films were dispersions of hard particles in a continuous softer phase. The best compromise of properties was with 25 to 35% of hard phase (MMA) [59].

Still another approach is to use thermosetting latexes (Section 9.4); this permits use of low T_g latexes that form films without the need for coalescing solvents but that reach adequate hardness through cross-linking. For example, an undisclosed latex that cross-links by autoxidation is reported to permit formulation of zero VOC gloss latex paints [60]. An acrylic latex that oxidatively cross-links, Rhoplex HG-700, is recommended for gloss paints. It is used with an associative thickener and a surfactant that promotes leveling. The latex has a MFFT of 16°C. Films of the paint gain block resistance rapidly with full development of cross-linked properties over a period of a month. Paint films show a 20° gloss of 50 to 60 and a 60° gloss of 80 to 90. VOC is reported to be $150\,\mathrm{g\,L^{-1}}$. Adhesion to old alkyd paint surfaces and exterior durability are reported to be excellent [61].

Satisfactory later gloss enamels having low VOC have been reported by combining associative thickeners and a cross-linking later [60]. An associative thicker (hydrophobically modified polyacrylic acid ammonium salt) increases open time to permit wet lapping and improves freeze-thaw resistance. This permits elimination of propylene glycol thus reducing VOC [60].

Acrylate–urethane dispersions have also been reported to give, exterior latex paints with good gloss and exterior durability [62].

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33

Special Purpose Coatings

The term *special purpose coatings* designates industrial coatings that are applied outside a factory. In 2002, they accounted for about 20% ($3.15 billion) of the value of U.S. coatings shipments [1]. Although the volume is the smallest of the three classes of coatings, it is substantial and the value per unit volume is the highest. Separate profit figures are not available, but historically, the operating profit percent for entrenched suppliers is also the highest. Many different end uses are involved; our discussion centers on four of the larger markets: maintenance, marine, automobile refinish, and aircraft coatings.

33.1. MAINTENANCE PAINTS

The term *maintenance paints* is generally taken to mean paints for field application, including paints for highway bridges, refineries, factories, power plants, and tank farms; not usually included are paints for office buildings or retail stores, which are classified as architectural coatings. For many maintenance paints, a major requirement is corrosion protection (Chapter 7). Sometimes, the terms *heavy duty maintenance paints*, *anti-corrosive paints*, *protective coatings*, or *industrial paints* are used, all implying that the paints must perform more effectively in aggressive environments than trade sales paints. Although selling prices are important, the major economic demands of customers emphasize proven performance, the time interval to be expected between repainting, and service, rather than the cost of the paint. The frequency of repainting in a factory is especially critical, since production may have to be shut down for repainting.

Since no laboratory tests adequately predict field performance of maintenance coatings, potential customers want to inspect actual field use examples of a coating system being recommended to them. State highway departments and the larger oil, chemical, and

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construction companies employ specialized engineering groups responsible for working both with coating suppliers to select appropriate coatings for their company's needs and with applicators to specify the application parameters. These groups also serve as inspectors to see that the coatings are applied properly. Records are kept of surface preparation, application conditions, coating composition, and coating supplier; and the performance of coatings on the various installations is monitored. The composition of the coatings is a major variable, but surface preparation and application procedures are also critical to performance. The *Steel Structures Painting Council* is a valuable source of information about the effects of such variables in its *Steel Structures Painting Manual* [2]. The problems of predicting the service life of coatings are discussed in the introductory paragraphs of Chapter 4, and the status of corrosion testing and performance prediction is described in Section 7.5. As discussed in those sections, reliability theory is a potentially powerful tool [3].

The most commonly used method for surface preparation has been sandblasting. It can be very effective for removing surface rust; it also roughens the surface, increasing the contact area with the coating, which in turn promotes adhesion. However, sandblasting creates hazardous dust: small particles of silica and paint debris, often containing toxic pigments. Elaborate and expensive containment systems are necessary to prevent worker exposure and contamination of the environment. As discussed in Section 6.4, many modifications and alternatives to sandblasting are being studied. They include dry abrasive blasting with a variety of other media, and ultrahigh pressure hydroblasting at pressures above 25,000 psi. Whatever the method, only a relatively limited area should be cleaned at a time, and primer should be applied as soon as possible. One of the authors was asked to explain why there had been a massive failure of coatings on a Taiwan oil tank farm located only a few hundred meters from the sea. The tanks had been carefully sandblasted and a high performance coating system had been used. However, there was a delay of some days between sandblasting and coating. In the meantime, spray from the sea deposited salt on the surface; the primer was sprayed over salt-contaminated steel. The salt crystals dissolved in water that permeated though the coating, leading in a few weeks to blistering and massive failure.

The coating system must be carefully selected for the particular installation. Most systems include at least two types of coatings: a primer and a top coat. Frequently, more than one layer of primer and/or top coat is applied, and in some cases, a combination of primer, an intermediate coat, and top coats is used. Primers provide the primary corrosion control, but intermediate and top coats also have significant effects on corrosion protection by reducing oxygen and water permeability of the combined films. Top coats also serve to protect the primer and provide other properties, such as gloss, exterior durability, and abrasion resistance. Three classes of primers are used: barrier primers, zinc-rich primers, and primers containing passivating pigments.

33.1.1. Barrier Coating Systems

As discussed in Section 7.3, a requirement for a barrier system primer is that it have excellent wet adhesion. The primer should have a low viscosity continuous phase with slow evaporating solvents to permit as rapid and complete penetration as possible into microscopic cracks and crevices in the metal surface. Amine-substituted binders are particularly resistant to water displacement. Phosphate esters such as epoxy phosphates have also been shown to enhance wet adhesion (Section 13.5). The T_g of the fully reacted binder should generally be only a little above the ambient temperature at which the curing is to be carried out. If the T_g of the fully reacted cross-linked film is too high, the rate of the cross-linking reaction becomes mobility controlled, and the reaction may stop prior to complete conversion (Section 2.3.2).

Two package (2K) primers formulated with bisphenol A (BPA) and/or novolac epoxy resins in one package and a polyfunctional amine in the other are widely used, since they provide good adhesion combined with excellent saponification resistance (Section 13.2). The novolac epoxy resins are prepared from novolac resins made with phenol, cresol, bisphenol A, and/or tetraphenolethane. To reduce viscosity, the triglycidyl ether of trimethylol propane (TMP) can be used as a reactive diluent. A coating formulated with the triglycidyl ether of TMP and a phenol–formaldehyde novolac resin showed better resistance to methylene chloride, acetic acid, and sulfuric acid than did one formulated with a bisphenol F resin [4].

Pot life is increased by using relatively high molecular weight (MW) epoxy resins and amine cross-linkers at relatively low solids, since this minimizes the concentrations of reactive groups. Especially when the solvents are slow evaporating, the vehicle can penetrate well into surface irregularities. Pigmentation should be high but somewhat below the critical pigment volume concentration (CPVC), to reduce permeability to oxygen and water and give a low gloss surface that enhances adhesion of top coat to the primer. Intercoat adhesion is further enhanced by applying top coat before cure of the primer is complete. Only a thin coat of primer is needed, but it is generally desirable to apply multiple coats of primer to assure that the entire surface of the metal has been coated. Sometimes, two different epoxy formulations are used: one as primer and the other for intermediate coats. To reduce VOC emissions, higher solids coatings are being adopted. As solids increase, the challenges of formulating coatings with adequate pot life becomes more difficult. The lower MW reactants in high-solids coatings increase the possibilities for toxic hazards.

Waterborne epoxy–amine primers are being used increasingly (Section 13.2.6). Novolac epoxy resins are frequently used in waterborne coatings since the higher MW does not affect viscosity. Novolac epoxies dispersed with a proprietary surfactant combined with a dispersion of a proprietary amine are reported to give excellent performance [5].

Alkyd formulations are used as primers, although their use is declining. 2K urethane coatings are also used as primers. Aromatic polyisocyanate prepolymers are chosen over aliphatic polyisocyanates due to their lower cost. They show strong adhesion to metals, including galvanized steel, concrete, and wood. Their resistance to saponification is a major advantage compared to alkyd resins in primers; this is especially important in coatings for galvanized steel and concrete, which have highly alkaline surfaces. Moisture-curable urethane coatings are also used as primers. Commonly primers are formulated with PVC $>$ CPVC, resulting in somewhat porous films. This permits water penetration through the film, minimizing the CO_2 bubbling from reaction with water.

The poor exterior durability of BPA and novolac epoxy–amine coatings limits their use as top coats to interior applications, for which their generally high chemical resistance makes them useful. An exception is that most epoxy–amine coatings do not resist acetic acid (or similar organic acids) very well. In contrast to inorganic acids, acetic acid dissolves in the films; this effect is promoted by the presence of amines, especially if cross-link density is inadequate. Novolac epoxy resins have a higher average functionality than BPA epoxies and generally provide greater organic acid resistance.

Generally, top coats have a different composition than primers. Chlorinated polymers such as vinyl chloride copolymer resins and chlorinated rubbers are used as top coat vehicles, since they have low moisture vapor and oxygen permeabilities (Section 17.1). Chlorinated resins require stabilization against photodegradation (Section 5.4). Polyvinylidene fluoride/acrylate copolymer latexes offer outstanding exterior durability [6] (Section 17.1.4). Since they are not cross-linked, they remain solvent sensitive and are therefore not appropriate for applications such as petroleum refineries and chemical plants. Use of chlorinated resins is limited by the high VOC required due to their high MW. Polypropylene has low water permeability and is being used for top coats on pipelines [7]. A system of an epoxy primer, an intermediate coat of a polar-modified polypropylene copolymer, and a polypropylene top coat is used. Since polypropylene is subject to photoxidation, UV stabilization is required.

Two package urethane coatings are used increasingly as top coats, due to lower VOC and high solvent resistance of the cured films; urethanes are particularly useful when abrasion resistance is an important requirement (Section 12.4). An important variable in 2K polyisocyanate–polyol coatings is the NCO/OH ratio. In ambient-cure systems, it is often found that a ratio of the order of 1.1 : 1 gives better film performance than a 1 : 1 ratio. A probable reason is that part of the NCO reacts with water from solvent, pigment, or air to give urea cross-links. To the extent this happens, two hydroxyls are unreacted for each water molecule; excess NCO minimizes residual unreacted hydroxyl groups. Solvent resistance is also improved. Since polyisocyanates are typically lower in viscosity than the polyol, excess NCO gives a lower VOC content [8].

2K urea coatings made from polyamines and polyisocyanates have the advantages that they cure rapidly even at freezing temperatures, have almost zero VOC, and have good low temperature flexibility. Aromatic amines react slowly enough that they can be used in 2K coatings. For example, MDI–polyoxypropylene prepolymers with aromatic amines are used in maintenance coatings for which gloss and color retention are not critical [9]. Roofs and floors can be walked on within 30 seconds after they are coated with such polyureas.

For 2K ureas that require exterior durability, hindered aliphatic amines are used. In one example, one package was a mixture of hindered and less hindered di- and tri-amines, and the other was HDI isocyanurate. The coatings had adequate pot life, tack free time of 2.3 minutes at 25°C, strong adhesion to a variety of substrates, chemical resistance, and exterior durability. No primer is required [10].

The chemistry of moisture-curable urethanes is described in Section 12.6, where it is explained that they are not actually urethanes, but ureas. These are one-package (1K) formulations that can cure at temperatures as low as 0°C, generally by reaction with moisture in the air. They have certain advantages over two-package (2K) maintenance coatings. The possibility of incorrect mixing ratios is eliminated, as are potential problems of mixing more 2K coating than can be used before the viscosity has increased too much for application or of not enough and running out before a work shift ends. A further advantage is that 1K formulations can be applied to damp surfaces. As compared to 1K systems that cure by autoxidation, moisture-curable coatings can have superior resistance to oxidation and exterior exposure (if aliphatic diisocyanates are used).

Compared with alkyd maintenance paints, moisture-curable urethanes generally exhibit superior abrasion resistance, chemical and solvent resistance, hydrolytic stability, superior adhesion retention over alkaline surfaces such as cement-based substrates or metal substrates, and with aliphatic isocyanates, superior exterior durability. Reference [11] provides a useful discussion of moisture-curable urethane coatings, especially for maintenance coatings. They are used for applications such as floor coatings, for which abrasion resistance and hydrolytic stability are especially important. They can also be applied at low temperatures and relatively high humidity. The coatings can be applied over metal when the temperature is below the dew point since the isocyanate groups react with the water condensed on the surfaces [12]. Reference [13] describes several examples of application to various bridges and other applications.

On the other hand, moisture-curable urethanes are more expensive than alkyds. A further drawback is that cure rates depend on the water content of the air; at low temperatures, higher relative humidity is required than at higher temperatures, since water content decreases with decreasing temperature for the same relative humidity. At high humidity and temperature, cure is rapid, but the carbon dioxide released by the reaction of isocyanate with water can be trapped as bubbles, especially in thick films. See Ref. [14] for a discussion of the effects of temperature and humidity and other application considerations.

A further consideration is that solvents, pigments, and other coating components must be essentially water free. Moisture-curable coatings are often used as clear, glossy coatings because it is expensive to remove adsorbed water from pigments. Molecular sieves can be used to adsorb water, but they reduce gloss. Pigmented moisture-curable coatings can be made using a water scavenger such as an alkyl orthoformate or *p*-toluene sulfonylisocyanate. Such water scavengers, especially sulfonylisocyanates, must be handled with care due to toxicity. Isophorone diisocyanate (IPDI) can be used as a moisture scavenger [15]; moisture-curable urethane coatings using IPDI are used on military vehicles. Oxazolidines are reported to be effective moisture scavengers for aliphatic isocyanate-based coatings, presumably with less toxic hazard and lower cost [16]. 4-Ethyl-2-methyl-2-(3-methylbutyl)-1,3-oxazolidine provides rapid water removal while not adversely affecting the stability or performance of a coating.

In most cases, atmospheric water is the curing agent, but in some cases spray application of liquid water or steam on the uncured film is recommended. A patent describes the use of steam fed spray application of moisture-curable coatings; cure is very rapid, and film thickness as high as 200 μm are feasible [17]. Through cure can also be accelerated by putting a hygroscopic liquid in a moisture-curable formulation. For example, *N*-methylpyrrolidinone [18] and γ-butyrolactone [19] have been used for this purpose [20].

2K waterborne urethane coatings have very low VOC emissions. A comparison of their performance with that of solventborne high solids 2K urethane coatings showed that when applied at 25°C (75°F) or below, the performance was similar. Under high humidity/high temperature conditions the films from the solventborne coating showed poor surface smoothness and appearance, whereas the waterborne coating had superior appearance. Five-mil films of the waterborne coating could be applied satisfactorily, but solventborne coatings are only recommended up to 2 mils. The waterborne coating was formulated with a water-reducible acrylic resin and a hydrophilically modified polyisocyanate [21].

Alkyd resins are still used, although their saponification resistance and exterior durability are inferior. Coatings based on alkyds are generally lower in cost and have intermediate VOC emissions. As a result of their low surface tension, alkyd-based coatings are less likely to develop film defects during application.

As described in Section 15.7, uralkyds have properties superior to those of alkyds. Studies indicate that the rate of water permeability in alkyd films is higher than in the uralkyd films [22].

Waterborne autoxidizable urethane coatings are being used (Section 15.7.2). A partial ester of linseed oil fatty acid with PE is reacted with MDI and then with maleic anhydride to form a maleated uralkyd [23]. The resin is diluted in 2-butoxyethanol, neutralized with TEA, and diluted with water. Polyunsaturated acid–substituted aqueous polyurethane dispersions (PUDs) are also being used. For example, a PUD made by reacting a diisocyanate with a diol, a fatty acid monoglyceride, and dimethylolpropionic acid (DMPA) is neutralized with an amine and then dispersed in water. Water acts as a chain extender for terminal isocyanate groups [24]. Hydrolytic stability of the aqueous dispersions is excellent. Films also have excellent abrasion resistance. Drying speed, color, and cost are dependent on the drying oil used. Aliphatic diisocyanates provide superior color retention and exterior durability at a higher cost. Cost can be reduced by blending in 10 to 20% of acrylic latex.

Corrosion protection generally increases as water vapor and oxygen permeability of the coatings are reduced (Section 7.3.3). High levels of pigmentation reduce permeability and cost, but also reduce gloss. Sometimes, low gloss intermediate coats are applied over the primer, followed by a high gloss top coat. Platelet pigments, such as mica and micaceous iron oxide, that can orient parallel to the surface of the coating as the solvent in the coating evaporates are particularly effective in reducing permeability. Pigmentation of the final top coat with leafing aluminum flake pigment is desirable because an almost continuous layer of aluminum forms at the surface.

Since zinc rapidly develops strongly basic corrosion products, alkyds are not suitable vehicles for galvanized steel. An extensive study showed that epoxy–polyamide primer with a urethane top coat gave the best performance on galvanized steel when exposed for $4\frac{1}{2}$ years at Cape Kennedy, Florida [25].

33.1.2. Systems with Zinc-Rich Primers

A typical modern coating for steel bridges consists of three layers: a zinc-rich primer, an epoxy intermediate coat, and a polyurethane top coat. The primer provides galvanic protection, the intermediate coat is a barrier, and the top coat is an additional barrier for enhanced weather resistance.

As discussed in Section 7.4.3, zinc-rich primers provide high performance either when the surface cannot be completely cleaned of rust or when complete penetration into surface irregularities cannot be achieved. The zinc acts as a sacrificial metal, protecting the steel from corrosion. To be effective, the level of zinc pigmentation must be such that $PVC > CPVC$. The high level of pigmentation assures electrical contact between the zinc particles and porosity that permits water to enter the film, establishing a conductive circuit with the steel surface. Even after a significant fraction of the zinc is consumed, the primer continues to provide protection, perhaps because the pores fill with $Zn(OH)_2$ and $ZnCO_3$, whose alkalinity may provide passivation [26] or perhaps because they form a barrier to water and oxygen. In most applications, top coats are required to protect the zinc against corrosion, reduce probability of mechanical damage, and provide a desired appearance. See Ref. [27] for a review of the types of zinc-rich primers together with their application and performance.

There are two classes of zinc-rich primers: inorganic and organic, each available in solvent-borne and waterborne formulations. The binder of inorganic zinc-rich primers is a prepolymer derived by reacting tetraethyl orthosilicate with a limited amount of water. The chemistry of cross-linking is described in Section 16.4. Cross-linking depends on moisture. When the coating is applied at low humidities, especially if the temperature is high, film properties such as abrasion resistance may be adversely affected [28]. If it is necessary to paint under hot and dry conditions, the coating should be mist-sprayed with water immediately after application. A review of the effects of zinc particle size and shape, extender pigments, and application techniques of ethyl silicate–based primers is available [29].

Organic primers command a share of the market by their advantages of greater tolerance to incomplete removal of oils from the substrate, easier spray application, and better compatibility with some top coats [30]. The binders in organic zinc-rich primers are often based on 2K epoxy–polyamine (polyamide) resins. Polyurethane binders are used increasingly. For example, the Michigan Department of Transportation recently adopted a urethane zinc-rich primer as its standard [31], replacing an epoxy zinc-rich primer [32].

In the older literature there is published evidence that in some circumstances, inorganic zinc-rich primers can provide better protection than organic primers. For example, in a seacoast environment, a six-year service life was estimated for inorganic primers compared to three years for the organic type [30]. More recently, however, organic zinc-rich primers have been adopted for many demanding applications, indicating that knowledgeable people expect them to be long lived. For example, in the early 2000s, zinc–epoxy primers were supplanting zinc–silicate primers in North Sea oil well applications [33]; the change is said to be driven by health, safety, and cost considerations as well as unspecified improvements in technology. Organic zinc–epoxy–urethane systems are favored increasingly and sometimes required in many U.S. states [34] and are typically used for onshore and offshore steel windmills [35].

Zinc-rich primers formulated with moisture-curable urethanes are used for new construction when the metal surface is blast cleaned to white metal conditions [36]. Reference [37] provides a discussion of variables in formulating such zinc-rich primers. Resistance to saponification is critical for a binder for zinc-rich coatings since the zinc reacts with oxygen and water, producing zinc hydroxide and zinc carbonate. Thus, urethanes are much more suitable than alkyd resins. Epoxy–amine 2K zinc-rich primers have been used widely, but the urethane primers have the advantage of being 1K coatings.

In response to the need to reduce VOC, waterborne zinc-rich primers have been developed. As of 2005 they had captured only a small fraction ($<3\%$) of the heavy-duty maintenance market in Europe, and early products admittedly performed poorly [38]. Both inorganic and organic waterborne zinc-rich primers are now available that are reported to rival solventborne counterparts in protective properties and have much lower VOC; different application methods are required [38]. For inorganics, a typical binder is a combination of potassium, sodium, and/or lithium silicates with a dispersion of colloidal silica [39]. Excellent performance on oil and gas production facilities in marine environments has been reported [40].

A challenge in using zinc-rich primers is proper selection and application of the top coat. The activity of the primer depends on maintaining its porosity by having PVC $>$ CPVC. If the top coat vehicle penetrates through pores in the primer, PVC of the primer is reduced to a level approximately equal to CPVC, reducing the effectiveness of the primer. Penetration of the continuous phase of a top coat into pores is controlled primarily by the viscosity of the external phase. Penetration can be minimized by applying a *mist coat* (i.e., a very thin coating) of top coat first. The solvent evaporates rapidly from a thin coating, so the viscosity of the continuous phase increases rapidly, minimizing penetration and sealing the pores. Proper application requires considerable skill, since excess mist coat in an area leads to increased penetration into the pores, but lack of coverage of an area results in insufficient sealing in that area, so the vehicle of the next coat of top coat will penetrate into the pores. Sealing the pores minimizes pinholing or bubbling during application of thick layers of top coat. It is desirable for the color of the mist coat to contrast with that of the zinc-rich primer to aid the sprayer in applying complete but not excessive coverage. After the mist coat is applied, application of further coats requires no special spraying skill. Since alkaline zinc oxide, hydroxide, and carbonate are present on the zinc surface, top coats in contact with the primer coat must be stable against saponification. Two package urethane, vinyl, or chlorinated rubber coatings are used. Often, an intermediate epoxy coat is applied to the primer, followed by a urethane top coat.

33.1.3. Systems with Passivating Pigment Containing Primers

When extensive film damage must be anticipated and when the substrate cannot be completely cleaned (especially when oily rust will remain), or when the coating cannot penetrate into the surface irregularities, passivating pigment primers are the primers of choice (Section 7.4.2). In contrast to the situation with baked OEM product coatings, for which passivating pigments are seldom appropriate, there are many cases in field applications for which they are preferred despite the fact that blistering is more likely to occur.

A range of primer vehicles is used. Alkyds have the advantage that they are relatively low cost and wet oily surfaces, but they are deficient in saponification resistance. Epoxy–amine primers provide greater saponification resistance and good wet adhesion. Epoxy ester binders are intermediate in cost and performance.

For many years, oil and alkyd paints with lead anticorrosive pigments were commonly used on bridges and other steel structures. They performed fairly well, especially since their relatively low cost made it economical to apply thick films. But repainting is a major problem—safe removal of the old lead paint and replacement with a lead-free coating is extremely expensive. Hare estimated a cost of \$54 to \$217 per square meter in 1997, which is probably much higher today [41]. Today, the emphasis is on coatings that will afford the longest possible intervals between repainting.

Zinc yellow was, for many years, the passivating pigment of choice (Section 7.4.2). However, zinc yellow is carcinogenic, and care must be taken to avoid inhaling or ingesting spray dust, sanding dust, or welding fumes; in some countries, its use has been prohibited. Zinc yellow is being replaced by other passivating pigments; possible replacement pigments are discussed in Section 7.4.2.

In recent years, the use of latex paint systems for maintenance applications has increased. When water is applied to a freshly abrasive blasted steel surface, there is almost instantaneous rusting, called *flash rusting*. Flash rusting occurs with latex paints. To avoid it, the formulation should include an amine such as 2-amino-2-methyl-propan-1-ol (AMP). Use of mercaptan-substituted compounds as additives to prevent flash rusting has also been recommended [42].

A paper has been published reporting on studies of factors influencing flash rusting and tests for evaluating it. Relative humidity during application is a major factor, especially when it is over 80%. Use of a "complex zinc compound in a mixture of anionic ionogenic solvents" gave better protection than a 10% aqueous solution of a 9 : 1 ratio of sodium benzoate and sodium nitrite solution. The composition of the latex affects the extent of flash rusting. A copolymer of acrylic acid, methacrylic acid, 2-ethylhexyl acrylate, and styrene gave good results. The easiest way to evaluate flash rusting is to apply pigment-free films to the steel since then there is nothing to hide the development of the red rust layer as it forms. A variety of other test methods are reported [43].

Since latex particles are large compared to the size of many of the crevices in the surface of steel, and since the viscosity of the coalesced latex polymer is extremely high, complete penetration into the crevices cannot be expected. Therefore, it is essential to use a passivating pigment. The pigment must be chosen such that the concentration of polyvalent ions is low enough so that package stability of the latex is not affected adversely, but is still high enough that it can serve its passivating function. Strontium chromate is less soluble than zinc yellow and is preferred. Zinc phosphate has been used. Among the newer passivating pigments, zinc–calcium molybdate and calcium borosilicates have been recommended.

Acrylic, styrene–acrylic, and vinylidene chloride/acrylic latex polymers are completely resistant to saponification. Special proprietary latexes are sold that provide enhanced adhesion to metal in the presence of water. It has been suggested that amine-substituted latexes are especially appropriate for wet adhesion. Use of 2-(dimethylamino)ethyl acrylate or methacrylate as a co-monomer is a way to incorporate amine groups on the latex polymer. Methacrylamidoethylethyleneurea has also found use as a wet adhesion promoting monomer. Another approach for enhancing wet adhesion is to use an alkyd or a modified drying oil to replace part of the latex polymer. The alkyd is emulsified into the coating. After application, as the water evaporates, the emulsion breaks and some of the alkyd can penetrate the fissures in the steel surface. Epoxy esters are more hydrolytically stable than alkyds and would be expected to provide better corrosion protection.

Owing to the high moisture vapor and oxygen permeability of most latex paint films, it is desirable to use some platelet pigment in the formulation. Mica is used in both primers and top coats. Final top coats using leafing aluminum (Section 20.2.5) are particularly appropriate. To avoid problems of the reactivity of aluminum with water, a special grade of leafing aluminum is mixed into a latex base paint just before application.

The need for reducing VOC emissions has been particularly critical in California. Since commercial paint suppliers did not have latex paints available for maintenance coatings for bridges, the California State Office of Transportation Laboratory undertook the formulation and application of latex paints to several highway bridges in order to evaluate their potential utility [44]. Latex primers were used in some cases and inorganic zinc-rich primers in others; in all cases, latex top coats were used. It is reported that some systems were still performing well after over five years field exposure. Based on the experience obtained, it was recommended that application should only be done when the temperature is above 10°C and when the relative humidity is less than 75%. Use of latex systems can be expected to expand as requirements for reduced VOC emissions become more stringent.

Traffic striping paints are a large-volume part of the special purpose coatings market. In the past, solventborne combinations of alkyds and chlorinated rubber formulated in fast-evaporating solvents were used. Glass bead pigments are used to increase reflectance of headlight beams back to the driver. Alkyds were displaced by preformed tape, epoxies, and polyureas

Latex traffic paints are used widely in Europe, and several U.S. states are putting them through final use tests. They have been compared to pre-formed tape, polyurea paint, and epoxy paint. Their useful life was found to be three years, not as long as the other paints but lower in total cost, including the earlier replacement. The epoxy paint was next lowest in cost but had the added disadvantage that recoat adhesion was poor and the old traffic paint had to be removed [45]. Thermosetting latexes are used exemplified by an ammonia neutralized binder consisting of a BA/MMA/MAA/acetoacetoxyethyl methacrylate latex made using dodecyl mercaptan for MW control, aminoethylaminopropyltrimethoxysilane, and a dimethylaminoethyl methacrylate/AA latex [46].

33.2. MARINE COATINGS

The marine coatings market includes coatings for pleasure craft, yachts, as well as for naval and commercial ships. Coatings for pleasure craft are commonly sold on a retail basis to the individual owner. A range of products is available; one for wood is spar varnish. The original spar varnish (Section 14.3.2) was a phenolic–tung oil varnish; the tung oil provides high cross-linking functionality, and the phenolic resin imparts hardness, increased moisture resistance, and exterior durability. Although some phenolic–tung oil is still used by traditionalists, the bulk of this market has shifted to uralkyds, which provide greater abrasion and water resistance (Section 15.7).

The larger part of the market is for commercial and naval shipping and some shore installations that are exposed to marine environments. A variety of substrate surfaces are coated, and many require special coatings. Reference [47] provides a useful overview of the market and products. A paper written in 2004 reports that the annual U.S. market for marine coatings by market is: U.S. Navy, \$4.6 million; commercial vessels, \$14 million; and the offshore drilling platform and related applications, \$48 million [48]. The global market is reported to be 500 million liters, of which 55 million liters are antifouling coatings [49]. The U.S. market is relatively small because most ships are painted in ports where regulations are less strict and labor costs are lower.

Coatings for exterior surfaces above the waterline are generally analogous to those supplied for heavy duty maintenance, as discussed in Section 33.1. Ultra high pressure hydroblasting is used to clean the surface; salt is a common contaminant in shipyards, and hydroblasting removes all salt from the surface. A primer must be applied soon after blasting to avoid recontamination. Inorganic zinc-rich or epoxy primers are used. In a study of the performance of a range of coatings over zinc-rich primers on panels exposed for 10 years in Jacksonville, Florida, inorganic zinc-rich primer with an intermediate epoxy coating and an aliphatic polyurethane top coat gave the best overall performance [50]. Inorganic zinc-rich primer with an epoxy second coat and a vinyl top coat received the next highest rating for overall exterior performance. Where the requirements are somewhat less demanding, a two component epoxy primer with a silicone alkyd top coat may perform adequately.

2K coatings formulated with an epoxy-functional silicone resin (Section 16.1.1) and a carboxylic acid–functional acrylic resin have been evaluated as marine coatings for topside application. They are reported to give superior exterior durability compared to urethane coatings, including less dirt pick up and easier cleaning [48].

The exterior durability requirements of coatings for ship superstructures are severe, since in addition to the direct UV, further UV is reflected off the water surface, and the humidity is also generally high. Alkyd coatings have been the standard; however, urethane coatings are being used increasingly because of their greater durability. Alkyds remain popular because they are relatively easy for crew members who are not trained painters to apply. Especially for interior paints, fire retardancy is important; chlorinated alkyd coatings have been recommended [51]. Latex paints are used to a minor extent; although initial gloss is lower with latex than with alkyd coatings, gloss retention and resistance to cracking are superior. The low solvent content of latex paints reduces the fire hazard of paint in storage on a ship. Deck paints have the further requirement of being skid resistant. 2K aliphatic urethane coatings satisfy the exterior durability and abrasion resistance requirements. Skid resistance is obtained by mixing coarse sand into the paint just before application.

For many ship bottom areas, 2K coal tar–epoxy coatings have been found to be particularly effective; they have also been used in ballast areas. The coatings must be handled with care in view of the potential carcinogenicity of components of coal tar. Coal tar is being replaced by petroleum derived hydrocarbon resins; in addition to lower toxicity hazard, the lighter color of hydrocarbon resins facilitates inspection in ballast areas. One package contains hydrocarbon resin, amine-terminated polyamide resin, and pigment; the other contains the epoxy resin. Multiple coats are applied to give a total film thickness on the order of 400 μm. The coatings have high chemical resistance and high dielectric strength. The latter property is especially important for ships that use zinc or magnesium sacrificial metal anodes to provide cathodic protection against corrosion (Section 7.2.2). Over properly prepared surfaces, the expected lifetime in seawater immersion is on the order of seven years [47]. Pigmentation with leafing aluminum enhances performance. To protect against environmental disasters, most oil tankers entering U.S. coastal waters are required to have a double-hull construction. This has increased the surface area of ballast spaces, which is as much as six times the outer hull area. The difficulty and high cost of repair work in double-hull construction dictates that the coating systems offer very long term protection against corrosion.

Fluorinated urethane coatings are used in tanks such as fuel tanks, septic tanks, and sometimes bilge tanks [52]. Fuel tanks must be protected against corrosion, since they are frequently filled with seawater ballast after the fuel is consumed. The lower free energy surface of the coatings simplifies cleaning.

The most challenging class of marine coatings is *antifouling coatings*. Spores and larvae of a variety of plants and animals, ranging from algae to barnacles, can attach to the underwater hull of a ship. The growth of plants and animals on ship bottoms increases the roughness of the hulls, which in turn increases the turbulence of water flow over the surfaces and drag; hence, speed decreases and fuel consumption increases. Removal of such growths requires putting a ship into dry dock. The economic penalty of fouling is very large. Review papers detail the variables involved, the history of antifouling coatings, and the status of the coatings available and the various approaches being worked on [49,53].

The major approach has been to apply coatings that contain biocides that leach out of the coating. The biocide must be a very general toxic agent. The leaching rate must be above a critical level required to kill all the organisms settling on the surface over a long period of time. Leaching rates decay exponentially in accordance with a first order release of biocide. The first biocide used on a large scale was cuprous oxide. Typical binders are solution vinyl resins containing rosin salts. The binder is water sensitive, so loss of cuprous oxide continues after the surface layer is depleted of cuprous oxide. To have sufficient cuprous oxide at the end of the life of the coating, the rate of loss of cuprous oxide in the early stages of use has to be excessive. The antifouling lifetimes of such coatings in actual use are on the order of 7 to 24 months.

The economic need was for a coating with a lifetime of 48 months or longer. Coatings based on copolymers of tributyltin (TBT) esters of methacrylic acid with conventional acrylates were developed. They are hydrophobic and fairly low in T_g. The TBT near the surface slowly hydrolyzes, liberating active biocide. As this happens, T_g increases and the surface becomes more hydrophilic. As a result, surface layers separate from the paint after they have released their biocide, exposing a fresh layer with more biocide. The rate of hydrolysis is controlled by the design of the copolymer and also by the incorporation of a slightly water-soluble pigment. Leaching of the pigment from near the surface of the film increases the contact area between polymer and water, increasing the hydrolysis rate. Part of the pigment can be cuprous oxide, to provide further biocidal activity. Since the rate of loss of biocide is controlled by the rate of hydrolysis at the surface, the rate of leaching is approximately linear with time rather than exponential. Furthermore, slow dissolution of polymer keeps the surface of the film smooth, which favorably influences speed and fuel consumption. These coatings are called *self-polishing coatings*. Depending on conditions, service lifetimes are up to five years.

When ships are in port, leaching of toxicants continues. In some harbors, concentrations of toxicant can build up sufficiently to affect marine life. There is concern about potential heavy metal entrance into the food chain, affecting fish that might be caught for human consumption. Therefore, regulations controlling biocide release are getting more stringent. In the mid-1980s, use of tributyltin compounds was banned on vessels less than 25 m in length, affecting most pleasure craft. The International Maritime Organization has drawn up legislation to restrict its use on all commercial vessels. If ratified, TBT will be banned as of the beginning of 2008 [53].

Use of copper based antifouling paints has again increased, and self-polishing copper acrylate coatings have been made available. However, their service lives are shorter than that of tin containing self-polishing coatings. Copper release by hydrolysis of the polymer is not sufficient to provide antifouling on its own; therefore, copper oxide and a biocide are used with it. An example of an organic toxicant is 4,5-dichloro-2-*n*-octyl-4-isothiazolin-3-one. It is reported to be an effective toxicant, and it degrades rapidly in seawater, so that there is no bioaccumulation [54]. Although copper is much less toxic than tin, some countries are banning its use as well.

Another approach to self-polishing antifouling coatings is the use of the zinc salt of hydrogenated rosin with a plasticizer such as oleic acid, Cu_2O, and a biocide. A study of laboratory evaluations of the rates of leaching and dissolution of the upper layers of the coating is available [55].

Intensive research in recent years has been aimed at attempts to find means of controlling fouling other than by use of toxicants [53]. It is a difficult problem. A promising approach is the development of coatings to which adhesion of fouling organisms is so limited that fast ship movement through the water or underwater brushes or hoses are sufficient to remove any fouling without dry docking. They are used on fast ferries, naval ships, and some motor boats. The coating is applied over an epoxy primer for corrosion protection. Service life is over three years, and the excellent leveling properties give a smooth surface, which reduces drag. Research is directed at improving abrasion resistance and tear strength of silicone elastomer coatings. Use of volatile methylsiloxanes, which are exempt under VOC regulations, as a solvent permits use of higher MW elastomeric silicones in the binder, thereby improving the physical properties [56]. Unfortunately, speeds of 18 to 22 knots are needed to remove most of the growths [53]. Ships such as freighters and tankers do not go that fast.

Coatings formulated with poly(4-hydroxystyrene) applied to the bottom of motor boats reduce drag and significantly decrease fuel requirements. The same coatings were applied to sea plane floats and permit take off with much shorter taxi distances before lift off [57].

A paper is available that discusses the requirements for a coating from which biogrowths are most easily removed. The polymer in the coating should have a flexible, linear backbone which introduces no undesirable interactions and a sufficient number of surface-active side-chain groups that are free to move to the surface to give the desired low surface free energy. The polymer should have a low elastic modulus and give a surface that is smooth at a molecular level, to avoid infiltration by a biological adhesive, leading to mechanical interlocking. The backbone and the surface active side chains should exhibit high molecular mobility. The thickness should be such as to control fracture mechanics at the interface. Furthermore, the polymer should be chemically stable for long periods in a marine environment. Polysiloxanes with side chains of nonafluorohexylmethylsiloxane or trifluoropropylmethylsiloxane are possible examples of polymers that could meet the requirements [58].

Self-polishing coatings that contain no biocides are being developed. One example is based on copolymers of a fluorinated monomer (e.g., 2,2,2-trifluoroethyl methacrylate), an organosilyl monomer (e.g., trimethylsilyl methacrylate), and other (meth)acrylic monomers. The erosion rate is adjusted by adjusting the proportions of monomers [59].

33.3. AUTOMOBILE REFINISH PAINTS

The value of coatings for cars and trucks outside assembly plants is almost as large as that for OEM automotive coatings, discussed in Section 30.1. Some refinish paints are used for overall finishing of cars and new trucks in special colors, but the largest segment of the market is for repair. When a car has been in an accident and a fender is straightened or a new door is installed, these parts must be coated so that the color matches the color of the original coating. There are major technical problems meeting the demanding application and performance requirements, and also major marketing and distribution problems. Hundreds of types of cars are made each year, each in as many as a dozen different colors. Although most cars on the road are five years old or less, many are well over 10 years old. If there is an accident involving a 15-year-old Jaguar, the owner expects to be able to bring it to a repair shop and have that section of the car painted to match the rest of the car. Furthermore, the *body shop* expects to be able to call the paint distributor and have the necessary liter of paint delivered by the next day.

The refinish industry is under increasing pressure to reduce emissions, complicating the technical challenge. The national limits for VOC emissions are much more liberal than those for many states, such as California. The present national EPA regulations permit: wash primer, 780 $\mathrm{g\,L^{-1}}$; primers and primer–surfacers 580 $\mathrm{g\,L^{-1}}$; primer–sealer, 550 $\mathrm{g\,L^{-1}}$; single-/two-step top coats, 600 $\mathrm{g\,L^{-1}}$; top coats/three or more steps, 630 $\mathrm{g\,L^{-1}}$; multicolor top coats, 680 $\mathrm{g\,L^{-1}}$ [60].

In some cases, coating manufacturers make and stock small containers to match the colors. These are ready to be shipped to dealers and repair shops before the first new car comes off the assembly line. However, these “factory packaged” colors are limited, due to inventory costs and the variations in color shade at the OEM manufacturing site. In most cases, the manufacturers provide formulations and tinting color bases to distributors (or larger repair shops) to permit matching any original color. Establishing the formulations requires great color matching skill, especially for metallic colors.

Both air dry and force dry (65 to 80°C) coatings are used. The heat in force dry coatings makes a large difference in enhancing the quality of the repair. In Europe and Japan, most shops are equipped with force dry ovens. In the United States, use of force dry ovens is increasing, but there is still a significant fraction of repair shops that use air dry coatings.

Repair of damage after an accident is usually accomplished with replacement parts, as labor costs to bump out dents have become too high. Replacement parts are usually received from the manufacturer coated with electrodeposition primer. In some cases, the damaged panel is repaired, then surface preparation is critical. The old coating surface must be cleaned to remove dirt, tar, and wax by scrubbing with detergent, rinsing thoroughly, and drying; in some cases solvent cleaners are required. Scuff sanding may be required to remove chalky pigment and degraded polymer. If the old paint is cracked, it must be sanded down to bare metal. Any breaks through to metal require that the edge of the area be feathered out, that is, sanded with a bevel so that there is a smooth change in film thickness. When bare metal is exposed, it must be washed free of grease with solvent.

A primer–surfacer is applied after checking whether the coating on the car can withstand the primer–surfacer solvent. Current OEM coatings give no problem, but if the car has been refinished in the relatively recent past, the coating might be only partially cross-linked and lift when solvent is applied to it. In the past in the United States and still in South America and Asia, the most common primer–surfacers are made with nitrocellulose–alkyd binders. To achieve fast dry, a medium oil length, rosin-modified, tall oil alkyd is used [61]. The rosin modification increases the T_g of the alkyd. The primers are highly pigmented, for example, with a PVC of 38% and sometimes even higher. The use of nitrocellulose with rosin-modified alkyd and high levels of pigmentation permit sanding the primer–surfacer within 30 minutes after application. The primer is sanded smooth with fine grit paper, and the spray dust is removed. Application solids of such primers is low. Stricter VOC controls and OEM warranty repairs are forcing the use of epoxy and urethane primers, which also give superior performance. In areas with the most restrictive VOC regulations, waterborne undercoats are being used. The initial products have been formulated with acrylic latexes or polyurethane dispersions. Drying of these coatings is dependent on humidity, and the time required for drying in high humidity is excessive. They are being replaced by thermosetting 2K waterborne epoxy (Section 13.2.6) or urethane (Section 12.8) primers.

The *eco-efficiency* of a UV cure primer compared with 2K urethane and epoxy primers has been reported [62]. The VOC of the UV primer was 1.7 lb/gal compared with 4.7 lb/gal for the 2K urethane and 4.4 lb/gal for the epoxy primer. Only one coat was needed for the UV primer, in contrast to two for the others. Curing time was 3 minutes compared with 25 and 20 minutes for the urethane and epoxy primers, respectively. The material cost for the UV primer was substantially higher, but the higher cost is largely offset by lower labor, energy, cleanup, and rework costs. Furthermore, the capacity of the shop was increased by 25%. The primer is in commercial use. BASF was awarded a presidential green chemistry award for the development in 2005.

Waterborne 2K primer–filler coatings based on acetoacetate–amine systems are being investigated. One package contains a polyacetoacetate such as trimethylolpropane triacetoacetate; the other contains an emulsion of a polyamine compound such as the reaction product of a low MW BPA epoxy resin and a polyamine such as diethylenetriamine neutralized with acetic acid. The primers show good stability, good pot life, excellent adhesion, fast curing, and sandability [63].

Two broad classes of refinish top coats are used: lacquer (thermoplastic) and enamel (thermosetting). A major application advantage of lacquer is fast dry; they have short *out-of-dust* times (i.e., the time required for the film to become sufficiently dry that dust particles do not adhere to the surface). There tends to be a great deal of dust in the air in repair shops, and fast dry is a major advantage, reducing contamination of the freshly applied coating. A disadvantage of acrylic lacquers for refinish is that when dried at room temperature, their gloss is not high enough. To match the gloss of the OEM applied coating, refinish lacquers must be polished with rubbing compound, adding to the cost.

In acrylic refinish lacquers, thermoplastic acrylic polymers with high methyl methacrylate content (Section 2.2.1) are blended with cellulose acetobutyrate (CAB) and a plasticizer such as butyl benzyl phthalate. Gloss retention is good but inferior to current OEM coatings. Application solids are low (10 to 12 NVV) and VOC emissions are very high. Lacquers are now used in North America only for antique car restoration and by the do-it-yourself market. They are still being used in countries, where there are few environmental regulations, such as in parts of Central and South American countries.

The other broad class of refinish top coats is enamels; there are several types. The oldest and lowest in cost are alkyd enamels; the alkyd is a medium oil, isophthalic, soy, or tall oil alkyd (Section 15.1). These enamels have several advantages in addition to low cost. Fewer film defects such as crawling or cratering occur during application, due to their low surface tension. Their gloss is high enough to match OEM monocoats without polishing. VOC emissions are substantially less than with lacquer. On the other hand, out-of-dust time approaches half an hour, and if recoating is necessary, it must be done within four hours after application or after 24 hours. At intermediate times, when the film is partially cross-linked, a second coat of enamel can lead to lifting. Gloss retention of alkyd coatings is poorer than that of OEM coatings or refinish lacquer.

The properties of alkyd enamels have been improved in several ways. Triisocyanates such as isophorone isocyanurate (Section 12.3.2) can be added just before spraying. They serve as auxiliary cross-linkers, reacting with free hydroxyl groups of the alkyds. This supplemental cross-linking reduces out-of-dust time and recoating problems. Another approach is to use methacrylated alkyds (Section 15.4), which give shorter out-of-dust times but cross-link less rapidly, so the films remain sensitive to gasoline for a protracted time. Another type resin is made by reacting an acrylic resin made with glycidyl methacrylate as a co-monomer with drying oil fatty acids. Films from such a vehicle show out-of-dust times and durability approaching that of acrylic lacquers and superior to that of alkyds. Since the relatively high T_g acrylic backbone provides the necessary initial dry, driers are not needed to accelerate the oxidative cross-linking. The absence of driers improves exterior durability.

With the increasing use of base coat–clear coat finishes (Section 30.1.2), corresponding coatings for use in refinishing were required. The base coat must be able to hide with two coats. Relatively low solids are required to permit alignment of aluminum or other flake pigments. Solvent evaporation must be relatively fast to allow clear coat to be applied within an hour without disturbing the flake orientation. Acrylic lacquer was used initially for refinish base coats but to accelerate drying is being replaced with a binder based on a polyester with cellulose acetobutyrate, and to assist in fixing the flake, a polyethylene–polyvinyl acetate wax suspension as a rheology control. Such base coats have a relatively high VOC and are used with very high solids clear coats (up to 85% weight solids), so that the combined VOC is within regulations.

Waterborne base coats based on either acrylic latexes or polyurethane dispersions are being made available. These waterborne coatings have a volume solids of 15%, which permits flake orientation comparable to OEM coatings. Treated aluminum flake must be used to avoid hydrogen evolution (Section 20.2.5). Rheology control additives are also required. Relative humidity conditions affect the drying speed; the coatings can be force dried or air dried with high volume dry air flow to remove most of the water before applying the clear coat.

Two package urethane enamels have become the most important for clear coats. Thermosetting hydroxy-functional acrylic resins similar to those used in OEM coatings can be used together with a polyfunctional isocyanate cross-linker. Polyfunctional aldimines and hindered amines are being used to further increase solids (Sections 12.4 and 25.2.2). A copolymer of an adduct of glycidyl versatate and methacrylic acid, butyl acrylate, styrene, and methyl methacrylate with low viscosity HDI isocyanurate is used as a vehicle for a high-solids clear coat [64]. Unsymmetrical HDI trimer (HDI iminooxadiazenedione) has been recommended for use in 2K acrylic clear coats for refinishing since 1 to 3% higher solids can be applied as compared with HDI isocyanurate coatings [65]. Use of *t*-butyl methacrylate as a comonomer in acrylic polyols permit somewhat higher solids, a 1-hour pot life, a tack free time of 35 minutes, and a higher gloss than that of other acrylic polyols. Use of EPA exempt acetone and 4-chlorobenzotrifluoride as part of the solvents permits making a 3.5 lb/gallon VOC [66]. For applications where the volatility of acetone is acceptable but the ketone structure is not, methyl acetate is an alternate exempt solvent. Recently, the EPA ruled that *t*-butyl acetate is accepted as an exempt solvent; its use awaits state inclusion in implementation plans.

Bicyclic orthoesters are used commercially with polyisocyanates in very high gloss 3K clear coats. The third component is the catalyst to promote hydrolysis of the orthoester and reaction of the resulting hydroxyl groups with the isocyanate component. Clear coats with a pot life of 4 hours are reported with 230 g L^{-1} VOC that flash off in 1 to 2 minutes and dry in 5 minutes at 60°C [67]. A patent application discloses the use of 2-butyl-2-ethyl-1,3-propanediol-spiroorthoester prepared by reacting 2-butyl-2-ethyl-1,3-propanediol with tetraethylorthosilicate, together with HDI isocyanurate as cross-linker and DBTDL as catalyst. The DBTDL acts as a catalyst for both the hydrolysis of the orthoester and the reaction of the resulting hydroxyl groups with the isocyanate. Pot life is reported to be 7 hours [68].

Silylated acrylic resins have been developed that are reported to combine good appearance, mar resistance, acid resistance, and exterior durability [69]. The silyl groups are introduced using 3-trimethoxysilylpropyl methacrylate as a co-monomer. After application, the resins are moisture-curable through the silyl group (Section 16.4). Very fast cure refinish clear coats can be formulated using pentaerythritol tetraskis-3-meraptopropionate, HDI isocyanurate, and a $Zr(AcAc)_2$ catalyst. Ambient temperature cure time is reported to be 10 minutes, and at 60°C, 4 minutes [70].

Dual thermal and UV cure clear coats are being investigated for refinishing. 2K coatings with a polyisocyanate in one package and a hydroxy-functional urethane/acrylate oligomer were used. The coatings were first cured at temperatures in the range 40 to 60°C followed by UV curing. The isocyanate cross-linking served to give acceptable properties even in shadow areas when the films were UV cured. The mar and chemical resistance are reported to be superior to a conventional 2K urethane clear coat [71]. A UV cure coating system for spot repairing has been patented. A pigmented primer–surfacer with a BPA epoxy acrylate and hexanediol diacrylate vehicle and a mixture of acylphosphine oxide and hydroxyacetophenone type photoinitiators, is applied, UV cured, and sanded. A pigmented base coat formulated with an aliphatic polyurethane acrylate and a mixture of acylphosphine oxide and hydroxyacetophenone type photoinitiators is applied and UV cured. A clear coat with the same vehicle as the base coat, to which a benztriazole UV absorber and a HALS compound are added, is applied and UV cured [72].

Monocarboxylic acid–modified polyesters cross-linked with HDI or IPDI isocyanurate have also been recommended [73]. Durability of these coatings is in the same range as OEM coatings, and they give high gloss without polishing. Out-of-dust times are intermediate between lacquers and alkyd enamels. The out-of-dust times can be reduced by increasing the amount of catalyst (often dibutyltin dilaurate), but pot life is also reduced. Refinish shops cannot generally afford dual-mixing guns, so the pot life has to be at least long enough to permit complete spraying of a car—over an hour. (See Section 25.2.2 for discussion of approaches to formulating coatings with reduced VOC and increased pot life.)

VOC emissions have been reduced by changing from conventional air spray guns to high volume low pressure air guns (HVLP). HVLP guns permit better transfer efficiency and hence lower paint use and lower VOC emissions (Section 23.2.1).

Although paint suppliers emphasize the need to wear masks and to mix and apply the paint in a well-ventilated spray booth, some refinishers do not follow recommended safety precautions. Especially if cross-linkers with some volatile diisocyanate components are supplied, sprayers can develop respiratory problems. Some shops will not use 2K urethane coatings. Refinish coating suppliers are pursuing non-isocyanate cross-linking systems. It is important to bear in mind that any reactant that can cross-link hydroxyl, carboxyl, or amine groups on a synthetic polymer can also cross-link proteins. Any such cross-linker will be toxic. A new system must be designed in which the reactive component is not volatile and has a high enough MW to minimize permeation through the skin and membranes.

A significant aftermarket product is truck bed lining. The principal coating is a black pigmented 2K urethane applied with dual feed spray guns. Fast gel coatings are needed to avoid sagging owing to the film thickness of more than 100 mils. The isocyanate is MDI/polyethylene glycol diol prepolymer. The resin package is a combination of polyether diol and triol with an aromatic diamine. The black pigment is to protect the binder against UV degradation. An aliphatic 2K coating has also been developed that permits colors that match the color of the truck. The isocyanate is HDI isocyanurate, and the resin package binder is a combination of polyester polyols, a polyaspartate, and aliphatic diamine. The amines are necessary to have a short gel time, The aliphatic coating can be applied as a sole coating, or to reduce the cost the aromatic product can be applied at a film thickness of about 120 mils followed by 40 mil of the aliphatic coatings as a top coat [74].

33.4. AIRCRAFT COATINGS

The U.S. market for aircraft and aerospace coatings in 1990 was estimated to be $60 million [75]. The majority of the business is for exterior primer and top coats for aircraft—roughly 50 : 50 for commercial and military aircraft.

Excellent adhesion and corrosion protection are required for a range of substrates: aluminum, aluminum alloys, and composite plastics. The high strength aluminum alloys used for aircraft structures are more vulnerable to corrosion than is ordinary aluminum. The coatings must resist swelling by phosphate ester hydraulic fluids, lubricating oils, and fuel. Swelling resistance is usually obtained by relatively high cross-link density. However, the coatings must also have good flexibility at low temperatures and excellent abrasion resistance while the aircraft is flying through dust, rain, or sleet at high speed. Military aircraft in the Middle East must be repainted very frequently due to abrasion. Flexibility and abrasion resistance tend to decrease with increasing cross-link density.

Achieving strong adhesion to aluminum requires surface treatment. Chromate based treatments have been used, but the toxicity of chromates has required the development of chromate free treatments. See Section 7.3.2 for a discussion of various treatments. Epoxy–amine primers are generally used (Section 13.2). For aircraft exteriors they are generally topcoated with urethanes. For interior areas, such as in hold or cargo areas, internal structural members, and wheel wells, the primers are generally not top coated except for special applications. The interior coatings are expected to last for the life of the aircraft and are not stripped and recoated as exterior coatings are. As aircraft are used beyond their original design lifetimes, there can be problems. For example, in military fuel tankers, which are often older than their pilots, fragments of primer come loose from the inside the wings and clog fuel filters. These primers are generally formulated with polyfunctional novolac epoxies (Section 13.1.2) with amido-amines or amine adduct curing agents to give relatively high cross-link density and maximum resistance to lubricating and hydraulic fluids. Passivating pigments are used to control corrosion in the case of breaks through the film. Strontium chromate is preferred over zinc yellow, since its solubility in water is somewhat lower, and therefore the rate of leaching of the pigment from the film by water is lower (Section 7.4.2). Strontium chromate also has greater heat resistance than zinc yellow.

Primers for exterior surfaces are designed with lower cross-link density by using only, or primarily, BPA epoxy resins. Amine-terminated polyamides (Section 13.2.2) are usually used as the cross-linking agents. The long chain fatty acid parts of the polyamides provide good wetting to the metal surface and flexibility to the final film. Cross-linking is catalyzed with 2,4,6-tris(dimethylamino)phenol. The lower cross-link density provides greater flexibility and permits easier stripping of the coatings for repainting. Strontium chromate is used as a pigment, and again owing to toxic hazard, chrome free primers are being evaluated.

Top coats are almost always 2K urethane coatings. Most commonly, hydroxy-terminated polyesters are used with isocyanurate trimers from hexamethylene diisocyanate or isophorone diisocyanate; commonly, a high isocyanate/hydroxyl ratio is used so that the coatings are partially moisture cured (Sections 12.4 and 12.6). Cross-linking is catalyzed by organotin compounds.

Aircraft coatings have had relatively high solvent contents, but there is pressure to reduce VOC emissions. Waterborne epoxy–amine primers are being used increasingly [30] (Sections 13.2.6 and 26.3). Some reduction of solvent in top coats has been achieved by using lower MW resins and polyisocyanates, but progress has been limited by the requirements for rapid dry at ambient temperatures, which is harder to achieve as the MW is reduced. Very fast reacting coatings requiring dual spray show promise of very low or even zero VOC. Aldimine based coatings are being evaluated (Section 12.4).

The exteriors of airplanes are frequently repainted. The biggest problem is not application of the new paint, but removal of the old paint. The paint strippers that have been used for many years contain substantial amounts of methylene chloride, which is toxic and environmentally undesirable. Studies are under way to eliminate the use of strippers by using mechanical methods for paint removal. The removal method must not weaken the metal or composite plastic substrate. For example, sandblasting will remove coatings, but also erodes the metal surface. Alternative blasting media such as plastic beads, dry ice pellets, and crystalline starch are being investigated (Section 6.4.1).

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Perspectives on Coating Design

Formulation of coatings is a challenging assignment. Sometimes, scientists look down their noses at the coatings formulator without realizing that the task of formulating a new coating can be more technically challenging than much so-called “pure” research. Any coating must meet a multitude of requirements. There are innumerable possible raw materials, combinations, and proportions. Test methods are generally subject to large ranges of error and frequently do not give results that predict use performance well. The formulator is faced with variable substrates and application methods. There are commonly severe cost constraints. Frequently, the volume of any one coating is too limited to justify expenditure of large amounts of time; furthermore, time available to solve the problem is usually limited. In fact, as one looks at the complexities of the field, one sometimes wonders how a useful coating ever gets formulated.

Historically, the problems of formulation were somewhat eased by following a procedure of making small modifications of coatings known to be satisfactory. Over time, excellent coatings were formulated in this way. This approach of continuous improvement, with a focus on the customer’s needs and close contact between the formulator and the customer’s engineering group, continues to be important. However, it has become necessary to make major changes in formulations in less time than was formerly used to make even small changes. This need results from a variety of factors, but particularly from the introduction of VOC emission controls and the increasing number of raw materials identified as having potentially serious toxic hazards.

Most of this chapter is written from the perspective of the United States, but our experience teaching courses in many countries around the world indicates that the differences in the challenges to coatings design in different countries are small compared with the common denominators.

Organic Coatings: Science and Technology, Third Edition, by Zeno W. Wicks, Jr., Frank N. Jones,
S. Peter Pappas, and Douglas A. Wicks

The challenge of formulation is intensified by the need for increasing productivity and creativity. We all want more of the good things of life, but the only way this desire is made possible for the population as a whole is to increase the aggregate productivity. Some politicians and some uninformed segments of the population tend to associate productivity problems with production line workers. Clearly, there is need for increased productivity of labor, but overall productivity depends on the efficiency with which management, sales personnel, accountants, clerical personnel, and laboratory personnel, including formulators, work. In the inimitable words of Pogo: "We have met the enemy and they is us."

At least as important, and perhaps more important, is the need for increased creativity in formulation. Some of the problems facing the coatings formulator seem impossible. Some of them are, in fact, impossible, but many "impossible" problems aren't really impossible but require creative visualization of ways around the supposedly insuperable hurdles. Enhanced creativity should be a critical component of most aspects of people's lives, and the need for creativity is especially important in technical people, including formulators.

The coatings industry has been known as an industry with a relatively low profit margin. It is commonly argued that more money cannot be invested in research and development because of low profit margins. Actually, the inverse is probably truer. Profit margins are low because a large fraction of the technical effort is spent trying to copy competitors' products and/or by applying the same old ideas as those being used by every other formulator rather than focusing on innovative research and development.

There is no magical single route to increasing creativity and productivity. This chapter provides some ideas based on the accumulated experience of four technical people who have worked in different aspects of the coatings field. Other people will have other suggestions; the particular approach is not important, but the end result is critical.

There are several important aspects involved in working on a formulating problem. Although, to a degree, these are sequential steps, continuous review and reevaluation of these aspects is essential as the work progresses.

1. Define the problem. The first stage in working on a formulating problem is to define it. This seems so obvious that one would think that it need only be mentioned in passing. However, experience shows that inadequate definition of the problem is a large factor in unsuccessful technical projects. Appropriately defining a formulating problem is in itself a difficult and relatively time consuming effort, but effort invested at this stage often saves time overall. It is particularly critical to define a coating problem in terms of performance requirements. The statement "Formulate a coating to meet Specification Number XXXX with a 30% reduction in VOC emissions" does not define the performance requirements in most cases. Very often, the specification is based on quality control tests that a satisfactory previous coating happened to pass, but quality control tests are not designed to predict performance of a new product. Consequently, an effective formulator must know or find out what the actual end use requirements are.

One should also examine closely the statement of a problem that he or she receives. On one occasion, a laboratory was asked to formulate a "harder" coating; this was done and the customer accepted the new formulation, but after some months of use, the customer complained loudly that the new coating had a poor wear lifetime. The customer really wanted improved abrasion resistance and assumed that greater hardness would provide it. The customer was mistaken, but the fault was not really his; the fault was that of the coating formulator, who didn't ask: "Why does the customer think that he wants a harder coating?" There is great need for direct contact and interaction between the customer and the formulator who works on a problem.

It is not adequate to define a problem as: "Match competitor A's Coating No. YYY at a lower cost." First, this definition propagates a self-fulfilling prophecy—that profits in the paint industry will continue to be low. Second, by the time the work has been finished, the competitor may have produced a better product than YYY, and thus a match for YYY is no longer adequate to get the business. Third, the difficulties of analysis, especially for additives, are such that one can seldom analyze a competitor's formulation precisely enough to duplicate it. Matching the laboratory test results of the competitor's product does not assure that the product performance will be equal. The only satisfactory definition of the technical aspects of a project is a listing of detailed performance requirements. In any list of this sort there is a range of degrees of importance of the various needs. Some are essential requirements, others are important, still others would be "nice if we could do it," and still others are in the category "As long as we are pipe dreaming, why not put this goal down, too?" The laboratory worker should clearly understand how each of the performance needs fit into such a scale.

Applicable regulations must be known—not just current regulations, but best estimates of what they will be over the lifetime of the potential project. No one can predict future regulations accurately, but a choice as to goals from this point of view must be made. After all, assuming that current regulations are going to continue unchanged is also a prediction of the future. Toxicity problems should be assessed, taking into consideration possible future developments. Starting a new study of a corrosion protective primer based only on zinc yellow pigment, with a target date for significant sales five years or so ahead, is risky, since it is known that zinc yellow is a human carcinogen.

Test methods must be agreed on. Few laboratory tests are adequate predictors of use performance. Since coatings are complex compositions and end use requirements are variable, there is a real danger in relying on any one test. Some widely used tests, such as salt spray tests for corrosion protection, have repeatedly been shown not to correlate with end use results (Section 7.5). It is absurd to base decisions for a major research project on whether or not the product will or will not pass a salt spray test. The problem of evaluation should be faced in advance. A variety of tests relating to mechanical, spectroscopic, and thermal properties should also be carried out using coatings with known field performance as standards for comparison. Dickie has published a methodology for integrating the results of laboratory performance tests, field history, environmental factors, design parameters, and the fundamentals of degradation to predict service performance [1]. The problems involved with predicting the service life of coatings have generally been underestimated. See Ref. [2] for a review of the problems of prediction and the proposed use of reliability theory for developing better methodologies.

Cost requirements are an integral part of the definition of a project. The formulator must know what the real permissible upper cost is, not just the amount to which some salesperson hopes the cost can be kept down. Similarly, the timing requirement must be known. Some projects have to be finished by a certain date. Some do not have a specific deadline, although obviously, the sooner they are finished, the better. Unrealistic cost and time goals can lead to wrong decisions in project planning. The technical person has the obligation to let any possible time slippage or cost increase be known to others as soon as he or she is aware of it.

The potential value of a project should be compared with the estimated total cost of the project. Some companies use elaborate discounted cash flow methods of analyzing the potential value of a project. Our experience has been that such analyses have killed many good projects along with bad ones. It should be recognized that estimates can be used to "prove" that any project will or will not be economically sound. On the other hand, there have been frequent occasions when a little thought would have shown that there was no sensible possibility of a return approaching the potential cost of the project.

Unfortunately, misunderstandings about the definitions of projects are all too common. A way of minimizing such misunderstandings is to have the person who will be doing the work write out his or her understanding of the project. It is far better to take the time required to reach consensus on a project definition at the outset than to risk disagreements midway or even near the project's end.

2. Do a background search. Too often, laboratory workers jump on their horses and ride off in all directions. First, one should assess the available knowledge. Review the pertinent scientific literature, review (with appropriate concern for bias) suppliers' technical data bulletins; and review any pertinent background with fellow workers, in the company's files, and on the Internet. Discussions with technical employees of raw material suppliers are often very helpful. Discussions with the customers' technical and engineering personnel can also be useful. Increasingly, companies are accumulating computer data banks that compare actual field performance with composition variables; such data can provide useful ideas.

It is particularly critical to be sure that a problem is not impossible. Some problems *are* impossible, and there is no point in working on them. No amount of wishful thinking will ever permit the development of a flat jet black paint or a white paint with gloss equal to that of a high gloss jet black paint (Section 19.10.1). No one can match the color of a gloss coating at all angles of illumination and viewing with that of a low gloss coating (Section 19.9.1). No one will ever make a kinetically controlled one package coating with six months of package stability at 30°C that will cure in 30 minutes at 80°C (Section 2.3.2). Stop such projects before they start.

3. Identify the approaches. Commonly, a technical person starts working on a project based on the most obvious approach to the problem. This approach is probably the same one that his or her counterpart in a competitor's laboratory will select. The greatest opportunity to apply creativity comes early in a project. Devise all of the approaches you can to solving a problem; solicit ideas from fellow workers. Don't be dissuaded by veterans who say: "We tried that 20 years ago and it didn't work." Assess the merits of their comments, but in 20 years, many other things have changed; what didn't work then might work now. Set the problem aside for a few days and try again to come up with really different ways by which the problem might be solved. Open up your mind; get out of ruts. Having accumulated a variety of possible approaches on which to work, try to assess their merits and pick the one or two most promising. Sometimes, the one picked will be the first approach identified, but commonly, it is not.

As the basic understanding of the factors controlling the performance of coatings increases, the opportunity for basing experimental approaches on sound scientific understanding increases. It is sad to see the failures to apply known understanding. To take an obvious example, it is well established that in room temperature–cure coatings, cross-linking may become limited by the availability of free volume. If the T_g of the fully reacted system is significantly above room temperature, the cross-linking reaction will slow and probably stop before completion. Why bother to prove this again? Why not start out with combinations of raw material that can react fully? Yet it is common for paint formulators to be given a sample of a new raw material—say a cross-linker—and substitute it in a formulation they are using, only to find out that it doesn't work. In many cases, just looking at the formulation will tell you not to bother even running the experiment, but rather, to change the resin being cross-linked to fit with the characteristics of the new cross-linker.

Understanding the principles that control exterior durability (Chapter 5) permits a better estimate of the durability of a new coating than any laboratory tests available. Using this knowledge permits one to concentrate efforts on compositions that have a reasonable chance of being appropriate. A person who understands recent work on corrosion protection can make a better prediction regarding corrosion protection by some new formulation by looking at the formulation in the light of corrosion principles (Chapter 7) than can be predicted by running salt fog chamber tests. Understanding the scientific principles gives a head start on the formulation of a coating with improved performance.

It is appropriate to repeat a theme that recurs throughout the book: Volume relationships, rather than weight relationships, are almost always the critical values. A good motto for a coatings formulator is: "Think volume."

Understanding relationships between properties and compositions is approaching the stage at which one will be able to design the binder for a formulation from first principles. We know what factors control T_g; we know what factors control cross-link density; we have some good leads as to the factors that control the breadth of the glass transition region; and we have a fairly good understanding of the relationships of these three characteristics with the performance of films. The day is not far off when it will be possible to design a resin and cross-linker for an end use without having to rely as much as is necessary today on trial and error. But this will only be true for the formulator who studies the advances in basic understanding and then tries to apply the principles.

4. Consider experimental approaches. The complexity of modern coatings and the increasingly stringent performance requirements being demanded by customers coupled with an industry wide reduction in technical support staff requires that efficiency of laboratory activities needs to improve continually to have a company remain competitive. Except in the simplest projects, two major factors face the experimental worker. First, most test methods used in the coatings industry are subject to considerable variation in results, and there are many possible variables and different possible responses in many different end uses. Second, there are almost always conflicting requirements based on performance, process, and economic considerations. To address these challenges, the coatings developer needs to choose carefully which experiments to run, use the most efficient laboratory approach to get the data needed, and make efficient use of all the data that are available.

Statistical experimental design and statistical analysis of data are particularly applicable to coatings formulation, since productivity can be increased by the use of statistics. Proper experimental design permits acquiring more information, with a higher degree of confidence in the results, with fewer experiments. Applying design concepts before starting at the bench can facilitate choosing which experiments are the most important.

Students are still being taught in school that "thou shall ***never*** change more than one variable at a time." This commandment should have just one word changed, so that it reads "thou shall ***always*** change more than one variable at a time." There are two major problems with changing only one variable at a time. First, there are so many potential variables and levels of those variables that one could still be changing single variables years later. Second, changing one variable at a time does not permit identification of interactions among variables. For example, the best catalyst at one temperature is not necessarily the best catalyst at another temperature. The best pigment for a coating that must have excellent exterior durability made with one class of binder is not necessarily the best pigment to use with a different class of binder.

The strength of experimental design is that it permits changing multiple variables simultaneously in ways that permit separation of the effects of the different variables and identification of interactions among the variables. It can also identify variables that many of us tend to ignore related to operator biases and those that come from running an experiment over and over, resulting in either an improvement or a reduction in skill at doing that experiment. Many books are available to provide background in experimental design. Although relatively old, Ref. [3] is a useful introduction because it uses examples from the coatings industry to illustrate the advantages and limitations of various types of experimental designs. More extensive coverage may be found in Ref. [4]. Courses in experimental design are available; every coatings formulator should take such a course. Any plan for a project of significant size should include statistical experimental design.

Perhaps the most important application of experimental design is to evaluate the robustness of a formulation after the basic components are settled upon. Many formulators do all of the development work using one batch of the raw materials or raw materials from only one source. The production environment will always provide many sources of variability; raw materials come with producer specifications that show ranges of product properties that will be acceptable, production processes at both manufacturer and end user have predictable variations, and purchasing departments are known to change raw materials based on favorable pricing. Each of these variations, either alone or synergistically, has the ability to affect product performance negatively. Failure of the formulator to anticipate changes that could happen after he or she finalizes the formulation can and indeed does lead to major failures in the field, with a corresponding financial impact. Proper application of experimental design will allow for evaluation of the interplay between variables by testing raw materials and processes at the extremes of their specifications.

Data analysis is also of critical importance. How many replicates are needed to obtain a test result with a 90 or a 95% confidence limit? Chemists, particularly, are used to standard deviations and do not seem to realize that 10 ± 2 means that there is about a 1 : 3 chance that the "real value" is greater than 12 or less than 8. Commonly test results subject to wide variations are used to decide between two formulations, the differences between which are small compared to the errors in the test results. The worrisome thing is not that poorer materials may be accepted for further development, but that good ideas may be discarded because of erroneous test results. It is desirable to analyze data obtained from statistical experimental designs, since this gives the opportunity of allocating the differences in results between the different variables, the different interactions, and *error*. Error is the unexplained remaining difference. If it is large, there can be two possible explanations: The test methods may have error ranges larger than the differences being investigated, or there may be one or more important uncontrolled variables. In either case, before proceeding further, one should do something about the test results either by increasing the number of replications and/or by identifying the other variable(s).

Laboratory methods and practices in many coating laboratories have not changed substantially over the last 50 years. Of course, there have been improvements in measuring methods, product specifications, and some productivity tools, but life for a modern formulator is still a sequential process of manually preparing one or two formulations at a time, manually preparing samples, and manually measuring properties, all followed by manual entry of results into a lab journal or spreadsheet. Even with an intelligent research plan, coupled with selection of reliable nonsubjective testing methods, this process leaves a lot to be desired in terms of efficiency, reproducibility, and accuracy.

Although there are current restraints, notably cost, combinatorial or high throughput methods are considered because of their potential importance in the coatings industry. These methods essentially make use of the advancements in computers, automation and analytical methods to address the laboratory experimentation with an eye on efficiency, reproducibility, and accuracy. In a fully integrated high throughput laboratory, the entire process is controlled by a central computer system that tracks composition, samples, and test results through four major steps:

1. Advanced software populates a database space (known as a *library*) based on formulation parameters selected by the researcher. This includes calculating weights and volumes of the various ingredients, specifying the process conditions and times, and determining in what order the experimental steps are conducted.
2. The information within the library is converted into instructions for a sample preparation robot that will combine all ingredients, mix, heat, and carry out the reactions as specified. Any deviations and the actual weight volume used are stored in the database and connected to the library description.
3. From the mixing and reacting steps, samples are transferred automatically to containers used for analytical measurements (multiple copies can prepared) and the analysis is performed with results sent back to the central database and connected to the library description.
4. At the end of the experiment, the database program automatically generates a custom report that is sent to the researcher requesting the study.

Aside from the opportunity to prepare large numbers of samples, several other key benefits arise out of the automation process described above. First, connectivity of results from experiment to formulation composition is automatic and in a standardized format. Second, record keeping accuracy increases dramatically as all information in the integrated computer system is obtained and maintained digitally. Third, the reproducibility and accuracy of measurements is improved as human error and bias is taken out. This is especially true in time dependent experiments; robotic systems can be programmed to do a routine in exactly the same amount of time, every time.

The stages usually found in a high-throughput process are:

- *Primary screening*. Large numbers of experiments are run and tested for only one or two properties that are considered knockouts if they fail to reach a given level. For many applications in catalyst or drug discovery fields, this primary screen may be used on tens of thousands of samples for a given application in a single day. For a coatings application, such a knockout might be: Does the sample thermally yellow more than a certain amount on storage at 100°C? Samples that do not meet the criteria are tagged as rejects, whereas those that exceed the criteria are tagged as “hits” and are selected for further testing.

- *Secondary screening*. The most promising hits from the primary screening are prepared in larger sample sizes and tested for a larger number of properties using more advanced techniques that will allow a clear ranking of a sample potential versus others and versus a known standard. Such tests might be run on hundreds of samples over a period of weeks, and again, hits are selected for further evaluation.
- *Tertiary screening*. The select number of hits from the secondary screening are passed through traditional laboratory experimentation and testing to validate earlier results and assign a final rank to those that go into full blown development.

The major benefit of this process of sequentially screening out guaranteed failures, followed by screening out by key performance characteristics, is the increased probability of choosing the best candidate to undergo full blown development.

Application of combinatorial and high throughput methodologies is rapidly being implemented in the materials sciences and formulation science. A number of international conferences regularly feature these methods for polymeric materials, and university researchers are also setting up national competency centers for this purpose. An excellent overview for material science has been prepared by Potyrailo and Amis [5]. In 2002 the U.S. National Institute of Standards and Technology (NIST) initiated a Combinatorial Methods Center to develop metrological standards for formulation science fields [6]. The involvement of national laboratories such as NIST is very important in terms of establishing traceable standards around which new high throughput analytical methods will be developed.

High throughput developments for preparing coatings raw materials and specifically coatings formulation and testing are rapidly increasing. Successful application to formulation of UV curable hard coats for plastics [7], blocked isocyanate systems [8], antifouling coatings [9], and thermostabilizers, among others, has been shown. However, reading the reports of successful applications reveals that there is as yet no standardization in the coatings industry and that major hurdles are yet to be overcome before this becomes a common tool. Key concerns related to samples and to implementation are:

- Automated sample preparation of pigmented systems has not been reported.
- Edge effects in small films can have a major impact on measured properties.
- Off the shelf testing solutions are not available.
- Clear cost–benefit benchmarks of the technology are not documented.
- The cost of implementation is far beyond that of all but the largest companies’ resources.

Universities and contract laboratories can be retained to perform high throughput research for corporations.

The latter two points should raise a level of concern as one contemplates getting involved. As discussed earlier, experimental design and data analysis, have clear applicability to coatings with immediate benefits that greatly exceed any investment, but that relationship is not so clear for high throughput methods. Within the area of pharmaceuticals with billion-dollar annual profit potentials or in catalyst development for olefin polymerizations, where a few percent improvement in performance is worth tens, if not hundreds, of millions of dollars in profit, it is easy to justify an expenditure of \$10 million to improve success. Very few opportunities of this size are available in the coatings marketplace, so care must be taken not to jump in too fast and to do so only after careful consideration.

5. Perform the work. One should think first, but one must also work, and work efficiently. One can think through what has to be done one or more days before working, so as to mesh together as many different tasks as possible. In general, it is desirable to identify the most difficult goal of the project and concentrate initial efforts on this aspect of the problem. If the most difficult problem cannot be solved, there is no need to solve the relatively easy parts of the task. Time management is one of our most critical needs. It is fashionable to attend seminars on time management, and indeed, they may help, but primarily, each individual needs to think through how he or she can spend his or her time most effectively. Plans and the problem definition should be reviewed frequently; the situation may have changed, and you may end up solving a problem that is no longer there. In complex problems involving several people from different disciplines, planning procedures that permit monitoring progress in all aspects of the project should be used.

6. Write a report. Most technical people detest writing reports, but in a discipline such as coatings, there is need for continuous accumulation of data. Writing a report forces one to review the work so far and plan the next steps. Valuable parts of reports are the experiments that did not work. Unsuccessful experiments represent a wealth of information that can be used to solve production problems with a current product, to minimize future work, or to meet the requirements of a coating for a different application. Unsuccessful experiments are also useful for preparing patent applications in activeness. It is particularly critical to get the results of actual field uses and the performance obtained into the database.

Standardization of the reporting of trials and results is very important, especially given the increase in electronic data storage. The report on a new formulation should spell out the reasons for inclusion of each of the components in the formulation. Consistent and accepted nomenclature have to be adopted, and analytical results have to be standardized and be nonsubjective. Otherwise, when others look at, or query, the formulation results years later, they may not have any idea why a certain component is there, what it really is, or what the results mean. This situation will complicate the reformulation that often becomes necessary, for example, by a change in the customer's process, and may render the data unusable for future comparative research.

The coatings field is frustrating because there are so many variables to deal with, but this is also what makes it fun and challenging. The primary factor controlling success is enthusiasm to tackle and solve complex problems.

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Organic Coatings: Science and Technology, Third Edition, by Zeno W. Wicks, Jr., Frank N. Jones, S. Peter Pappas, and Douglas A. Wicks