High-performance organic coatings

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Contents

18 High-performance organic coatings for wastewater treatment plants 388

D DHAGE, EWAC Alloys Ltd., India

19 Anticorrosion organic coatings for the automotive industry 407

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Introduction

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Corrosion is a natural process and many metals and alloys used in industrial applications need protection in order to minimize or prevent corrosion. There are various methods of corrosion control which include better design, choice of better materials, protection by inhibitors, cathodic and anodic protection, and protection by coatings. Among these, coating is the simplest and most widely used method.

Steel is used all over the globe in a huge number of applications. Steel, however, is a very reactive material even in normal environmental conditions, corroding in moist air. It needs protection wherever it is used. Whether it is a steel structure, steel frame, steel tank, overhead steel pipe or underground cross-country pipeline, all need corrosion protection. The most common method to protect steel from corrosion is paint coatings.

A paint coating is basically a polymer resin, dispersed in a solvent, modified by additives to achieve specific properties and pigments for providing colour, corrosion protection and other important properties. The nature of the coating revolves round the type of resin that is used, whether alkyd, epoxy, urethane, vinyl or polyester. High-performance properties can be achieved by adding different kinds of pigments, which give not only colour and opacity but also strength, lower permeability and, in turn, longer life. High performance can also be achieved by using solventless systems which not only give higher thickness per coat but also are environmentally friendly because of their low volatile organic content (VOC).

Any discussion of coating is incomplete unless it considers surface preparation and paint application. Surface preparation is a key aspect of paint coatings: any mistake at this stage will compromise the coating. It is advisable to carry out proper surface preparation by following a suitable standard and measuring its anchor profile. New paint formulations or surface tolerant coatings able to cope with partially cleaned surfaces, are important requirements for maintenance of offshore structures, chemical plants, refineries and power plants where surface cleaning may be difficult.

Paint application has become a very specialized subject. Today it is important to know about not only traditional methods of paint application by brush and roller but also the use of more sophisticated techniques such as airless spray, electrostatic powder application, together with the special application skills required to apply elastomeric polyurethane, polyurea and many other fast-curing polyester coatings. Methods for the maintenance of paint coatings are also increasingly important.

Despite proper application, paint coatings do fail prematurely. It is very important to understand what causes the paint to fail and what the various remedial measures are. Another issue in paint coatings is to estimate the life of the coating. It is very important to correctly estimate paint life. Are conventional testing techniques adequate or do we need new methods to estimate the life of a coating? Lastly, it is essential to incorporate good paint inspection and quality assurance techniques both during paint application and afterwards. The importance of supervisors, coating inspectors and others responsible for maintaining quality should be emphasized. They should be provided with good theoretical and practical training.

This book covers a range of key issues in the effective use of high-performance organic paint coatings, including important industrial applications, offshore structures, underground pipelines, automotive coatings, coil coatings, coatings for rebars and concrete structures, coatings for ships and in other aggressive environments.

Part I

General issues

1

Key issues in applying organic paint coatings

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1.1 Introduction

A paint coating can be best described as a coating system, which consists of four main stages:

- Surface preparation
- Primer application
- Application of an intermediate coat
- Application of a top coat.

For any coating to be effective, all four steps are essential. Negligence in performing any of the above steps can reduce coating performance and service life. Surface preparation is the most important of these stages. This topic will be discussed in the next chapter.

The role of primer is very important. An organic coating applied without a primer may act as a barrier coating. However, severe corrosion can occur to the substrate if the coating is damaged. In the presence of a suitable primer, such corrosion of the substrate can be prevented. As an example, a zinc-based primer, applied before the main coating, protects the substrate from corrosion through a cathodic protection mechanism, in case the coating becomes damaged during service. There are several other advantages of the primers which will be discussed in the following section.

An intermediate coat is the main coating which provides barrier protection to the substrate. The intermediate coating may be applied as one coat or more, depending upon the severity of the environment. The top coat can sometimes be the intermediate coat only. However, if the intermediate coat is an epoxy or any other coating which is UV sensitive, it must have a top coat which is UV resistant. Further details are given in the following sections.

1.2 Primers

A primer is defined as a first coat before the main coating is applied. There are several advantages of primers:

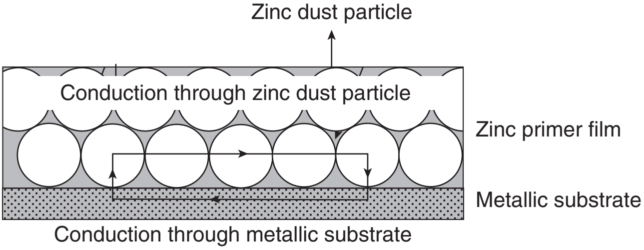
- A primer application can provide a corrosion-resistant barrier.
- For thin sheets and strips, where shot blasting is not possible because of bending of the strip, a primer application can act as a means to create a suitable rough surface. This is usually achieved by conversion coatings, such as phosphating or chromating coatings. The process involves cleaning the specimen, followed by dipping it in a suitable chromate or phosphate solution, which converts the surface of the steel substrate to a phosphate or chromate of iron.
- In the case of a partially cleaned surface, primer application is essential to improve the wetting properties of the surface.

Most of the primers used for providing corrosion resistance to the coating are zinc-based. Several reviews have highlighted the importance, advantages and limitations of these primers and their difference from alternative techniques such as conventional hot dip galvanization [1–3]. Zinc-rich coatings are of two types:

- Organic zinc-rich coatings
- Inorganic zinc silicate coatings.

An *organic zinc-based coating* is usually a dispersion of zinc dust in an organic resin. The organic resin may be alkyd, epoxy or polyurethane and is usually used as a base for the corresponding organic coating. It is usually a colloidal solution of zinc in the organic resin as shown in Fig. 1.1. The bonding of the coating is resin based. The performance of an organic zinc-rich coating depends upon the amount and purity of zinc dust used. A small amount of zinc dust can give a coating some inhibitive properties. However, cathodic protection is achieved only when the zinc dust concentration is more than 75% by weight.

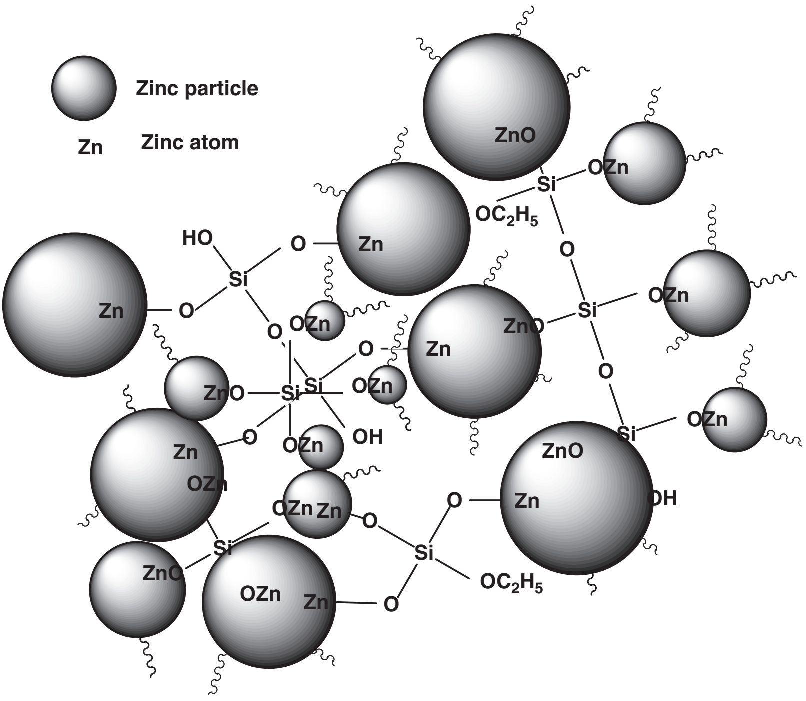
An organic zinc coating can be single-component or two-component. A two-component coating is more effective than a single-component coating. Other organic zinc-rich coatings can be made by the addition of zinc phosphate in an organic resin. Such coatings can be applied on the fully cleaned or partially cleaned surfaces.



1.1 Effect of zinc on the coating performance of the organic resin.

An *inorganic zinc silicate coating* is entirely different from an organic zinc-rich coating. Here also, zinc dust is added in an organic resin, but in this case the organic resin is an active one which bonds strongly with the zinc atom, which in turn forms a chemical bond with the substrate [1]. Hence inorganic zinc coatings are applied only on very clean surfaces having a surface finish equivalent to or better than *S*a $2\frac{1}{2}$. The active organic resin used is ethyl silicate to which more than 80% of good quality zinc is added. Figure 1.2 shows how an ethyl zinc silicate coating forms a strong bond with the substrate.

An inorganic zinc silicate (IOZ) coating, when applied along with two coats of epoxy and followed by one polyurethane top coat, can give a life of more than 5–6 years in an aggressive environment, while the same coating without IOZ will not have a life of more than 2–3 years. An IOZ coating, if applied alone, can also last for six months to one year in a relatively moderate environment, compared to an organic zinc-rich coating which may survive for as little as a few hundred hours. Furthermore, while an organic zinc-rich coating cannot sustain a temperature of more than 150°C, an IOZ coating can withstand a temperature of more than 450°C.



1.2 Structure of an inorganic zinc silicate coating.

IOZ is the most common coating applied on heat exchanger components in power plants.

Shop primers are special kinds of primer that have a longer life than the normal organic zinc-rich primers. A shop primer such as red oxide in epoxy is a well-known primer used in the ship industry and other heavy machinery construction. Along with the advantage of having a longer life than the conventional primers, shop primers can be painted on as a single coating together with a top coat without surface preparation or another coat of the primer.

1.3 Intermediate and top coats

The intermediate and top coats are generally organic paint coatings. Based upon the kind of environment, application technique and climatic conditions, different types of paint coatings can be chosen. The range of coatings can be classified as follows:

Conventional coatings

- Alkyd
- Epoxy
- Polyurethane
- Chlorinated rubber
- Coal-tar
- Vinyl
- Polyester

Advanced coatings

- Solventless coatings
- Glassflake-modified coatings
- Fluoroelastomeric coatings
- Polysiloxane coatings
- Polyurea

Conventional coatings are basically solvent-based coatings and can be of one or two components. A one-component coating is simply a solution of a resin in a solvent. These are also called lacquers. They provide a coating which remains on the surface after the evaporation of the solvent. These coatings do not give very strong corrosion protection and also do not have good rigidity, strength, etc. In a two-component system, the coating dries by reaction between the resin and the hardener which cures with time and becomes hard. The coating becomes harder by strong crosslinking between the resin and the hardener. The following sections deal with different types of coating and also look at ways of improving coating properties.

1.4 Curing mechanisms

Coatings dry by several mechanisms. The simplest is by evaporation of the solvent. Whether the paint is one-component or two-components, in solvent-based coatings solvent evaporates, leaving the resin on the substrate. In a two-component system, crosslinking of the coating also proceeds simultaneously.

The second most common mechanism is reaction with oxygen. Oil-based coatings such as alkyd coatings dry by the reaction of oils with oxygen. Because this process is very slow, it takes several days to completely cure an alkyd coating. The third main mechanism of curing is the chemical reaction between resin and hardener in two-component systems. As the resin and the hardener or catalyst are mixed, crosslinking starts and with time the hardness of the mixture increases till it becomes the complete solid.

The fourth mechanism is radiation curing, where the paint is dried by exposing it to microwave radiation or UV radiation. In the fifth case, the paints are dried by heating. This process is called stoving. In coil coatings, where the strips are coated online, the immediate coated strip is passed through a long furnace, maintained at a fixed temperature. The coated coil travels through this furnace. It is important that the coating temperature does not rise above 150°C, above which many coatings disintegrate.

1.5 Pigments

Pigment is an essential constituent of a coating. It is a common perception that the main role of pigment in a coating is to provide color and opacity. However, pigments can also be added for several other important reasons. The main functions of pigments are summarized below:

- Providing color and opacity
- Strengthening of paint resin
- Providing barrier properties
- Enhancing corrosion resistance
- Adding functional properties such as heat resistance and fire protection.

It is difficult to classify pigments meaningfully [4]. The traditional classification is in terms of organic and inorganic pigments. There is significant variation in the properties of these two groups. Inorganic pigments are heat resistant with long durability and are often costly. Organic pigments have varying properties with respect to durability, heat resistance and cost. In the last few years, the use of nanopigments has also become significant. Very common pigments such as ZnO, SiO_2, TiO_2, Al_2O_3, etc., when added as nanopowders, have significantly improved the performance of paint coatings [5]. It has been found that only 0.03% of ZnO added as a nanopowder in a waterborne coating improved the mechanical, corrosion and UV properties several times [6]. In the same way addition of 0.3% of nano-alumina improved abrasion and scratch resistance of an alkyd-based waterborne coating by almost 10% [7].

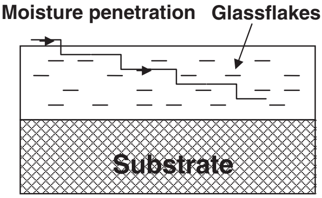
1.5.1 Color and opacity

While inorganic pigments normally give high opacity and are often dull in color, organic pigments are usually bright and normally transparent. Table 1.1 lists some of the organic and inorganic pigments that are commonly used for giving different colors to paint coatings.

The most important pigment used in many coatings is titanium dioxide, commonly known as universal white pigment. Its high refractive index gives high opacity and a pure white color to the coating. More than 70% of organic pigments belong to the azo group, especially in the yellow, orange and red colors. Many of the non-azo pigments are classified as polycyclic pigments. They are organic compounds with more than one five- or six-membered ring in their chemical structure. Phthalocyanine and quinacridone are also included in this category [4].

Table 1.1 A list of a few selected organic and inorganic pigments

Inorganic pigments		Organic pigments	
Carbonates	White – colorless	Isoindolinone	Yellow, orange
Oxides	White, green, yellow, red, brown	Quinophthalone	Yellow
Sulfates	Colorless	Anthrapyrimidine	Yellow
Ferrocyanides	Blue	Flavanthrone	Yellow
Chromates, molybdates	Yellow, orange, red	Perinone	Orange, red
Silicates	White, colorless, blue	Carbazole	Violet
Carbon	Black	Perylene	Red, maroon
Metallic	Aluminum bronze	Benzimidazolone	Yellow, orange, red, brown
Sulfides, sulfoselenides	White, yellow orange, red	β-naphthol	Red, orange



1.3 The tortuous path being followed through a coating cross-section with an ideal distribution of glassflakes.

1.5.2 Strengthening of paint resin

The principle of strengthening paint resin using a pigment is to form a composite matrix by adding some inorganic pigment material as particles, fibers or flakes. Depending upon the size, thickness and distribution of the particles, fibers or flakes, in addition to the increment in the strength of the matrix, there is enhancement of the permeability resistance of the coating.

As an example, adding glassflake as a pigment provides strength to the coating and inhibits moisture permeation, thereby enhancing the life of the coating. This is characterized typically by a random distribution of flakes in an epoxy matrix. If we now consider, for example, an ideal distribution of flakes in cross-section as shown in Fig. 1.3, it can be seen that the path which a permeating pollutant, for example moisture, chloride, etc., will follow will be several times longer than the path followed without glassflake incorporation. This results in the enhancement of coating life.

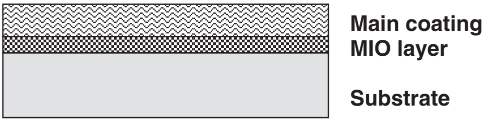
The addition of glassflakes, their size and distribution are very important in imparting the optimum benefit to the coating properties. An ideal composition has been found to be achieved with glassflakes about 0.04 mm in size up to a concentration of 15% [8].

1.5.3 Providing barrier properties

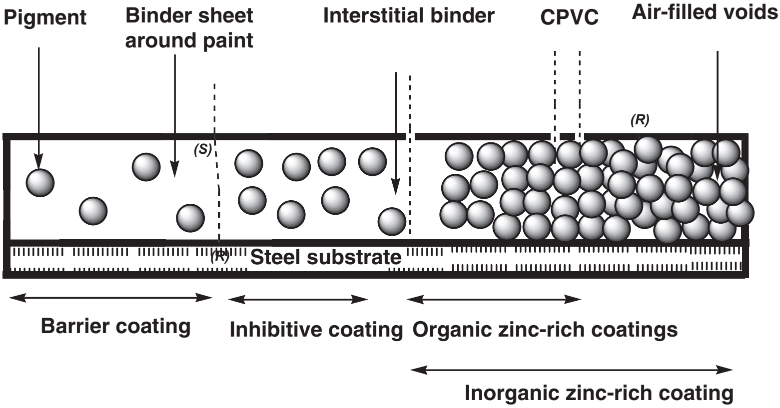
Micaceous iron oxide, commonly used in Europe and to a lesser degree in the United States, has lamellar (platelike) particles. Any relatively large-sized pigment particle, even if it is not plate-shaped, will increase the permeating path of moisture and will result in a barrier-type protection. Mechanism of barrier protection by micaceous iron oxide is shown schematically in Fig. 1.4. The moisture which can penetrate the organic coating is resisted by a lamellar micaceous iron oxide internal layer next to the substrate.

1.5.4 Enhancing corrosion resistance

An organic coating applied on a steel substrate is called a simple barrier coating, as the organic coating just separates the steel substrate from the



1.4 Mechanism of barrier protection by lamellar micaceous iron oxide layer.



1.5 The change in properties of a coating by changing the pigment concentration.

environment. In the case of any damage to the coating, the substrate surface would be exposed to the environment, resulting in its corrosion, because there is no additional protection to the steel surface. By the addition of certain pigments, this corrosion can be reduced. Depending upon the type and concentration of the pigment, the coating will become slightly modified as a result of passivity on the surface, while a large concentration of the pigment may fully protect it sacrificially. The presence of zinc pigment in a small concentration of zinc (pure dust, zinc chromate or phosphate) can provide protective properties to the paint as shown in Fig. 1.5. The coating under these conditions has better properties than a pure barrier coating with no inhibitor at all. As the concentration of the pigment increases, the barrier properties of the coating change to inhibitive properties. A sufficient increase in the concentration of the pigment may result in an organic coating which can give a complete cathodic protection to the steel surface even if the organic coating is damaged. This happens when more than 70% of zinc dust is added into the organic resin. Such a coating is called an organic zinc-rich coating. The inhibitive pigments are usually water soluble. Whenever

Table 1.2 Classification of various pigments

Active pigments	Barrier pigments
Principal functions:	**Principal functions:**
• Anti-corrosion effect on steel by electro-chemical mechanism • Inhibiting anodic or cathodic areas	• Anti-corrosion effect on steel by barrier mechanism • Ultraviolet (UV) radiation absorption providing film protection
Examples:	**Examples:**
• Zinc metal pigments • Zinc chromate pigments • Zinc phosphate pigments • Red lead pigments	• Micaceous iron oxide (MIO) pigments • Aluminum pigments • Glassflake pigments • Talc pigment extender • Mica pigment extender

paint coatings are exposed to a moist environment, with the permeation of some moisture from the environment to the coating, the pigment dissolves and reaches the surface of the steel. It passivates the steel and so inhibits corrosion [9].

The role of these active pigments is thus quite different from that of barrier pigments. Active pigments result in an electrochemical reaction to form a passive layer, while barrier pigments provide a physical barrier to the movement of corrosive species. Table 1.2 differentiates the role of active corrosion pigments from those of barrier pigments.

1.5.5 Functional properties such as heat resistance and fire protection

There are several pigments which, when added in paint, enhance its heat resistance properties or make it fireproof. The addition of intumescent chemicals, which on burning cause thick char formation, prevent a steel structure from losing its mechanical properties and hence give additional time for safe evacuation of people and valuables. Pigments such as tetrabromobisphenol-A hexabromocyclododecane are flame retardants which remove hydrogen and hydroxyl radicals in the gas flame phase, thus stopping it from spreading. Phosphorus-containing compounds act in the solid phase of burning materials. When heated, the phosphorus reacts to give a polymeric form of phosphoric acid (PO_3), causing the material to char. Examples of phosphorus-containing flame retardants include ammonium polyphosphate, red phosphorus metal and organics. Ammonium polyphosphate is preferred for coating applications.

1.6 Additives

Additives are important constituents of paint systems which modify a specific property of the paint coating. The performance of paint systems from two manufacturers, having the same resin, hardener and pigment, may not be the same because of the use of different additives to improve various other properties of the paint coatings such as wettability, surface tension, reaction to UV light, dispersion, etc. Each specific property is taken care of by a different additive and its concentration. A broad classification of various additives can be given as:

- Wetting and dispersing additives
- Surface additives
- Defoamers
- Anti-skin additives
- Preservatives
- Ultraviolet stabilizers.

Wetting additives reduce interfacial tension between pigment particles and resin. They also reduce sagging and settling of paint. Silicones and acrylic copolymers are well-known surface additive chemicals. They reduce surface tension, improve slip and control surface flaws. In the same way, different chemicals are added to avoid foaming of paints (for example, mineral oils or polysiloxane). Other chemicals protect paint from attack by fungi and bacteria. For this purpose, various biocides are added [9].

One of the biggest problems of paints is their stability in UV light. White paints usually go yellowish, and dark-colored paints become faded due to exposure to UV light. Chemicals such as phenyl salicylate and 2-hydroxy 4-methyl benzotriazole act as UV absorbers and hence prevent the paint from deteriorating.

1.7 Alkyds

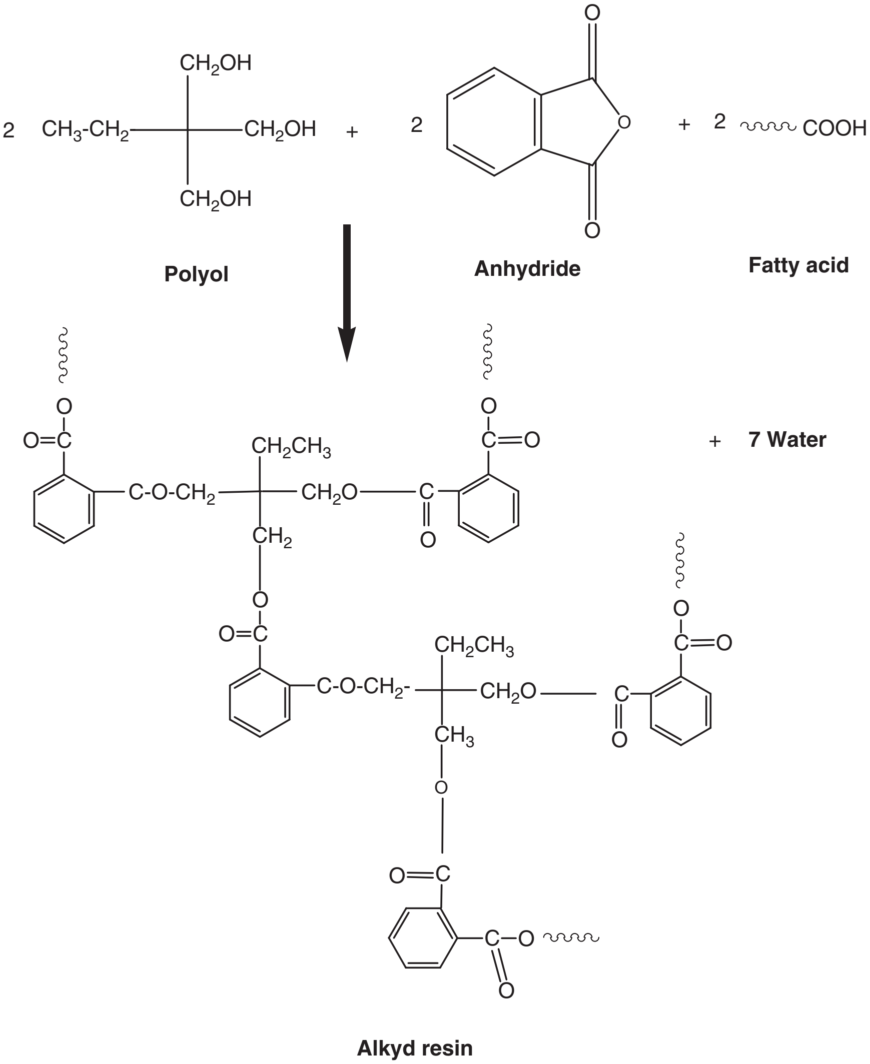
Organic paint resins can be either natural or synthetic. Examples of natural resins are:

- Rosins, from sap exuded from pine trees
- Shellac, a secretion of a coccid insect
- Copals, derived from vegetable remains.

Use of these resins in paint applications is limited. Synthetic resins are used as film formers for both protective and decorative coatings. Since they have improved properties such as better resistance to moisture, chemical and UV attack, compared to the natural resins, they are used in a variety of different service environments as corrosion protective coatings [9].

An alkyd resin is synthesized by reacting an oil with an acid and alcohol. The principal raw materials are oils (castor oil, soya bean oil, etc.), fatty acids, polyhydric alcohols (glycerol) and dibasic acids (phthalic acid). Figure 1.6 illustrates the formation of an alkyd resin.

Alkyd coatings possess properties derived from the drying oils used in the manufacture of the alkyd resins. Properties such as drying time, hardness, color and moisture sensitivity all depend on the drying oil, its type and the



1.6 Formation of an alkyd resin from alcohol, fatty acid and a dibasic acid.

degree of unsaturation. Soya bean oil has been shown to give good drying rates and good color retention. However, linseed oils generally dry faster but darken on exposure to light. Castor and coconut oils have good color-retentive properties and are used as plasticizing resins because of their non-oxidizing characteristics. The extent of the reaction of the oil with the resin influences the protective ability of the applied alkyd coating. High-solubility oil resins (2 l/kg) have poor moisture and chemical resistance and longer drying times. Low-oil alkyds (0.80 l/kg) are fast-drying coatings and have good moisture and chemical resistance but are relatively hard and brittle [9].

The drying mechanism of an alkyd coating initially involves a solvent evaporation mechanism followed by curing by auto-oxidative crosslinking of the oil constituents. Alkyd coatings do not have strong chemical resistance and hence cannot be used in highly aggressive environments and are generally not preferred for any immersion application. They are, therefore, used in environments which are not vulnerable to pollution. The biggest advantage of these coatings is their low cost and their ability to adhere nicely to poorly prepared, rough, dirty or chalked surfaces.

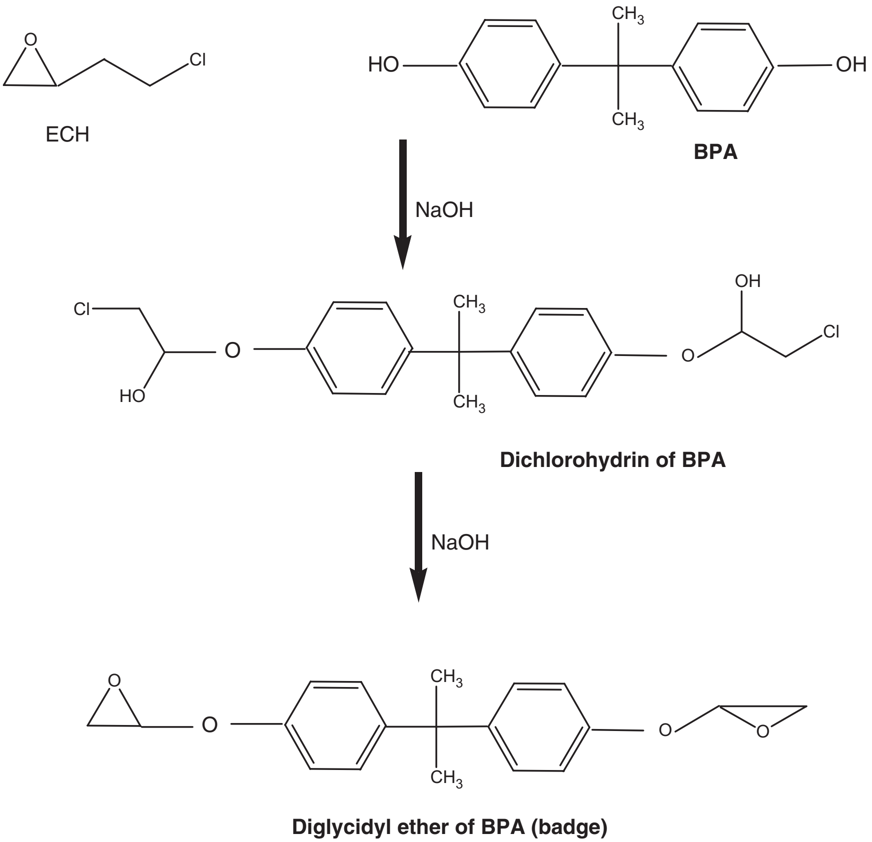
It is possible to enhance the properties of alkyd coatings. Several properties such as corrosion resistance, weathering, and mechanical properties such as hardness and abrasion, can be modified by addition of other resins. An example is the modification of alkyd resin with the incorporation of other resins, is given below. Phenolic resin improves gloss retention, water and alkali resistance. Phenolic alkyd resins have performed satisfactorily in water immersion conditions, where ordinary alkyd resins fail.

Alkyd resins with vinyl modification are commonly formulated as universal primers. The alkyd constituent improves adhesion, film build-up and thermal resistance. The vinyl modification enhances chemical and moisture resistance. These coatings are used frequently as shop primers or as tie coats between different generic coatings, for example over inorganic, zinc-rich primers or between alkyd primers and epoxy topcoats [9]. Other modifications such as incorporation of epoxy resin also provide alkyd coatings with improved chemical and moisture resistance. Though relatively costly, these are used by equipment manufacturers for appliances, machinery, pumps and valves.

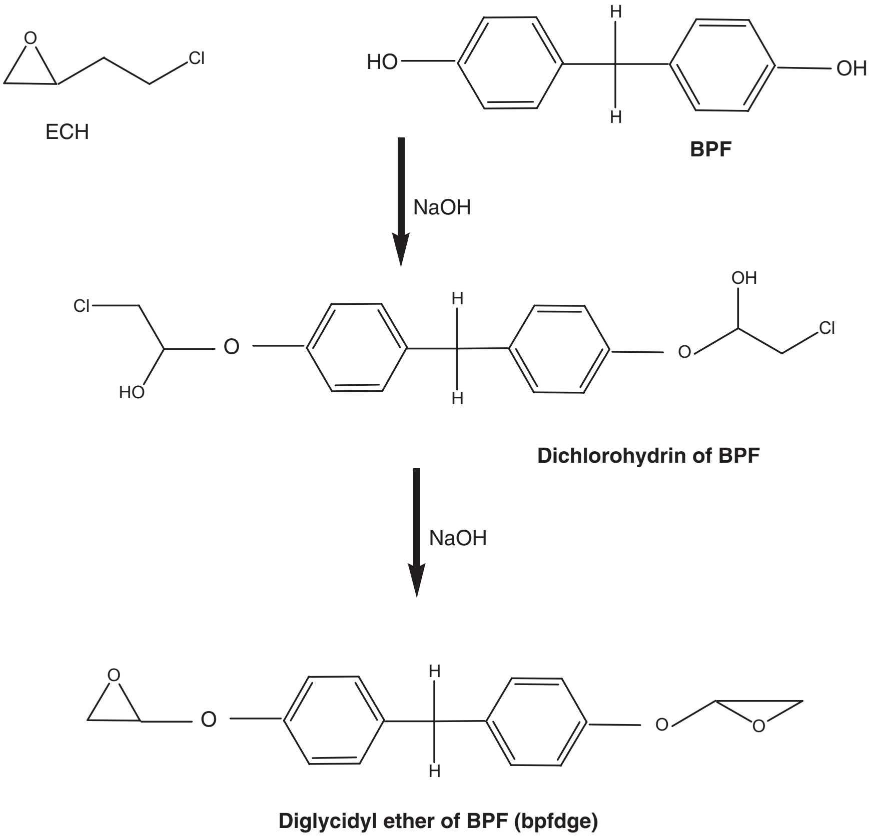
The most widely used modification of alkyd coatings is the addition of silicon. A silicone intermediate is added to the alkyd resin in quantities up to 30% to provide polymers with greatly improved durability, gloss retention and heat resistance. Moisture resistance is also greatly improved by the silicone modification, and this type of paint is used extensively as marine and maintenance paint. Further improvements in drying time of the coating and enhanced resistance to chemicals, moisture, weathering and abrasion is provided when alkyd resins are reacted with isocyanates to form so-called uralkyd or urethane oil coatings.

1.8 Epoxies

Epoxy is perhaps the most commonly used resin for industrial protective coatings. It is derived from bisphenol-A (BPA) and epichlorhydrin (ECH). This combination of raw materials yields a series of related compounds that, prior to crosslinking, have an epoxide group at each end of the molecule, and an alcoholic hydroxyl group as a mid-chain pendant. Crosslinking takes place preferentially through the terminal epoxy groups and to the mid-chain hydroxyl groups. Figure 1.7 shows the formation of a basic epoxy resin monomer, diglycidyl ether of BPA, from the starting raw materials, ECH and BPA, while Fig. 1.8 shows the formation of diglycidyl ether of BPF, from the starting raw materials of ECH and bisphenol-F (BPF). These two epoxy monomers are the base for the large number of epoxy-based coatings which are used for corrosion protection. Figure 1.9 shows the role of various



1.7 Formation of an epoxy (diglycidyl ether of BPA) from epichlorhydrin and bisphenol-A.

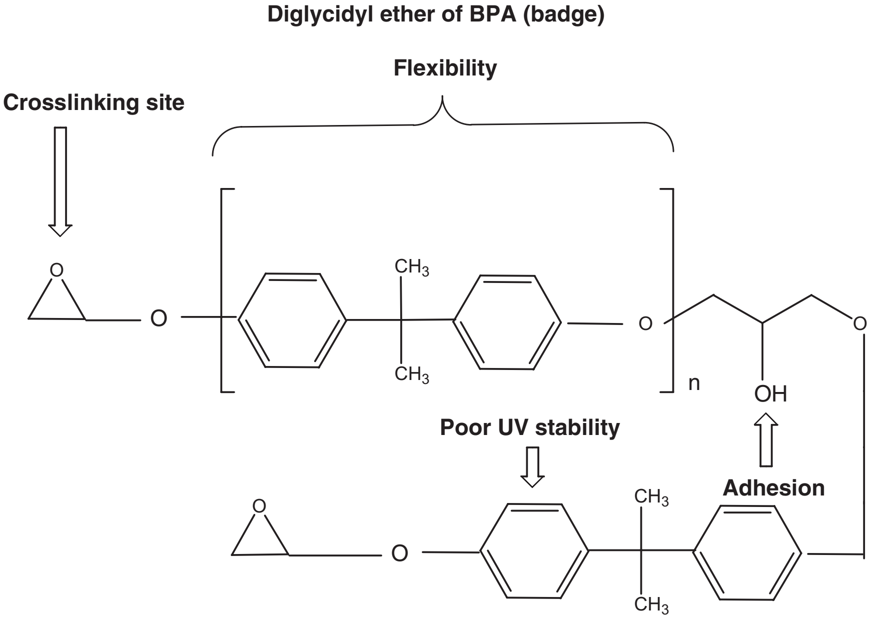


1.8 Formation of an epoxy (diglycidyl ether of BPF) from epichlorhydrin and bisphenol-F.

components of epoxies in providing functional improvement in the properties. As an example, the adherence of an epoxy coating is provided by polar groups such as —OH. The stretchability and flexibility of a coating comes from the chain length of the polymer.

The protective properties of epoxy coatings result from reaction with a very active reagent called a hardener. The role of this reagent is to provide crosslinking between the polymer chain and the hardener. It is rightly called a hardener since, as the reaction progresses, the coating hardens and finally becomes solid. The most common hardeners for epoxies are usually a polyamine or a polyamide. Figure 1.10 shows a typical crosslinking reaction with BPA and an amide curing agent.

The crosslinking results in making the coating rigid. Such a coating has lower permeability and hence better corrosion resistance. The extent of crosslinking depends upon the number of epoxide groups in the epoxy resin

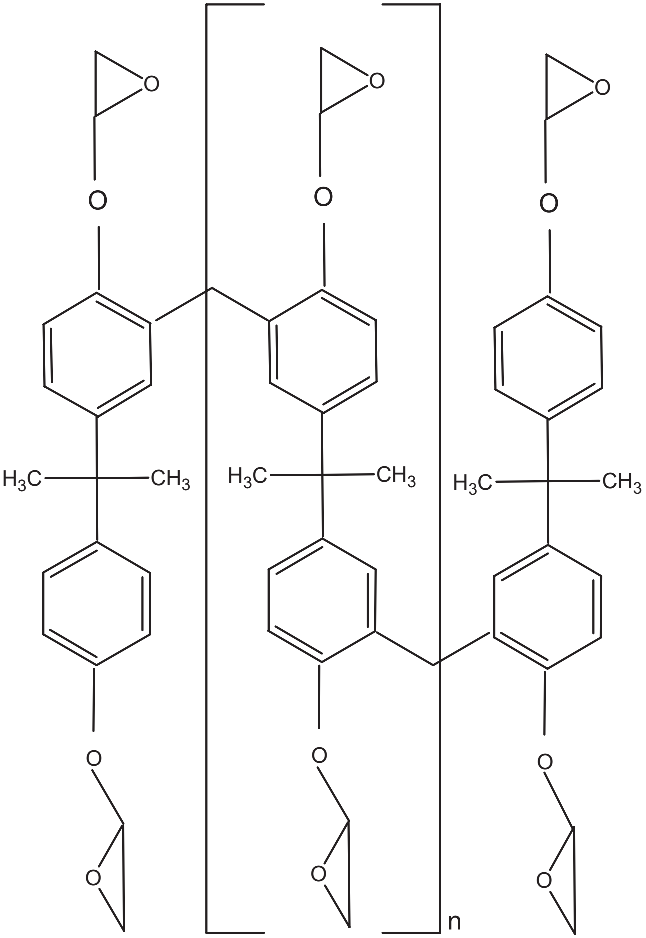


1.9 Various properties that epoxies gain from structure of polymer.

chain. The greater the number of epoxide groups, the higher will be the crosslinking. The resultant coating will be rigid, acts as a strong liner to the substrate and can provide high chemical, erosion and abrasion resistance. One such epoxy resin is novolac epoxy resin, which is formed by the reaction of formaldehyde with phenol, having three phenolic groups per monomer [10]. When it reacts with epichlorhydrin, it forms a resin having three epoxide groups (Fig. 1.11).

This resin on crosslinking forms a hard, dense, rigid coating, which provides greater hardness as well as resistance to high temperatures. The high temperature resistance of these coatings is effective up to about 250°C. The resin also has high chemical resistance but high brittleness and lack of toughness and flexibility.

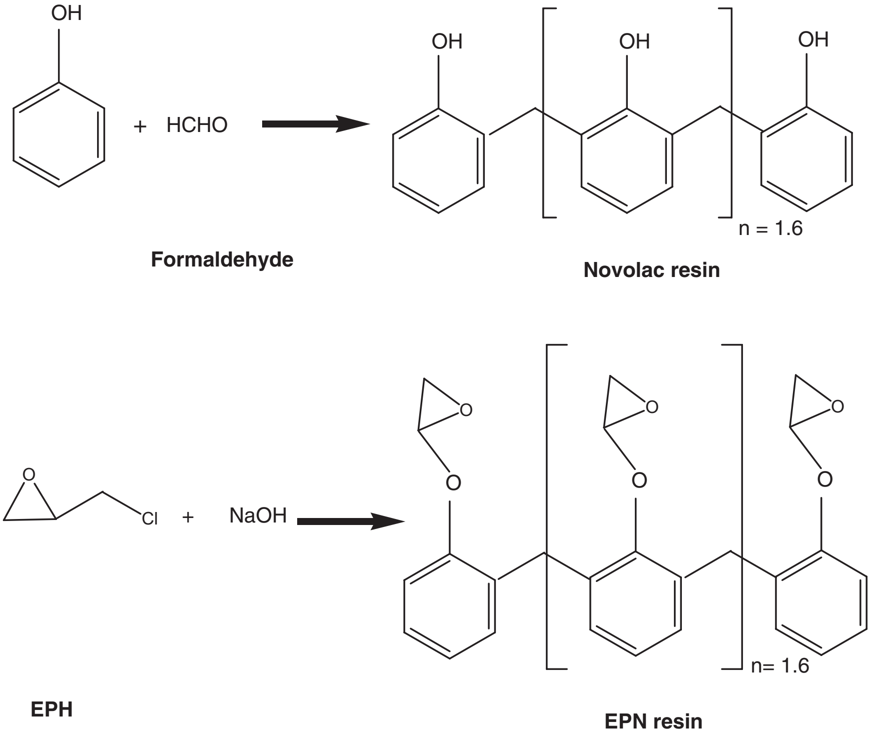
Polyamide and polyamine hardeners result in different properties. While the polyamines (diethylene triamine, hydroxy ethyl diethylene triamine, bishydroxy diethylene triamine) are relatively small molecules with a low molecular weight compared to the epoxy resin, they lead to tight crosslinking and high chemical and moisture resistance. Polyamide curing agents are the condensation products of a dimerized fatty acid with the polyamine. With amine groups at the ends, they allow crosslinking to occur lengthwise irrespective of the fact that the polyamide molecule is much larger. The prominent differences in their properties are shown in Table 1.3.



1.10 Mechanism of crosslinking.

Table 1.3 Differences in the coating properties achieved by different hardeners

With polyamide as hardener	With polyamine as hardener
Larger molecule with respect to epoxy	Smaller molecule with respect to epoxy resin
Tight crosslinking, making the coating rigid	High crosslinking, still retains good flexibility and flow
Lower water resistance	Excellent water resistance
Excellent chemical resistance	Good chemical resistance
High solvent and alkali resistance	Lower solvent and alkali resistance
Low UV light resistance	Better UV light resistance



1.11 Formation of Novolac epoxy resin which has three epoxide groups per monomer.

1.9 Coal-tar epoxies

Coal-tar enamel coatings are cheaper coatings which have excellent barrier properties. However, these coatings have poor dielectric properties and higher permeability. They also have poor mechanical properties such as brittleness, and their tendency to go hard at lower temperatures and to flow at higher temperatures limits their applicability to a limited temperature range. In order to improve the properties of coal-tar coatings, an epoxy is added to produce a coal-tar epoxy coating. The level of epoxy varies from formulation to formulation, with a range from 25% to 40% [11]. The epoxy resin is packed separately in one pack, while the second pack consists of well-refined coal-tar pitch with a hardener polyamide. The two packs are mixed just before use. The crosslinking reaction is the same as that described earlier for epoxy resins. Active hydrogens from the amine crosslink with the epoxide groups and, in some conditions, the hydroxyl groups of the epoxy resin. The coal-tar acts as a filler within the crosslinked epoxy matrix. This gives better flexibility and good dielectric properties to the coal-tar.

The coating thickness, which can range from 125 to 300 μm, has better toughness, adhesion, UV resistance and thermal stability and extremely high moisture resistance. The polyamide-cured coal-tar epoxies have higher water resistance, are more flexible and are easier to topcoat. They are very commonly used in walls immersed under water such as sea walls and barriers, as well as on piping above ground level.

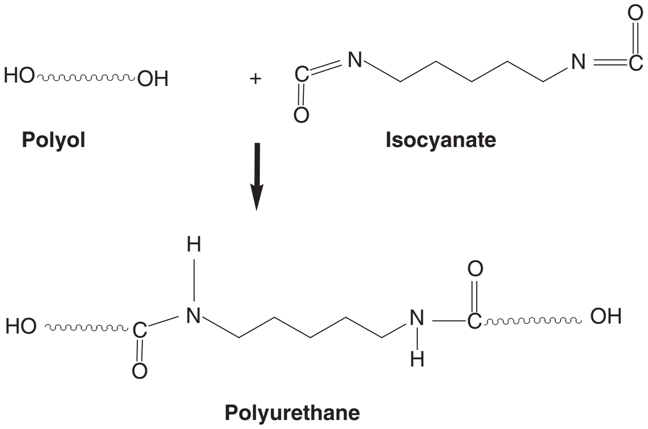
1.10 Polyurethane coatings

The urethane monomer is formed by the reaction of an isocyanate (—N=C=O) with an alcoholic group (—OH) as shown in Fig. 1.12. A quick reaction occurs because of the high reactivity and affinity of the isocyanate group for the active hydrogen of the polyolhydroxyl. The extent of crosslinking depends on a number of factors, such as the type and configuration of both the isocyanate and polyol materials, temperature, etc. The reaction also requires a catalyst.

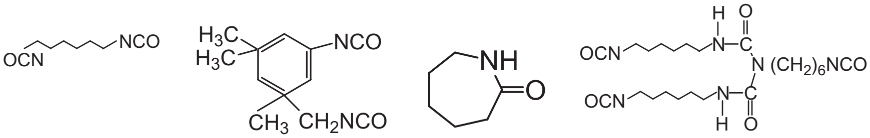
The important constituents of a urethane coating are isocyanates. The properties of a polyurethane coating depend upon the type of isocyanate as well as on the type of polyol. One of the greatest advantages of polyurethanes is their resistance to UV. For this reason, they are used as top coats on various epoxy and other intermediate coats. Two main categories of the isocyanates are:

- Aromatic isocyanates
- Aliphatic isocyanates.

As can be seen in Fig. 1.13, an aromatic isocyanate is one which has an unsaturated hydrocarbon or benzene or phenolic group. All isocyanates



1.12 Formation of urethane monomer from the reaction of an isocyanate with a polyol.



1.13 Structures of various isocyanate molecules.

except the second in Fig. 1.13 are aliphatic. The main difference in the two types is in their UV resistance. While polyurethanes formed using aliphatic isocyanates are resistant to UV light, aromatic polyurethanes are severely affected in UV light. They chalk and lose gloss and color when exposed to UV light. The aromatic isocyanates have properties very similar to that of epoxy with the exception of poorer chemical resistance.

The most important monomeric diisocyanates used for coatings are toluene diisocyanate (TDI), 4,4-diphenylmethane diisocyanate (MDI) and 1,6-hexamethylene diisocyanate (HDI). They are normally converted into isocyanate-terminated polymers or adducts of polyols such as hydroxyl-terminated polyesters and polyethers. The molecular weight of these isocyanates can be increased by self-reaction in the presence of catalysts to form dimers and/or trimers. Aliphatic isocyanates are more expensive and react more slowly but allow the formulation of non-yellowing, light-stable coats with a high gloss finish. One of the most important aliphatic isocyanates is HDI [9].

Polyols react with isocyanates to form a polyurethane film. A polyol consists of large molecules (commonly acrylics, polyesters, polyethers, epoxies, vinyls and alkyds) that have been reacted with di- or polyfunctional alcohols such as propylene glycol, trimethylolpropane, pentaerythritol and others. The most common industrial polyurethane coatings are two-component coatings. The first component is the isocynate prepolymer while the second component is the hydroxyl-terminated polyol. Just before application the isocyanate and polyol constituents are mixed, and crosslinking proceeds via the isocyanate-hydroxyl functions and liberates carbon dioxide gas.

In general, the characteristics and properties of the urethane coating depend predominantly on the properties of the polyhydroxylated coreactant. Tremendous improvement in the properties of the polyurethane coating takes place when polyol has various prepolymers such as acrylic, polyester, polyethers, epoxies or vinyls. Acrylic urethanes are perhaps the most widely used urethanes for corrosion protection and atmospheric service. They have excellent weatherability, gloss and color retention and good chemical and moisture resistance. Polyester urethanes are tightly crosslinked and have great chemical and moisture resistance, but they are not as flexible and tough as the acrylic urethanes. They are used in exterior chemical environments in which acid fumes or highly corrosive conditions are encountered. They also have high gloss, are light fast and have a good appearance.

1.11 Moisture-cured polyurethanes

One of the limitations of polyurethane coatings is that they are very sensitive to moisture. Therefore, for application of polyurethane coatings, the relative humidity must be low (preferably lower than 60). This makes them usually difficult to apply in highly humid environments such as coastal and offshore. A moisture-cured polyurethane is based upon the reaction of isocyanates with the hydroxyl group in water (H–OH) to form a unique class of coatings known as moisture-cured urethanes. These are single-pack coatings. They use an isocyanate prepolymer that, when applied, reacts with moisture in the air to form a tough, hard, resinous film. Because of their rapid rate of reaction, aromatic isocyanates are used almost exclusively in moisture-cured urethanes. When applied by air spray, they form a tough, glossy, highly protective chemical and solvent-resistant film. These days moisture-cured polyurethane is used as a primer. One of the best applications of moisture-cured polyurethane is as a maintenance coating, because moisture-cured polyurethanes can be applied on partially cleaned surfaces, followed by an intermediate epoxy or aromatic polyurethane coating and an aliphatic polyurethane as top coat [9].

There are several other resins which are used sparingly in several different applications. The most common are polyesters and vinyls. Polyester coatings include oil-free, acid or hydroxyl functional polyester resins. They are mainly composed of coreacted di- or polyhydric alcohols and dibasic or tribasic acid or anhydride, and are thinned by normal solvents. They are relatively expensive resins and are used for long-lasting applications such as automotive clear coats and steel coil coatings.

The term vinyl resin commonly refers to polymers and copolymers of vinyl chloride, which is a cheap monomer, whose polymer possess good color, flexibility and chemical resistance. Vinyl resins are used in coatings for strips in venetian blinds and for bottle tops where extreme flexibility and extrusion properties are required. They are also used in heavy duty and marine coatings where toughness, elasticity and water resistance are the main requirements. They also have application as thick coatings on coil strip building facings. Polyvinylidene fluoride dispersion is now used as the highest durability coil coating on aluminum.

1.12 High-performance coatings

A high-performance coating can have one or more of the following characteristics:

- High corrosion resistance in highly aggressive environments
- Can be applied in high relative humidity (more than 90%)
- High thickness (DFT) can be achieved per coat
- Provides resistance to weathering, especially UV light
- Good mechanical properties such as high impact strength, abrasion resistance and hardness.

Some situations in which high-performance coatings can be applied are in the splash zone of offshore structures, underwater in sea and rivers, on damp surfaces, in highly acidic and alkaline environments such as pickling units, in the battery chamber of a ship or submarine, in sewage disposal units, seawater transport through jetties, etc. The requirements of such paint coatings are:

- High chemical resistance (as in epoxies)
- Solventless so that a large thickness can be obtained per coat
- Long life and structural stability that can be obtained by addition of pigments such as glassflakes and fibers.

A good example of a high-performance coating is a solventless epoxy system. Solventless resins are those which do not use any solvent in paint formulation. There can be several advantages of using such coatings:

- These coatings are eco-friendly as they do not contain any solvent and are thus free of volatile organic content (VOC).
- They can be applied to give a higher coating thickness per coat.

A comparison of solventless and solvent-borne coatings is summarized in Table 1.4.

The most common solventless coatings are epoxy-based. These are used as linings in highly corrosive environments, such as for seawater jetty pipes for condenser cooling, tank linings and offshore structures. These epoxies are usually low molecular weight polyfunctional liquid epoxy resins, and the hardeners are polyamines which provide crosslinking, giving highly tough, corrosion- and erosion-resistant linings. Presence of a tertiary amino phenolic catalyst, such as tri(dimethylaminomethyl) phenol can produce polymerization of the epoxy resin with itself. Silicone resins may be added as flow agents, and dibutyl phthalate can be added as a plasticizer [9].

Further improvement in the coating life can be achieved by adding glassflakes, which not only improve the strength of the coating but also help in increasing the tortuous path as discussed earlier, and thus enhance the life of the coating [12]. Such glassflake epoxy coatings have high corrosion and erosion resistance. They are used in highly corrosive and erosive applications such as in the splash zone on offshore structures. Their short curing time coupled with high thickness per coat make them the right choice for

Table 1.4 Comparison of solventless and solvent-borne coatings

Property	Solventless epoxies	Solvent-borne epoxies
State	Mostly liquid epoxy resin	Solid or semisolid epoxy resins
Hardener	Low-viscosity amines	Medium/high-viscosity amides
Pigments	Yes – depending upon color and other required properties, e.g. color pigments are very common, glassflakes are usually added for high strength	Pigments and additives essential to obtain useful properties such as color, UV absorption, etc.
Solvents	Usually no solvent is required, but sometimes thinners are added to adjust the viscosity for smooth application	Solvent essential to dissolve resin, pigments and additives
Application	Usually by airless spray	Using brush, roller and airspray
Plural components	Always	Can be single-component or two-component
Curing	Chemical reaction of two components	By solvent evaporation as well as chemical reaction
Pot life	Usually small	Relatively larger
Edge protection and filling of pits	Solventless coatings because of low viscosity as well as due to application by high-pressure airless technique protect the edges very well and the paint reaches down into the pits, giving a smooth finish even after coating on a highly pitted surface	Edge protection is very poor and uneven surface is seen after paint coating on a pitted surface
Safety and health hazard	No risk of explosion, good skin protection as there is no or only a little VOC.	Forced ventilation necessary to reduce explosion risk due to VOC, and skin protection needed

offshore platform piles which usually get very little drying time. These coatings can be applied in the brief dry period between low and high tides. The life of these coatings has been predicted to be more than 10 years for a coating thickness of 1000 μm. The only problem these coatings face is deterioration in UV light. Severe cracking and chalking may take place after continuous exposure for several thousand hours.

Other very common solventless resins are polyester coatings. Isophthalic-based polyester systems or polyester modified with vinyl ester are the best examples of such applications [13]. These coatings with glassflake addition are found to be very suitable for the splash zone. They have an advantage over epoxy systems as they do not get chalked or crack on exposure to UV light.

One of the most common solventless resins is an elastomeric polyurethane coating. This is perhaps the most common coating used as a floor coating. The main advantages of elastomeric coatings are their quick drying time and very good elastic properties [14]. They are also becoming very important coatings for rehabilitation jobs for pipelines. Their quick drying property is being used for girth welding coating for pipelines, although solventless epoxy is preferred for this application, as there is less wastage due to the relatively longer curing time.

For underwater applications and for applications on damp surfaces a hydrophobic system of epoxy is usually recommended. The principle of such a coating is that when it is applied underwater, it replaces water very quickly and sticks on the steel surface [15]. The full curing, however, takes place within 24 hours in water. Such coatings have been found to have a longer life under water. It has been found that aliphatic polyamine curing agents displace water from wet surfaces in order to make a permanent bond with the substrate; they form the basis for today's cutting-edge underwater epoxies.

For highly acidic and alkaline environments, there cannot be any better coating than poly vinylidene difluoride (PVDF) coatings, which resist strong acids and alkalis and also have strong UV resistance. PVDF coatings are now being used in external wall claddings on aluminum as aluminum composite panels, and a life of 25–30 years is assured with no maintenance [16].

Long gloss retention and high temperature resistance can be achieved by polysiloxane coatings. Polysiloxane coatings can have excellent gloss retention up to 15 years and can be used as heat-resistant coatings up to a temperature of 600°C [17]. Another class of high-performance coatings are the fireproof coatings, especially intumescent coatings [18]. These can be organic resin based or inorganic coatings. The principle of these coatings is to create insulation with the char produced on burning with the help of some chemicals added into the resin. This inhibits the degradation of the mechanical properties of the underlying steel and hence gives enough time to rescue people and valuable assets from the building. Some of these coatings are described in great detail in the application section, later in this book.

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2

Surface preparation for organic paint coatings

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2.1 Introduction

Surface preparation is perhaps one of the most important aspects of paint coatings. It has been found that more than 75% of paint failures take place due to poor surface preparation. What do we mean by surface preparation? The different methods of surface preparation and the procedures and standards followed will be dealt with in this chapter.

Surface preparation basically means creating a surface suitable for paint application, a surface that can give strong adhesion to the coating. The main components of surface preparation are surface cleanliness and anchor profile of the surface. Both are obtained by blasting the surface with suitable abrasives which remove the unwanted debris on the surface and give a suitable profile.

Before one goes for blast cleaning, the surface must be pre-cleaned. Depending upon the source of the substrate, it may have different kinds of impurities. A substrate lying in the open for a long time may have dust and rust. A substrate lying in a working space may have grease and oil, while a component near the seashore may have many corrosion products and salt deposits on its surface. Thus it must be pre-cleaned before blasting treatment is carried out. The following systematic steps are required before a surface is subjected to blasting:

1. **Assessment of surface condition.** A thorough examination of the component to be painted is a must. It is important to identify welded areas, mill scale and defects on the surface due to fabrication.
2. **Remedying design or fabrication defects.** In order to have a uniform surface for blasting, all the defective areas must first be repaired and dents removed. If the surface is pitted, it must be cleaned by removing all corrosion products; it is especially important to remove spatters near the weld.
3. **Pre-cleaning.** This is required to remove various impurities on the surface by one of the following methods:

   - Solvent cleaning
   - Hand tool cleaning
   - Power tool cleaning
   - Flame cleaning
   - Acid pickling.
4. **Inspection/documentation.** This is the most important aspect of surface preparation. It helps in checking that all the steps are being followed. It also helps later to know where errors have occurred, and it helps in eliminating surface preparation as one of the reasons for failure of paint in case of a dispute.

Only then can blasting take place.

All the above activities of pre-cleaning are carried out according to standards. The standards used for surface preparation are set by:

- NACE (National Association of Corrosion Engineers)
- SSPC (Steel Structure Painting Council)
- ISO.

Details of these standards are summarized in Table 2.1.

2.2 Blast cleaning

For paint coatings, it is important that the surface should be clean. However, mere cleanliness of the surface is not the main requirement. Surface roughness, which is measured by the anchor profile, is the necessary requirement. The one and only method to achieve both the highest degree of cleanliness and a reasonable surface profile is blast cleaning. This is a process in which very hard particles called abrasives are forced on to the object; they not only remove the unwanted corrosion products, paint debris and mill scale from the surface but also create the required roughness by their impact. Since the speed and kinetic energy of the abrasives is important, compressed air at a pressure of about 1000 psi is used to accelerate the particles, causing the abrasives to move at a speed of up to 200 m/s [1].

The SSPC has published reference cleanliness standards for abrasive blast cleaning (SSPC Painting Manual, Volume 2). The National Association of Corrosion Engineers (NACE) has established similar standards. They are summarized in Table 2.1. Each degree of cleaning stipulates a percentage of the surface that must be free of contamination.

2.2.1 Blast cleaning techniques

Conventional blast cleaning generally falls into four categories:

- Pressure blasting

Table 2.1 Various standards for surface preparation

Surface pre-cleaning method	Process involved	SSPC Standard	NACE Standard	ISO-8501 Standard
Solvent cleaning	Cleaning with water, acetone, acid, base or any other solvent, by either spraying, swabbing or dipping	SP1	–	–
Cleaning by hand tools	Remove loose mill scale, rust, paint. Tools used: wire brush, scrapers, chisel, knife, chipping hammer	SP2	–	S12 or S13
Cleaning by power tools	Hard, strongly adhered rust, paint coatings, etc. Tools used: grinding wheels, vibrating wire brush, sand wheel	SP11	–	–
Blast cleaning	Full white metal (contamination <5%)	SP5	NACE 1	Sa3
	Near white metal (contamination <15%)	SP10	NACE 2	Sa2$\frac{1}{2}$
	Commercial cleaning	SP6	NACE 3	Sa2
	Virtual cleaning	SP7	NACE 4	Sa1

- Centrifugal blasting
- Vacuum blasting
- Wet blasting.

Pressure blasting

Perhaps the most common method of abrasive blast cleaning is pressure blasting, in which the blasting medium is stored in a pressure vessel, connected by a hose to an air compressor. The other components are moisture and oil separator, air coolers and driers, nozzle, and safety-related equipment.

The air compressor is the source of energy for pressure blast cleaning. The extent of blasting is in direct proportion to the volume of air (cubic

Table 2.2 Efficiency of a blast cleaning process as a function of nozzle size and air availability

Blast nozzle orifice size (inch)	Air required in cfm (cubic feet per minute) for various efficiency at different nozzle pressure		
	60 psi	80 psi	100 psi
$\frac{1}{4}$	67	85	103
$\frac{3}{8}$	151	191	232
$\frac{1}{2}$	258	340	413

feet per minute) through the nozzle. A large compressor can support big nozzles. The larger the orifice size of the nozzle, the more efficient it is in blasting. The relationship between the nozzle size and the air pressure required for a particular efficiency is given in Table 2.2.

The efficiency of pressure blasting depends upon the following:

- Condition of the substrate (whether the scale is category A, B, C or D)
- Quality of surface to be blasted – Sa1, Sa2, Sa2$\frac{1}{2}$ or Sa3
- Availability – pressure of air
- Nozzle type and size
- Distance of nozzle from the surface.

Usually,

- 100 psi at nozzle gives 100% efficiency.
- 80 psi at nozzle gives 66% efficiency.
- 66 psi at nozzle gives 50% efficiency.

The most important part of the abrasive blast technique is the nozzle, which is identified by the size of its orifice. Diameters are usually measured in sixteenths of an inch. For example, a 4.76-mm ($\frac{3}{16}$-in.) diameter orifice is designated No. 3, a 7.94-mm ($\frac{5}{16}$-in.) diameter orifice is designated No. 5, and so on. Nozzles are commonly available up to 15.9 mm ($\frac{5}{8}$ in.) in diameter [1]. The size of the nozzle should be large enough to maintain a pressure of air at 100 psi at the nozzle exit, which gives an efficiency of 100%. Another important aspect is the quality of nozzle material. A nozzle coated with tungsten carbide gives the nozzle a much longer life (~1500 h compared to 3–4 h for an uncoated nozzle tip) as it does not erode due to interaction with hard abrasives. Production cleaning rates can be increased by as much as 30–50% with the use of a venturi nozzle as opposed to a conventional 'straight bore' nozzle. Longer nozzles, from 127 to 203 mm (5 to 8 in.), will more easily remove tightly adherent deposits and increase cleaning rates [1–3].

In an industrial unit used for continuous blasting of big components such as pipes or I-beams entering the blaster on a conveyor belt, there are several guns inside the blast chamber which blast the rotating pipe moving with a pre-adjusted speed. The clean member comes out from the other side.

In order to achieve better blasting efficiency, it is advisable to optimize the following parameters:

- The proper balance of abrasive and air is achieved when the abrasive air stream from the nozzle is 'bluish' in color [1].
- The angle of the nozzle to the surface can range from 45 to 90°. To remove rust and mill scale, an 80–90° angle to the surface is preferred. This angle is also suitable for dislodging contaminants from pitted surfaces. A slight downward angle also directs the dust away from the operator. To peel old paint and layers of rust from the surface, a 45–70° angle to the surface is most productive.
- The closer the nozzle is to the surface, the smaller the blast pattern. With a small pattern, the abrasive is concentrated in a smaller surface area, resulting in an impact at greater speed and more force. A distance of only 152.4 mm (6 in.) may be required to remove tight mill scale and heavy rust, but a 457.2-mm (18-in.) nozzle-to-surface distance may be most effective for removal of old coatings. Each pass should be straight and at the same distance from the substrate to give a uniform pattern.

Abrasive cleanliness [1]

Abrasive materials contaminated with oil or chemical residue can lead to surface contamination. Abrasives should be monitored for cleanliness using one of the following techniques:

- The 'vial test' is referenced in SSPC Painting Manual Volume 2, Abrasive Specification No. 1, 'Mineral and Slag Abrasives' (SSPC-AB 1). With this test, if the abrasive is contaminated, the top of the water in the vial will reveal a film of grease or oil.
- The abrasive also can be tested for chemical contamination by performing a conductivity test, as per ASTM D4940. However, water-soluble contaminants such as salt will not be detected using these tests.
- If water-soluble contaminants are present, a litmus paper test of the water in the vial will tell if they are acid or alkaline. If neutral, a drop of 5% silver nitrate solution should be added to the water. The formation of a white precipitate will indicate the presence of chlorides. Alternatively, after the water has evaporated, if these contaminants are present, salt crystals would be detectable.

Ambient conditions

One of the most important requirements of blast cleaning is proper atmospheric conditions. A blasted surface has a large surface area. It is prone to flash rusting as soon as wet conditions are available. Thus while carrying out the blasting one should maintain suitable conditions. The work should be halted if temperature, relative humidity, dewpoint or surface temperature deviate from the contract requirements. Most importantly, the surface temperature should be at least 3°C higher than the dewpoint for final blast-cleaning operations. This precautionary step will preclude moisture formation on the surface.

Centrifugal blast cleaning

The principle of the centrifugal blast cleaning technique is to allow abrasives to impact the steel surface from various directions by rotating wheels with blades. The bladed wheels rotate rapidly to propel the abrasive at speeds of up to 90 m/s. It is a relatively fast cleaning technique, capable of throwing approximately 10 times the amount of abrasive per minute than an air blaster can [1]. Further, it consumes less energy and blasting abrasive. The recycling of the abrasives is possible after separating them from the rust, mill scale and other impurities. The degree of cleanliness of the surface can be changed by controlling the speed of the conveyor or the velocity at which the abrasive is thrown towards the steel surface.

Vacuum blast cleaning

Surfaces may be contaminated with toxins such as lead-based paints and dust which when inhaled can cause serious health problems. It is advisable that such surfaces be prepared using the vacuum blasting process. In this method, the blasting nozzle is connected to a vacuum chamber. Due to this, the dust, abrasives and coating debris are sucked into the vacuum chamber while blasting is being carried out. The abrasive is separated from paint debris and sent for recycling. Thus the highest level of surface preparation can be achieved using vacuum blasting [1].

Wet blasting

In many applications, when blasting is carried out by steel shot, there are dangers of fire caused by sparks initiated by the abrasives hitting the metal substrate, especially if the substrate is in a refinery, oil or gas installation facility or petrochemical plant. Dry blasting can be disastrous in such areas. Wet abrasive blast cleaning involves the incorporation of a small amount of water into a dry abrasive blast-cleaning operation. Methods, equipment and techniques are similar to dry abrasive blast cleaning, except that a modified nozzle is used in which water is either injected into the blast stream or introduced to the abrasive as a ‘collar’ around the exit stream.

2.2.2 Types of abrasives

The surface effects produced with various abrasives can range from deep cutting to gentle scouring of the surface. Important factors to consider in selecting an abrasive include the following:

- Type of surface to be cleaned
- Shape of the structure
- Type of material to be removed
- Surface finish desired
- Required profile
- Breakdown rate of the abrasive
- Reclamation of the abrasive
- Hazards associated with the use of the abrasive
- The area in which the abrasive will be used and any dangers to the surroundings.

Some of the most common abrasives used for surface preparation are as follows:

- Chilled iron grit or shots
  - widely used, variety of grades, excellent for general purpose, very hard
- Crushed slag – Cu slag, Al slag, coal slag
  - for use once only (cheap)
  - in Cu slag, SiO_2 (38%), Al_2O_3, TiO_2, Fe_2O_3, FeO (42%), MnO, MgO; CuO is only 0.47%
- Naturally occurring grits
- Ceramic grits
  - expensive, effective cutting action, effective at lower pressure, reusable.

Each type of abrasive cleans in a different way and leaves a slightly different surface texture. There is a recommended physical and chemical property reference for mineral and slag abrasives as defined by SSPC-AB 1. In addition, several ASTM test methods exist that deal with all abrasives and include the following: C128, C566, C702, D1125, D4417, D4940 and E1132.

2.2.3 Important characteristics of abrasives

Size, shape and hardness of abrasive particles decide their efficiency. Large abrasive particles will cut deeper and thus provide a deeper surface profile. Hard particles generally cut deeper and faster than soft and brittle abrasives. Table 2.3 compares the cleaning efficiency of various kinds of abrasives for a fixed nozzle size (9.5 mm) at a pressure of 100 psi.

Table 2.3 Cleaning efficiency of various kinds of abrasives for a fixed nozzle size (9.5 mm) at a pressure of 100 psi

Abrasive type	Abrasive consumption rate (kg/m^2)	Extent of cleaning (m^2/min)
Silica sand 16/40 mesh	12.69	0.44
Garnet 36 grit	17.58	0.33
Aluminum oxide 36 grit	15.13	0.42
G-40 steel grit	26.85	0.28
Copper slag 16/40 mesh	15.13	0.40

2.3 Measurement of anchor profile

2.3.1 Comparing standard coupons

One of the simplest ways of measuring the blast profile of the blasted surface is by comparing it with a standard profile. Coupons are available with Sa2$\frac{1}{2}$ surface finish with anchor profile of 12–75 μm. The procedure consists of just keeping the comparator on the blasted surface and matching visually the closest profile.

2.3.2 Replica tapes

Replica tapes are very flexible cellulose tapes. When pressed on the surface, they acquire impressions of peaks and valleys. Thus by measuring the initial thickness of cellulose tape (without impressions) and the thickness after taking impressions, using a microgauge, the anchor profile can be measured. This is the most applicable method in the industry.

2.3.3 Dial gauge to measure the depth

A dial gauge is pressed gently on the blasted surface, which gives the anchor profile either on an analog scale or on a digital scale.

2.4 Measuring the impurities on the blasted surface

Of late this has become the most important requirement of surface preparation. It has been found that severe disbondment can take place if dust and especially chlorides remain on the blasted surface. Usually the dust contamination comes from the open application rooms, and chloride can come from either the environment or from the contaminated abrasives in continuous use for several runs. Dust is usually removed by cleaning the blasted surface just before it enters the coating booth, while chlorides are measured by adding silver nitrate solution in the water solution obtained by wetting a small blasted area. White precipitates of silver chlorides confirm the presence of chlorides. There are several commercial methods such as the test kit from Chlor-rid. [4].

2.5 Sponge jetting

Sponge jet is a low-dust abrasive blasting technique for surface preparation. It suppresses up to 99.9% of what would normally become airborne dust [5]. Sponge Media abrasives are manufactured with a tough, porous urethane sponge material, which controls or suppresses dust. Sponge Media particles flatten as they strike the surface, then expose the abrasive where they cut into the coating and substrate profiling. As the Sponge Media abrasives rebound, the porous urethane creates suction, entrapping dust. Compressed air is used to propel particles against the surface to be cleaned. After use, the sponge and debris are collected and loaded into a vibrating screen, and the reusable portion of the sponge is returned for additional blast cleaning.

The specialized equipment required for sponge jetting includes an air compressor, blast hoses and special blast nozzle, specialized blast pot, abrasive collection equipment (e.g., vacuums), and vibrating screen abrasive reclaiming equipment. Screens or tarps to isolate the work area along the ground are typically sufficient to capture the abrasive and debris for return to the separation system [1].

There are several advantages of sponge blasting, with a few limitations of slightly higher cost and low efficiency. The advantages of dust-free operation, with low paint debris with more chances of using recycled sponge abrasive, and surface cleanliness of the same or better quality than for abrasive blasting, overcome the limitations. Low waste generation compared to abrasive blast cleaning, with increased worker and public safety by minimizing adverse effects to the environment, are additional advantages.

2.6 Hydrojetting (water blasting)

Hydroblasting is a technique for cleaning surfaces that relies entirely on the energy of water striking a surface to achieve its cleaning effect. Abrasives are not used in hydroblasting systems. Consequently the problems caused by dust pollution and by the disposal of spent abrasives are eliminated.

It may be mentioned here that not all water-blasting techniques qualify as hydroblasting. As a matter of fact, depending upon the pressure of the water, the blasting method can be classified as water cleaning or hydroblasting. Water pressure up to 5000 psi usually does not remove any scale but helps in removing dust, soluble matter and other suspended impurities. Raising the water pressure to 10 000 psi just helps to remove loose contaminants, but adherent corrosion layers are not removed. However, such a pressure can cut steel plates.

Hydrojetting is usually described from a pressure of 10 000 psi to 25 000 psi. A pressure of 25 000 psi can be used to remove scales of grade A and B, but is not effective on scales of grade C and D. These days pressures of 25 000 psi to 45 000 psi are used to clean the thick corroded layers formed on the surface. The latter is called Ultra High Pressure hydrojetting. It can give efficient cleaning with water consumption of 8 l/min.

One precaution is required while using hydrojetting as one is handling water at very high pressure, thus the distance of the object must not be very far. It is expected that in order to get good efficiency from the hydrojet, the nozzle must be about 50 mm from the substrate.

The main advantages of hydrojetting are:

- It is a quicker process, several times faster than abrasive blast cleaning.
- For thick scales, only blasting needs to be carried out, without having to perform different steps of first removing the scales by power tools as is done in abrasive blasting, followed by the abrasive blasting itself.
- Because water is a solvent, many salts, dust and other impurities are removed in a single step, thus avoiding any pre-cleaning as is required in abrasive blast cleaning.
- No requirement for costly abrasives, nor any need of collection after the blasting process.
- Simple process of a high-pressure pump and a water tank connected to special nozzles which give a very high-pressure jet.

There are, however, several disadvantages of this process. A few important ones are as follows:

- A large amount of good quality water is required and hence the method is most suitable where water is available in plenty. Use on offshore structures and in remote areas is limited.
- Water blasting does not give an anchor profile as in abrasive blasting, hence paint adherence is a problem unless the profile is created by blasting with abrasives. There is an alternative of using abrasive water blasting or slurry blasting, discussed in the next section.
- Another disadvantage of water blasting is the flash rusting. This is a serious problem which has been solved in recent years by one of the following methods:
  - by flash blasting the surface after it is dried, or

  - by using inhibitors in water which can prevent rusting during hydrojetting.

  Both the above methods are actually difficult to adopt on site. Thus the alternative is to use special paint systems which are made especially for hydroblasted surfaces. Flash rusting poses one additional step, while addition of inhibitor in water is very costly and appears to be less effective, due to the large volume of water that is used in every cycle, with more make-up water.

- Another very serious problem is safety, as handling jets at 25 000 to 45 000 psi can be quite dangerous and can cause serious injuries. Hence specially trained staff are required to carry out water blasting. Of late, hydrojetting has become much safer as the water nozzles are part of a plate facing the substrate which slides over the surface by a trolley-type movement. Of course for uneven surfaces and small areas, jet nozzles are still in use.

A typical pump which creates a blast of 40 000 psi is more useful for cleaning very big structures very fast.

The safer way of hydroblasting is by the use of jet streams, where nozzles fitted on the base plate move smoothly on the floor or on the roof, with no danger from the high-pressure stream to the person handling the nozzle. Hydroblasting is also very fast.

2.6.1 Water abrasive blasting

Water abrasive blast cleaning uses high pressure water and abrasive to provide a cleaned and roughened surface. Basically, a small amount of abrasive is fed into the water stream. The equipment, methods and technique are similar to those for wet blast cleaning, except that an abrasive supply is provided for injection into the water stream. The advantages of wet abrasive blast cleaning include the control of dust emissions and aid in the removal of chemical contamination by the introduction of water. The advantages of water abrasive blast cleaning include providing a surface profile when compared to the water blast-cleaning method without abrasive. The limitations of wet abrasive blast cleaning include the accumulation of considerable amounts of abrasive on the surface because of a lesser amount of water in and around the abrasive stream, which requires an extra step of cleaning (washing) to remove the spent abrasive.

2.6.2 Slurry blasting

A slight modification of water abrasive blasting is where water and sand are mixed together in a pot and blasting is carried out with this wet slurry. Such blasting is quite efficient and provides the anchor profile also.

2.6.3 Hydroblasting standards

The steel surfaces produced by hydroblasting do not look the same as those produced by dry abrasive blasting or slurry blasting. This is because water on its own cannot cut, or deform steel like abrasives. Hydroblasted surfaces therefore tend to look dull, even before they 'flash rust'. In addition Grade D steel, with active corrosion pitting, shows a mottled appearance after hydroblasting. Mottling occurs when the corrosion products are washed out of the pits, leaving a bright patch, and the surrounding areas are left a dull grey, brown to black color. 'Flash rusting', i.e. light oxidation of the steel, which occurs as hydroblasted steel dries off, will quickly change this initial appearance. This standard gives advice on the recommended standard of hydroblasting and the acceptable level of flash rusting allowed prior to the application of coatings.

The standard consists of a series of color photographs, which depict the condition of unpainted steel surfaces prior to and immediately after surface preparation by hydroblasting. It then shows these surfaces with varying degrees of flash rusting.

Initial rust grades [6]

The various rust standards are described in ISO 8501-1:1988 as grades A, B, C and D. For hydroblasting two initial rust grades C and D are described in the surface preparation standard and the SSPC VIS-1-89 surface preparation standard of the Steel Structures Painting Council. The definitions are:

- Rust Grade C Steel surface completely covered with rust but with little, or slight pitting under normal vision
- Rust Grade D Steel surface completely covered with rust, on which general pitting is visible under normal vision.

Hydroblast standards [7]

The standard illustrates grade C and D surfaces prepared by hydroblasting to two different degrees of cleanliness. They are designated HB2 and HB2$\frac{1}{2}$ and are comparable to Sa2 and Sa2$\frac{1}{2}$ described in the ISO 8501-1:1988 surface preparation standard and to SSPC-SP6 and SSPC-SP10 of the Steel Structures Painting Council surface preparation standards. The definitions are given in Table 2.4.

2.7 Summary

Fundamentals of surface preparations are described. Different methods of pre-cleaning of surfaces, cleaning by hand tools, power tools and blast clean-

Table 2.4 Hydroblasting standards and degree of flash rusting

Hydroblasting standard	Surface appearance	Degree of flash rusting		
		Light	Medium	Heavy
HB2 Thorough Hydroblast Cleaning	The surface shall be free from visible oil, grease, dirt and from most of the rust, paint coatings and foreign matter.	Light tan-brown rust will partially discolour the original metallic surface.	Light tan-brown rust may be evenly distributed or patchy in appearance, but it will be heavy enough to mark objects brushed against it.	Heavy layer of dark tan-brown rust will completely obscure the original metallic surface.
HB2$\frac{1}{2}$ Very Thorough Hydroblast Cleaning	The surface shall be free from visible oil, grease, dirt, loose rust, paint coatings and foreign matter except for staining.			

ing are described in detail. Kinds of abrasives, measurement of surface cleanliness and of anchor profiles and impurities on blasted surfaces are also discussed briefly. Three important standards for surface preparation, namely NACE, SSPC and ISO, are described in detail. Hydroblasting, its applications, advantages and limitations, are also covered.

2.8 References

1. US document 1100-2-3400, Chapter 7, 30 April 1995.
2. *Steelwork Corrosion Control* by A. Derek Bayliss and D.H. Deacon, Reinhold Pub. Corp., 1967, p. 48.
3. *Metals Handbook*, ASM, 1990, p. 300.
4. www.chlor-rid.com
5. www.spongejet.com
6. Rust Grades, ISO 8501-1, 2007, *The Rust Grade Book*, LD3020, www.tqc.eu/en/products/article/68/150-850/
7. Hydroblasting Standards, downloaded from Akzonobel website, www.international-pc.com/pc/technical/tech_papers/hydroblast.asp

3

Techniques for applying organic paint coatings

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3.1 Introduction

As discussed earlier, coating is both an art and a science. While one needs to know the chemistry to understand various formulations, application of coating is an art. What this means simply is to achieve a good, smooth and protective coating. The skill of the applicator is the most important requirement to achieve this. Whether the coating is to be carried out by brush, roller or any sophisticated spray gun, conservation of paint and finish of coating depend upon how skilled the applicator is.

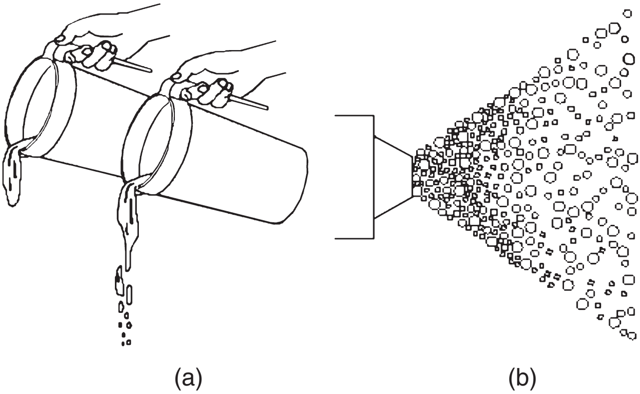
3.2 Application by brush and roller

Paint coatings can be applied by brush, roller, trawling, air spray gun or airless spray gun. Application by brush or roller is the simplest. Neither costly equipment nor a very skilled person is required. However, choice of a good quality brush or roller of the correct size, and methods to conserve paint, are some of the important requirements. Brush application is slow; quality of surface achieved depends upon the fatigue of the applicator. Because of this, there can be a problem in getting a uniform thickness and finish throughout the surface. Using a roller, the speed of application is usually increased by 4–5 times. Further, not all paints can be applied equally by brush or roller. Relatively low viscosity paints can be applied by either, but high viscosity paints give brush marks.

Before we start discussing spray application, it is important to understand paint atomization. Atomization is:

- Breaking up fluid into small particles (droplets)
- Collection of moving particles on the surface, known as spray
- Spray pattern can be created by variety of means.

As shown in Fig. 3.1(a) and (b), droplets of liquid paint are produced by interaction of liquid paint with a stream of air or with compressed air.



3.1 (a) Atomization of liquid drops by a stream of air; (b) atomization of paint by compressed air.

Atomization is directly related to the viscosity of the paint. A high viscosity paint will produce more atomization than a low viscosity paint as shown in Fig. 3.2.

There is a very good balance between the quantity of the paint (*Q*), its viscosity (*V*) and the total energy (*E*) required for atomization. This energy is provided by the pressure of the compressed gas. This is shown in Fig. 3.3.

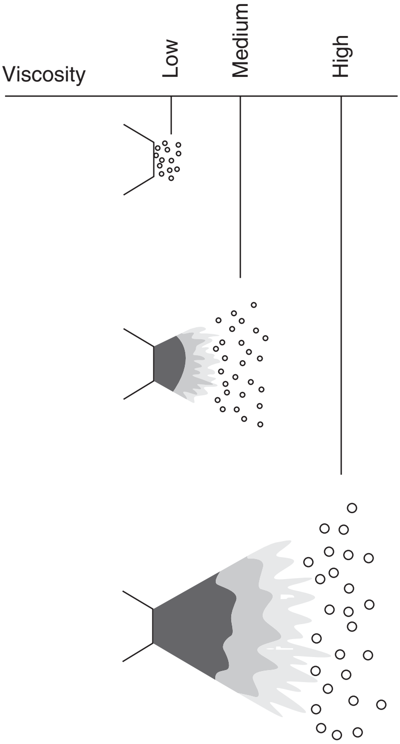
3.3 Spray application

There are basically two main types of spray processes: air spray and airless spray. In the former, compressed air is used to atomize the liquid paint, while the latter uses hydraulic pressure to atomize the paint. In air spray, compressed gas with a pressure of 20–100 psi is used, while in airless spray a pressure of 2000 psi or above is usually required. There are several other kinds of spray processes resulting from modification of these two basic processes:

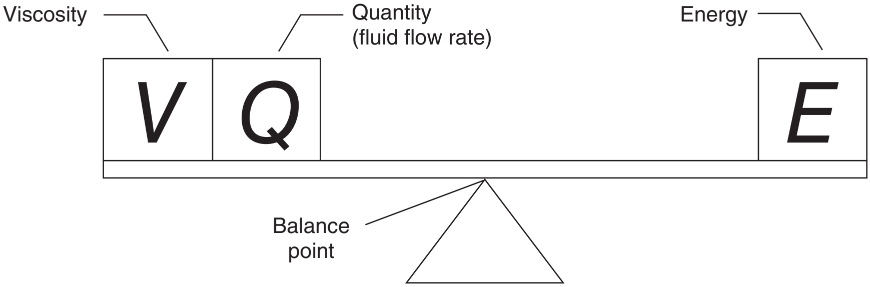
1. Air spray
2. High volume low pressure (HVLP) spray
3. Airless spray
4. Air-assisted airless spray
5. Electrostatic spray.

3.3.1 Air spray

Air spraying relies on compressed air for paint atomization. Compressed air from a compressor, connected to the nozzle, breaks the liquid paint into

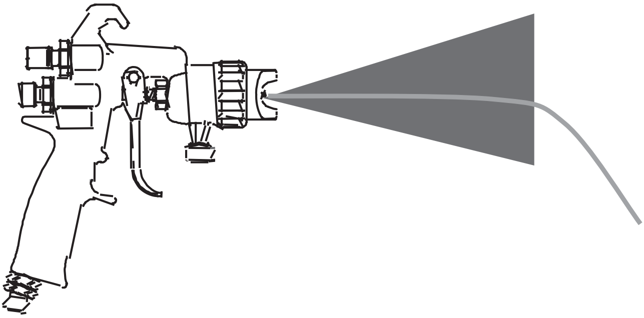


3.2 Effect of viscosity on the extent of atomization [1].



3.3 Balance between viscosity of paint, quantity of fluid and energy required for atomization [1].

tiny droplets that reach the surface and adhere to it. The main component of an air spray is the spray gun, which is not very expensive. It consists of a port from where compressed gas is introduced. It is connected to a compressor using a good quality hose long enough to reach the object easily. The second port in the gun is connected to a pot filled with liquid paint.



3.4 Schematic of an air spray gun (air pressure 20–60 psi) [1].

Table 3.1 Advantages and limitations of air spray

Advantages	Limitations
Fine quality of coating	Easy to over-atomize and cause excessive overspray
Flexible – operator control of all aspects of atomization including pressure, fan width, and fluid delivery	Not recommended for protective coating
Inexpensive equipment	Poor transfer efficiency
Low pressure safety	Cannot handle high solid paints

Compressed air at a pressure of about 40–60 psi forces liquid paint to break into liquid droplets which have enough pressure to reach the substrate surface. The transfer efficiency of this spray process is rather low and is estimated to be 25–30%. The reason for this is the strong rebound of the paint droplets from the surface. Many conventional spray guns require 4 l/s of paint flow to operate with a medium viscosity coating such as latex paints, some lacquers, sealers, alkyds and conventional epoxies. It is advisable to use a separator between the air compressor and the pressure pot, to prevent moisture and oil from reaching the coating. A schematic of an air spray gun is shown in Fig. 3.4. A proper gun is held about 18–22 cm from the surface of the object. By varying the volume of air and coating fluid at the spray gun, the amount of atomized coating can be regulated. The selection of fluid nozzle and needle size is another way to regulate the amount of coating exiting the fluid nozzle. Some of the properties of coating achieved by air spray gun are listed in Table 3.1.

For the application of certain coatings such as zinc-rich coatings, it is advisable that the pot should be equipped with a mechanical agitator to keep the zinc-rich coating in suspension so that the zinc does not settle on the bottom of the pot. If application stops and resumes after 15 minutes when spraying zinc-rich coatings, the entire length of the hose should be whipped to re-disperse the coating in the line.

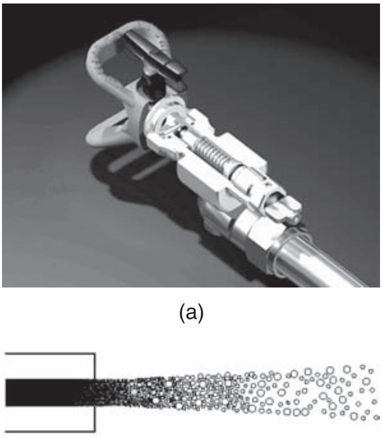
3.3.2 High volume low pressure spraying

One of the limitations of conventional air spray is its poor transfer efficiency. This happens because of severe bouncing of the atomized particles from the substrate surface after impact. If, however, the speed of the atomized particles is reduced, the bouncing can be reduced considerably, which will improve the efficiency of the coating. This is done with slight modification in the spray gun. The modified spray gun is called a High Volume Low Pressure (HVLP) spray gun. Simply by reducing the pressure of the compressed gas and using the same volume of liquid paint, the speed of the atomized particles is reduced, which in turn reduces the bounce back, thereby enhancing the transfer efficiency from 25–30% in conventional air spraying to about 40–50%. The high transfer efficiency attained reduces material costs and waste, and an HVLP spray is easy to set up and simple to operate.

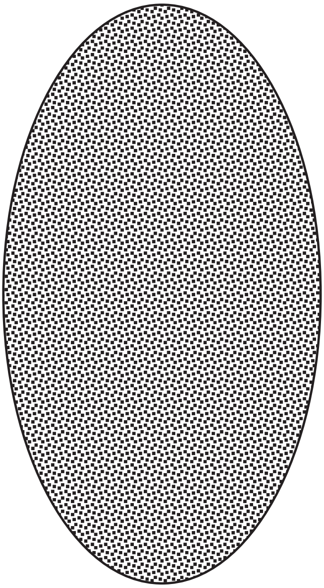
3.3.3 Airless spray

As the name suggests, an airless spray gun does not use compressed air. It uses a power source (an electric motor) to generate very high pressure of the order of 2000 psi. Further, with the help of a high pressure fluid pump, a high pressure fluid hose, and an airless spray gun with spray tip, a high concentration of atomized paint droplets can be created. The airless spray process is used for high performance protective coatings such as solventless systems which have high viscosity and require large pressure for atomization. Further, because of the very high pressure, the particles hit the surface with great force, thereby resulting in a coating of high bond strength. It may be noted that airless spray guns give a high protective property but a less smooth surface than is obtained using an air spray gun. Figure 3.5(a) shows a typical airless gun, and (b) shows the dense atomization obtained as a result of airless spray. Figure 3.6 shows the fan that is formed during spray on the coating surface.

The protective property and the DFT achieved on a substrate surface depend on the fluid pump which is the most important part of the hydraulic airless system. It multiplies the air input pressure to deliver material at pressures up to 4500 psi. A very common airless pump can give an output to input pressure ratio of 30 : 1, which corresponds to an output pressure

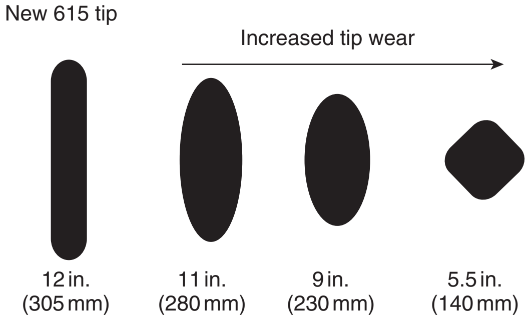


3.5 (a) A typical airless gun; (b) the dense airless atomization at 2000 psi.



3.6 A typical fan showing the atomization using 2000 psi pressure during an airless spray.

of 3000 psi for an input pressure of 100 psi. Other fluid pumps with output to input pressure ratios of 45 : 1, 63 : 1 and 80 : 1 are also available commercially. Such high pressure fluid pumps can give a coating thickness of more than 500 to 1000 μm in a single coat.



3.7 The continuous damage of the tip due to wear with use [1].

One of the most important parts of an airless spray is the choice of a tip. A large variety of airless spray tips are available. Its selection is based upon the type of material to be sprayed and the desired spray pattern. The tip orifice opening and the fan angle control the pattern size and fluid flow. There are no controls on the spray gun itself. Tip orifices vary in size to accommodate the viscosity of the coating being applied. Fan angles range from 10° (~100 mm spray width) to 95° (~430 mm spray width). For example, two tips with an identical orifice size of 0.381 mm but different spray angles (10° and 40°) will provide fan widths of 100 and 216 mm, respectively, and will have identical flow rates of 0.0145 l/s at 2000 psi [2].

Further, the quantity of the sprayed coating is determined by the orifice size of the spray tip. A larger orifice results in more fluid being delivered at a faster speed; however, this leads to poorer atomization. Dual or adjustable tips can be used with airless spray equipment. The tip size increases as the fan width increases. One of the most severe problems with a continuously working tip is its damage due to wear. This results in decreasing the fan width, resulting in more material at one place, which causes sagging. Figure 3.7 shows how the tip gets damaged due to wear. It is advisable to change the tip when its width starts decreasing. Other advice is to use tips coated with wear-resistant coatings, such as tungsten carbide tips which do not wear very fast and have a much longer life than conventional tips.

Safety is one of the main considerations. Care should be taken not to remove the spray gun from the hose, or the tip from the gun, until the pressure from the pump and in the line has been released. All high pressure airless systems should be sprayed and flushed in a well-ventilated area. These systems also should be grounded to avoid dangerous static sparking, explosion or fire when spraying or flushing the lines. Table 3.2 lists the advantages and limitations of the airless spray process.

Table 3.2 Advantages and limitations of airless spray

Advantages	Limitations
Provides higher film build-up capabilities, greater surface penetration and rapid coverage	Complexity in changing fan width makes this technique difficult for coating large structures with varying profiles
High viscosity products can be coated without solvents	Not a good surface finish expected
High bond strength of the coating	Not economical for small structures or small jobs
Good when large areas have to be coated	Not good for conventional solvent-borne paint systems
Higher transfer efficiency, 50–55%, compared to air spray	

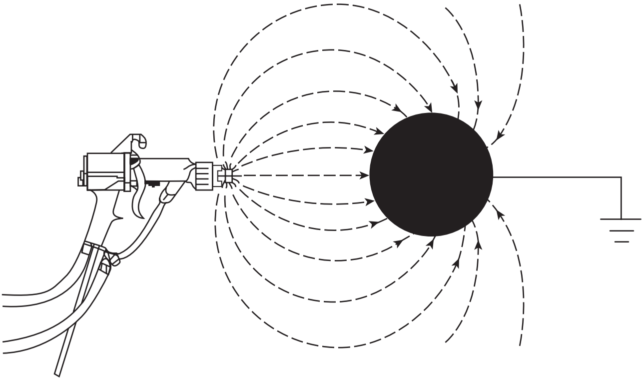
3.3.4 Air-assisted airless spray

In order to further increase the efficiency of the airless spray by 5–10%, and to improve the surface finish, air-assisted guns are used. The improvement in efficiency occurs because the gun operates at lower pressure and thus particles move less rapidly, which results in a better surface finish. These are basically airless guns with lower pressure, 800 psi plus fluid pressure. The process of atomization involves both the pressure created by the power source and that created by the compressed air. The compressed air pressure is about 20 psi. Such a spray gun has several advantages: fine atomization, reduced flow rate, higher transfer efficiency and low wearing of parts. It is used preferably for coating structural steel, tubing, engineering equipment, aircraft and ground support [1].

3.3.5 Electrostatic spray

In order to enhance the transfer efficiency of the paint, an innovative method is to charge the paint particles just before they are out of the nozzle and to ground the substrate. Because of the attraction of the charged atomized paint droplets to the substrate, the loss of paint or its rebound is minimal. This is illustrated in Fig. 3.8.

An electrostatic spray system can be of a simple airless atomization design or of an air-assisted one. The only difference is that for the charging of atomized droplets, additional high voltage is required. The charged particles come out from the nozzle and hit the substrate, which is positively biased. Thus the atomized particles are attracted to the object and rebound is minimal. This results in an increase in efficiency to about 75%. The advantages of using electrostatic spray include:



3.8 Schematic of an electrostatic gun [1].

- It reduces coating material loss.
- It reduces clean-up and maintenance time, increases production rates, and reduces the number of application steps caused by wrap-around.
- It results in improved atomization.

One of the most important applications of the electrostatic spray gun is in powder coating. For small components, the substrates are sprayed first with the powder and then passed into a hot chamber. The coating immediately melts and then fuses. In the case of bigger components such as pipelines, beams, etc., the component is first heated and then passed to the coating booth, where the powder is sprayed on the hot substrate, melting and fusing immediately. Such a coating has high adherence and flexibility and low holidays (very small regions on the coated surface where the paint failed to adhere).

3.4 Transfer efficiency

The transfer efficiency compares the amount of paint deposited on the substrate with the amount sprayed from the gun, as shown in Fig. 3.9. It is given as

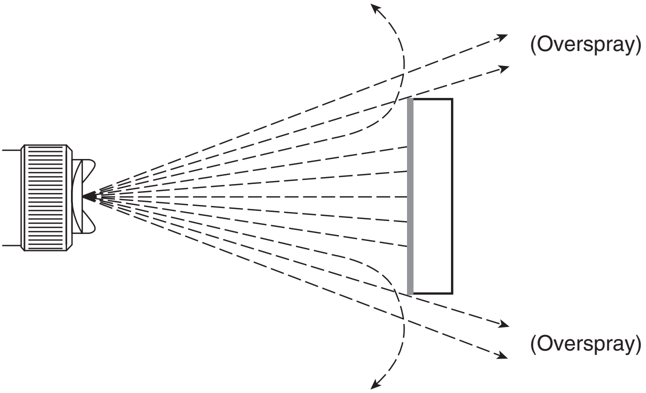
$$\text{Transfer efficiency (TE)} = \frac{\text{paint deposited on the part}}{\text{total paint sprayed}}$$

$$= \frac{W_p}{W_s} \times 100\%$$

where

W_p = weight of wet coating on the part

W_s = weight of liquid coating sprayed



3.9 Amount of paint deposited on the substrate compared with that sprayed from the gun [1].

Table 3.3 Comparison of the transfer efficiencies of various paint application methods

Application method	Air spray	HVLP	Airless spray	Air-assisted spray	Electrostatic spray
Transfer efficiency (%)	30	45	50–55	60	75

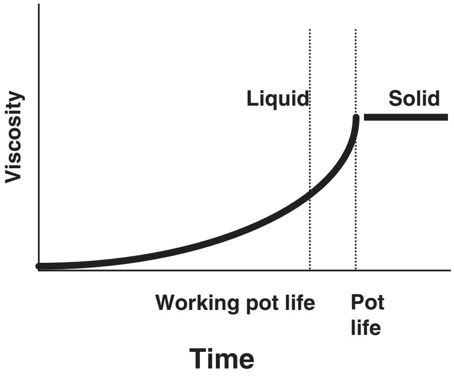
Table 3.3 compares the transfer efficiencies of various paint application methods.

3.5 Mixing components

It has been already explained in Chapter 1 that many high performance and protective coatings have two components: the resin and the hardener. Just before application, the components are mixed in the specified proportions and then application is started. There are two very important aspects of this mixing:

- Pot life
- Method of mixing.

Pot life is the time (beginning from the mixing of two components) at which the mixture of the two components turns into a solid. This happens because of a chemical reaction between resin and hardener, leading to an increase in viscosity due to the crosslinking of polymer chains. However, the application of paint cannot be possible till the end of the potlife, as it



3.10 The difference between pot life and working pot life [1].

will become solid in the hose and in the gun. Therefore a different term called the working pot life was introduced, which defines the time up to which the coating can be applied, either by brush or by a spray method. The two terms are well illustrated in Fig. 3.10. One important aspect of two-component paints must be explained here. In the case of solventless systems, it is advisable to start the coating application immediately after severe mechanical mixing. However, if the paint system is solvent based, it is advisable to wait some time after mixing the two components so that the two components come in closer contact with each other.

3.5.1 Type of mixing techniques

There are several ways in which two components are mixed:

- Hand mixing
- Batch mixing
- Mechanical mixing
- Electronic mixing.

Manual mixing

Manual or hand mixing is simple and does not require sophisticated equipment. It can be used where

- some materials ratios are not very critical
- production volumes/rates are low.

However, there are issues that must be addressed:

- Operator-related measuring and mixing quality issues

- Disposal of cans
- Large quantities of clean-up solvent
- Labor intensive.

Batch mixing

Batch mixing is a modification of hand mixing in which instead of physically adding new lots they are added by some replacement mechanism, so this requires more pressure pots. Such a system can be part of an airless spray package.

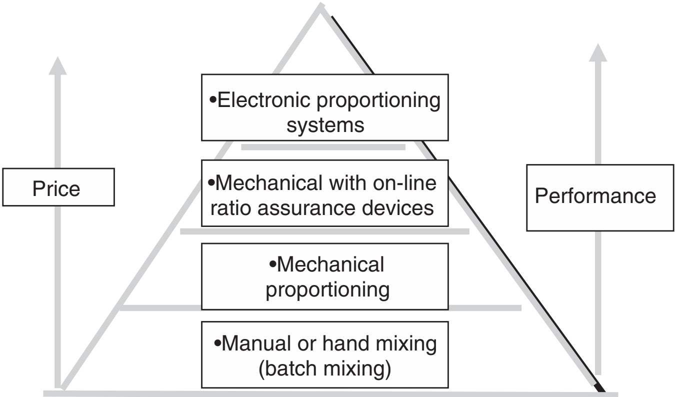
Mechanical mixing

Mechanical proportioners are next in line in terms of accuracy of mixing, as well as being less labor intensive. Mechanical mixing can work on some mechanical principle in which a fixed or variable ratio of two components is added after the running lot is exhausted. It is more accurate and faster and gives better results.

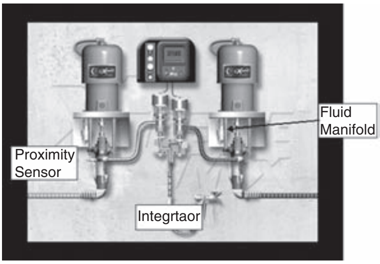
Electronic mixing

There are fully microprocessed systems that operate once all the parameters are well set up on a computer; they are fully automatic, highly productive, fast and accurate. The quality of coating obtained is uniform and is excellent.

The performance and cost involved in all three systems above are compared in Fig. 3.11. It is clear that the performance of more sophisticated, electronically controlled systems is excellent but one has to pay more.



3.11 Comparison of various mixing processes on the basis of performance and cost[1].



3.12 A two-component airless spray machine, where two components travel separately through Fluid manifold, enter Integrator, are mixed and sprayed immediately [1].

With the availability of several fast-curing coating systems, such as elastomeric polyurethane, polyester and very recently polyurea, which have curing times of the order of a few minutes down to 10 seconds, the latest machines are the most sophisticated. Figure 3.12 shows an example of an airless spray system in which two components reach independently through two different hoses and pumps at a speed proportionate to their mixing ratios. They keep on traveling independently till they reach an integrator, where they are mixed and immediately sprayed from the nozzle to the substrate. Polyurea has a curing time of 3–10 seconds. In normal spray pumps, the coating on mixing would become solid in the hoses and would damage the gun. Such a system is very useful for such applications.

3.6 Summary

A systematic approach to paint application techniques is presented with the principles of different techniques, methods of application, advantages and limitations along with some important applications in industry. The author acknowledges the help of Graco Incorporated for allowing the use of their diagrams used in training manuals, and the US foundation's detailed document EM 1110-2-3400 partially.

3.7 References

1. *Atomization, air spray and airless spray, concept and theory training*, Graco Inc., 1995.
2. *Coating applications*, US foundation document EM 1110-2-3400, 30 April 1995, Chapter 8.

4

Characterization, evaluation and testing of organic paint coatings

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4.1 Introduction

One of the important aspects of paint coating, after its formulation, is to know whether it has achieved the set composition and is able to meet its functional requirements. Also, it is important to know how the paint will perform in a particular environment. Thus it is necessary to test a few specific properties and also its performance to pre-qualify it for a specific job. Pre-qualification tests are also important for many industrial applications, before a large-scale coating work is planned. Thus paint characterization and its systematic evaluation is one of the most important aspects of paint coating. This is also important for the inspection and quality assurance of paint coatings.

Characterization of paint coatings can be divided into the following four categories.

1. Characterization of paint composition and physical properties such as:
    - % Volume solid – which in turn helps to calculate coating coverage
    - Non-volatile matter
    - Density
    - Viscosity
    - Volatile organic content (VOC)
    - Pigment volume concentration (PVC)
    - Wettability.
2. Measurement of paint properties during application such as:
    - Wet film thickness (WFT) and dry film thickness (DFT)
    - Drying time
    - Permeability
    - Water absorption
    - Mechanical properties of paint film and of coated substrate.
3. Performance testing and coating evaluation:
    - Salt spray

  - Humidity
  - Outdoor exposure
  - Immersion tests.
4. Paint durability and weathering tests:
  - Accelerated UV
  - Color, gloss and chalking resistance.

Durability of a paint system greatly depends upon various conditions including quality of paint systems, exposed conditions and other factors. Test methods for developing and monitoring the performance of paints are designed to simulate the conditions of usage. They are usually designed to accelerate the degradation process to which paints are subjected. Another facet of durability is the tendency to withstand abuse in various forms under conditions of use, and in this case the requirements of different markets dictate different methods of testing.

In order to evaluate the painted surfaces for properties such as weathering resistance, light resistance, corrosion resistance and adhesive strength, impact resistance and hardness by instrumental measurement or by visual inspection, suitable well-documented standards are used that specify the detailed procedure of evaluation. The most common standards for characterizing and evaluating paint coatings are those of the following organizations:

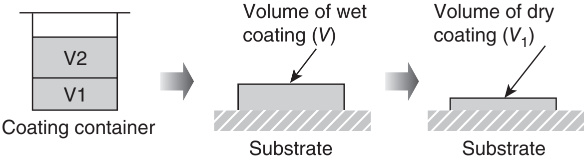
- American Society for Testing and Materials (ASTM)
- British Standards Institution (BSI)
- International Standards Organization (ISO)
- Steel Structure Painting Council (SSPC)
- National Association of Corrosion Engineers (NACE)
- Bureau of Indian Standards (BIS)
- German Standard (DIN).

The approach to characterize a particular coating depends upon its application requirements. Characterization and evaluation of paint coatings can further be divided into two parts:

- Tests carried out on coatings before they are applied to a substrate
- Tests carried out on coatings after they are applied to a substrate.

4.2 Tests carried out prior to application

In sections 4.2–4.10, tests that are performed on paint systems, such as volume solid, viscosity, VOC content, etc., are discussed in detail.



V_1 = Volume of 'non-volatile' components in coating

V_2 = Volume of 'volatile' components in coating

$V = V_1 + V_2$ = Volume of coating in container

$$\% \text{ volume solids} = \frac{V_1}{V} \times 100$$

4.1 Illustration of % volume solid.

4.2.1 Volume solid

Volume solid is the most important characteristic of a paint coating. The volume solid of a coating is simply defined as the amount of coating that will not evaporate, for example, resin (vehicle), pigment and other additives. The volume solid of a coating is best described diagrammatically as shown in Fig. 4.1.

$$\% \text{ Volume solid} = \frac{V_1}{V} \times 100$$

where V_1 = volume of 'non-volatile' components in coating
V_2 = volume of 'volatile' components in coating
$V = V_1 + V_2$

The % volume solid of a paint is important for the following reasons.

1. It is the measure of spreading capacity of a paint system.
2. It decides the dry film thickness (DFT) of a paint coating. A higher volume solid of a coating will give a higher DFT per coat. Based upon this, three different categories of paint systems are described:
    - Conventional solvent-borne coatings with % volume solid of 40–60%, usually giving a DFT of 50–70 μm.
    - High build (HB) coatings with % volume solid above 80%, usually giving a DFT of 80–100 μm.
    - Solventless coatings with % volume solid 99–100%. These are usually applied by airless spray gun to a DFT of 100–1000 μm, depending upon the gun parameters.
3. It can be used to calculate paint coverage. How much paint is required for a given surface area can be calculated from the % volume solid and

the DFT required. This is given by a term called the theoretical coverage rate, given by:

$$\text{Theoretical coverage rate} = \%\ \text{volume solid} \times 10/\text{DFT}$$

However, the theoretical coverage rate is not the correct value to calculate total coverage. Another term, called the practical coverage rate, is used which takes care of several losses that usually occur during application of paint. These include distribution loss, loss due to anchor profile, etc. Before going on to calculate the practical coverage, let us first study the calculation of % volume solid. It is calculated according to ASTM D 2697 [1]. For this, one first has to calculate its NVM and density.

4.3 Identifying non-volatile matter (NVM)

NVM is defined as the relative weight of total non-volatile matter in a paint – which could be resin, pigment and additives. This is calculated by a simple gravimetric method as follows:

1. Weigh approximately 2 g of paint sample in a lid and spread it across.
2. Place it in an oven at 105°C for 3 h or 120°C for 1 h.
3. Calculate the weight retained as a percentage.

4.4 Density

Density is the mass per unit volume. However, in paint coatings, it is measured as weight per liter (WPL). For this, a standard calibrated cylinder of volume 100 ml is used and is filled with paint. The difference in weight converted to 1 liter is the WPL. This is determined as follows.

4.4.1 Density cup method

For measurement of density of paint coatings, density cups can be used. Density cups are generally cylindrical in shape, which provides a large opening for easy filling, emptying and cleaning. The tightly fitted stainless steel covers have an upward slope to a small hole in the center to allow excess sample materials to be expelled without entrapping air bubbles, which in turn increases efficiency.

Measurement of density using density cups follows this sequence:

1. Weigh the thoroughly cleaned density cup and record the weight.
2. Fill the density cup with paint whose density is to be determined.
3. Put the cover on the density cup without any tilting. Care should be taken to avoid any kind of bubble entrapment to get more accurate results.

4. Paint overflowing after putting the cover on the cup should be carefully removed with absorbent cloth.
5. Weigh the filled density cup again.

After obtaining the weights of the empty and filled density cup, the WPL can be calculated using the following equation:

$$\text{WPL}=\frac{\text{weight of filled density cup(g)} - \text{weight of empty cup(g)}}{\text{volume of density cup (ml)}}\times 1000$$

Usually, the density cups are of volume 100 ml.

The significance of density (WPL) is as follows:

- If density is not within the specification, then there is a good chance that there can be some error in charging of the batch.
- It can act as a check on the solid content of the paint.

Now to calculate the % volume solid, we need to calculate the weight of paint in the wet condition. For this, the Archimedes Principle is used to calculate the applied paint in dry and wet conditions. For simplicity, water is used as the solvent, whose density is 1 g/l. The calculation is as follows:

- W_1 = weight of disc in air(g); W_2 = weight of disc in water (g)
- D = density of water (1 g/l)
- Volume of disc, $G = (W_1 - W_2)/\mathrm{D}$
- W_3 = weight of coated disc in air (g)
- W_4 = weight of coated disc in water (g)
- Volume of coated disc, $H = (W_3 - W_4)/D$
- Volume of dried coating = $F = H - G$
- Volume of wet coating, $V = (W_3 - W_1)/(\%\ \text{NVM} \times \text{WPL})$

The % volume solid is then calculated as below:

$$\%\ \text{Volume solid} = \frac{\text{volume of dried coating}}{\text{volume of wet coating}}\times 100$$

4.5 Practical coverage calculations

International Paint [2] devised a method to calculate the practical coverage. For this, a paint system with a % volume solid of 80% is chosen as an example. To apply one coat of DFT of 100 μm, theoretical coverage would be 80 × 10/100 = 8 m^2/l. This means that, to apply one coat of DFT of 100 μm, with a paint of % volume solid of 80%, will require 1 liter of paint to cover 8 m^2. However, in practice one finds that the paint required is much more than this value. This is mainly because of the following reasons:

There are several kinds of losses that occur during paint application. These can be classified as apparent and actual losses.

Table 4.1 Extra paint required as the surface roughness increases, as suggested by International Paint [2]

Surface	Blast profile	DFT loss*
Unblasted surface	0	0
Blasted with abrasives	0–50 μm	10 μm
Blasted with abrasives	50–100 μm	35 μm
Blasted with abrasives	100–150 μm	60 μm
Blasted with abrasives	150–300 μm	125 μm

*DFT loss is the additonal DFT required to compensate for the blast profile.

Table 4.2 Distribution losses for various paint application methods [2]

Application method	Type of structure	Estimated loss due to distribution
Brush and roller	Simple structure	5%
Brush and roller	Complex structure	10–15%
Spray	Simple structure	20%
Spray	Complex structure	40%

4.5.1 Apparent losses

Effect of blast profile during surface preparation

The quantity of paint used on a smooth surface is much less than the quantity of paint used on a blasted (rough) surface. Depending upon the blast profile, additional paint will be required. Table 4.1 lists the extra paint required for different anchor profiles of the substrate surface.

Paint distribution losses

A good quantity of paint is lost when applied by different application methods as given in Table 4.2. As can be seen, when applied by simple techniques such as brush and roller, the paint loss is much less compared to when it is applied by a spray process. Further, the loss is greater when the object is a simple structure, such as a flat surface, compared to when it is an object of complex shape such as round, curved, etc.

4.5.2 Actual losses

The other losses are due to paint application, paint wastage from spillage, paint handling such as retention in container, on brush or roller, or that remaining in the spray line, etc. Losses also occur due to premature gelling during application (e.g. due to improper mixing ratio, high temperature, etc.).

Further, there are fewer losses when the paint is one-component compared to when it consists of two components. In a two-component system, the loss due to crossing of pot life is often more. Estimated losses for one component are 5% maximum, while in the case of two components, the losses can be as high as 10%.

The difference between the theoretical and practical coverage can be illustrated using an example. Let us consider a two-component paint system with % volume solid of 80% and apply two coats of 100 µm each on a complex structure, with a surface finish of Sa$2\frac{1}{2}$ with an anchor profile of 50 µm. The theoretical coverage is 80 × 10/200 = 4 m^2/l. The practical coverage will be calculated as follows:

First coat

Required DFT	100 µm
Loss due to blast profile	10 µm
Loss due to distribution @ 40% (100 × 0.4)	40 µm
	150 µm
Loss due to application @ 5% (150 × 0.05)	7.5 µm
Loss due to wastage @ 10% (150 × 0.1)	15 µm
	172.5 µm

Extra paint required for the first coat will be 72.5%.

Second coat

Required DFT	100 µm
Loss due to blast profile	Nil
Loss due to distribution @ 40% (100 × 0.4)	40 µm
	140 µm
Loss due to application @ 5% (140 × 0.05)	7 µm
Loss due to wastage @ 10% (140 × 0.1)	14 µm
	161 µm

Extra paint required for the next coat is 61% more.

$$\text{Total loss for two coats} = \frac{72.5+61}{2} = 66.75\%$$

This means that 66.75% extra paint is required with respect to the theoretical quantity, i.e. 1.67 liters of paint is actually required instead of 1 liter. Therefore the practical spreading rate can be defined as:

$$\text{Practical spreading rate} = \frac{\text{theoretical coverage}}{\text{actual paint required}}$$

$$= 4\ \text{m}^2/1.67\ \text{liter} = 2.39\text{m}^2/1$$

$$\text{Overall loss factor} = (4-2.39)\times 100/4 = 40.25\%$$

$$\text{Utilization efficiency} = 60\%$$

Thus as seen above, the volume solid of the paint coating is an essential and most important factor which not only helps to determine the spreading rate of a paint system and DFT, it also helps in estimating the practical coverage of the paint, which is very important for a user when ordering a paint consignment.

4.6 Viscosity

The viscosity of paint is an important property. It is the measure of the flow of a paint system. It also decide whether a paint coating be applied by brush or roller or by an air spray or airless spray. The viscosity can also be estimated from its % volume solid. A paint with high volume solid has higher viscosity than a paint with lower volume solid. Viscosity is modulated by the selection of vehicle, binder, and its molecular weight; by the use of thixotropes or rheological modifiers, and most importantly by the selection of the type and amount of solvents to be employed [3].

Viscosity affects the mixing of the components of the coating during manufacture, its stability during storage, the ease with which it is applied to a substrate, and the manner in which it flows out to form a smooth layer, free of defects like runs and brush marks. Since many defects are related to the flow of paints, viscosity measurements can give a lot of information about the causes of paint failures or difficulties one finds during paint application.

Viscosity can be measured by a variety of instruments and techniques. In the paint industry, a number of measurement methods, from a simple flow cup to a computer-controlled rotation viscometer, have been established for the determination of viscosity. Using different viscometers, we can measure the viscosity of samples at low, intermediate and high shear rates.

4.6.1 Ford cup

This is the simplest method, in which a given quantity of paint is allowed to pass through a fixed size of orifice. Initially, the flow through the orifice is continuous. The point at which there is a break in the continuity of flow is the time in seconds which is used as a measure of the viscosity of the paint. Low viscosity paints are those with viscosity less than 40 s. Brush application can be possible up to a viscosity of 75 s. Paints with viscosity more than 75 s are viscous paints and need to be applied by air spray or airless spray.

4.6.2 Stormer viscometer

The Stormer viscometer is a rotation instrument used to determine the viscosity of paints. This method is intended for paints applied by brush or roller. It consists of a paddle-type rotor that is spun by an internal motor, submerged into a cylinder of viscous substance. The rotor speed can be adjusted by changing the amount of load supplied. The standard defines the consistency of a paint as the weight required to produce a rotation of 200 revolutions per minute. The standard also includes charts which enable the instrument weight and rotational speed data to be converted to Krebs units (a unit of viscosity measure unique to this instrument) [4]. It is also a convenient method for measuring the viscosity of a sample under low shear conditions. Table 4.3 relates viscosity as expressed in different units.

4.6.3 Rotational viscometer

This method uses a Brookfield-type rotational viscometer, which consists of a variable speed, electrically driven shaft onto which can be fitted a number of different spindles. The choice of spindle and rotation speed enables measurements to be carried out in the low to medium shear rate range, i.e. 0.1 to 50 s^{-1}.

The standard is intended for use with non-Newtonian samples and is particularly applicable to thixotropic paints. Methods are described for measuring the viscosity under constant and variable shear conditions.

4.6.4 Cone and plate viscometer

The cone and plate viscometer, as the name implies, consists of an electrically driven shallow cone whose vertex touches a rigid temperature-controlled plate. The test liquid fills the narrow gap between the cone and the plate, and the torque is measured either electronically or mechanically. The choice of cone geometry and speed of rotation enables a sufficient shear rate to be attained and this high shear rate corresponds to that produced during brushing, roller coating and spraying operations.

Table 4.3 Relationship between viscosity in different units (poise, seconds and KU) [4]

Poise	Ford cup (s)	Stormer viscometer (KU)
0.01	Out of range	Out of range
0.10	Out of range	Out of range
0.15	Out of range	Out of range
0.22	13.6	Out of range
0.32	15.3	Out of range
0.50	19.0	Out of range
0.65	22.0	Out of range
0.85	27.0	Out of range
1.00	30.0	Out of range
1.25	96.0	Out of range
1.40	40.0	Out of range
1.65	46.0	Out of range
2.00	50.0	Out of range
2.25	55.0	54
2.50	68.0	56
2.75	74.0	59
3.00	81.0	61
3.20	86.0	62
3.40	91.0	63
3.70	99.0	64
4.00	107.0	65
4.35	116.0	66
4.70	125.0	67
5.00	133.0	68
5.50	146.0	69
6.30	167.0	71
8.85	199.0	78
10.70	270.0	85
12.90	Out of range	95
17.60	Out of range	100
22.70	Out of range	105
27.00	Out of range	114
36.20	Out of range	126
46.30	Out of range	129
63.40	Out of range	Out of range
98.50	Out of range	Out of range
148.00	Out of range	Out of range

4.7 Volatile organic components

Volatile organic component (VOC) means any organic compound having an initial boiling point less than or equal to 250°C, measured at a standard pressure of 101.3 kPa. 'VOC content' means the mass of volatile organic compounds, expressed in g/l, in the formulation of the product in its ready-to-use condition. VOCs are the major concern of environmental protection agencies all over the world. In paint composition, organic solvent is the only volatile component, which in standard paint formulations serves as the carrier for paint pigment. When paint dries, the solvent (VOC) evaporates and causes several health problems due to inhalation, and therefore is the cause of great concern. Exposure to VOCs can trigger asthma attacks, create throat and eye irritation, nausea and headache among other health-related problems. Long-term exposure can lead to cancer and diseases of the kidney and liver. Some of the more common VOCs used in paint as solvents and preservatives include formaldehyde, xylene, toluene and benzene. VOC is measured by subtracting the % non-volatile matter (NVM), calculated above, from 100:

$$\text{VOC} = 100 - \%\text{NVM}$$

The most serious health effects caused by low concentrations of organic compounds in the air do not result directly from the compounds themselves, but from products of reactions that the compounds can undergo. The most notorious ingredients which can cause health hazards are the reaction of VOCs with nitrogen oxides, and sunlight. In the presence of ultraviolet light from the sun, VOCs and nitrogen oxides react to produce ozone, a very reactive form of oxygen that attacks lung tissue. Nitrogen oxides are produced by high-temperature combustion (such as from vehicle engines and power plants) and are therefore present in most populated places. Any additional VOCs will lead to more ozone, and thus more respiratory problems. The remedial measures are:

- Use paints with not more than 450 mg/l of VOC.
- Use solventless paint systems.
- Use waterborne paint formulations.

4.8 Pigment volume concentration

The paint industry describes the concentration of the vehicle and pigment in a coating based upon volume instead of weight, because many of the properties of coatings vary with volume and may be compared on this basis. Pigment volume concentration (or PVC) is defined as the 'ratio of pigment (in volume, measured in %) to the total volume of solids'. This is used to measure the extent of binder that is available to surround and protect the pigment.

The PVC is a comparison of the relative volumes (not weights) of total pigment and binder, and is calculated as follows:

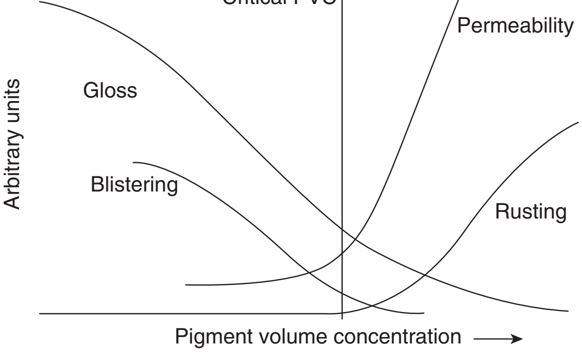
$$\text{PVC\%} = \frac{\text{volume of pigments}}{\text{volume of pigments} + \text{volume of binder}} \times 100$$

The PVC plays a major role in determining various properties of coating systems. It can also determine the sheen level of a paint. Pigment reduces the gloss of the paint. Incrementally increasing the pigment levels or using pigments of larger particle size, the finish of paint moves from a glossy to a more flat finish. The particle size of pigment has great influence on the properties of the coatings. Coarse pigments hide the surface whereas fine pigments remain transparent. With no pigments present, most binders would dry to form a clear, glossy film.

4.9 Critical PVC (CPVC)

CPVC is the point at which there is not enough binder to protect and surround all the pigment. Pigment particles of different size (poly-disperse) have a greater packing density than particles of the same size (mono-disperse). In the case of poly-disperse particle packing, the CPVC increases because the free volume between the large pigment particles can be filled with small ones. Also, fine lamellar fillers (e.g. talc) can fill the free volume between the larger particles.

Above the CPVC, void spaces are present. Below the CPVC, the pigment particles are separated by binder. Abrupt changes in many paint properties may occur at the CPVC, including mechanical, permeability and optical properties [5]. In addition to becoming lighter in color, with increasing void space, tensile properties decrease and porosity increases as the pigment volume concentration gets increasingly high, above the CPVC. The effect of pigment concentration on various properties of paints is shown in Fig. 4.2. It is clear from the figure that paints give optimum properties when pigment concentration reaches the CPVC value.



4.2 Effect of pigments on paint properties [5].

4.10 Wettability

Wetting is the contact between a fluid and a surface, when the two are brought into contact. When a liquid has a high surface tension (strong internal bonds), it will form a droplet, whereas a liquid with low surface tension will spread out over a greater area (bonding to the surface). Most wettability tests are based on determining the angle of contact of drops of liquid (paint, water, solvent) that have been placed on the surface of interest. This measures the angle between the surface and the surface of a liquid droplet on the surface. Generally, the lower is this angle, the better is the wetting. Perfect wetting has essentially no angle at all [6].

The contact angle θ and the surface energies of the materials involved are related by the Young–Dupré equation

$$\gamma_{\mathrm{sv}} = \gamma_{\mathrm{SL}} + \gamma_{\mathrm{LV}}\cos\theta$$

where γ is the surface tension between two substances and S, V and L correspond to the solid, vapor and liquid substances in a contact angle experiment respectively. This equation can be rewritten as

$$\gamma(1+\cos\theta) = \Delta W_{\mathrm{SLV}}$$

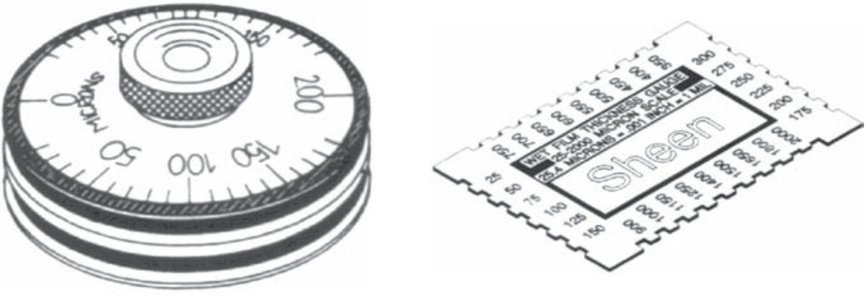
where ΔW_{SLV} is the adhesion energy per unit area of the solid and liquid surfaces when in the medium V. A contact angle of 90° or greater generally characterizes a surface as not wettable, and one less than 90° means that the surface is wettable.

The contact angle of a single liquid on a surface may be useful, but does not tell us the surface tension of that surface. A simple swab test for estimating the critical surface tension was developed many years ago by Hansen [7]. This wetting/de-wetting test is easy and quick and can be employed in the field or at a customer's plant. It works on curved and irregular surfaces, where accurate contact angles cannot be measured. The basics of the test is to swab the solvent onto the substrate and observe whether the strip of solvent stays in place or de-wets (crawls or retracts). The surface tension of the highest surface tension solvent that wets the surface without de-wetting is taken as the critical surface tension of the substrate.

4.11 Tests carried out on coatings after they are applied to a substrate

4.11.1 Thickness measurements

Dry film thickness (DFT) is the thickness of paint coating reached after the solvent has fully dried. Thus there can be an erroneous result on thick-



(a) (b)

4.3 Two types of wet film thickness measuring equipment: (a) the reducing curvature type; (b) the comb type.

ness when measured after full drying of the wet paint. In order to estimate the correct DFT that is required on a substrate, it is first estimated using a wet thickness method. The wet film thickness (WFT) meter is a simple instrument which, when placed over a wet painted surface, immediately gives the paint thickness. There are two types of instruments: the comb type having teeth on the edges, the depth of various teeth giving the WFT; and a spiral of varying thickness, which when rotated on a wet painted surface colors up to a certain length, which is calibrated in terms of the thickness of the coating. The two types of equipment are shown in Fig. 4.3.

The exact DFT can be estimated from the WFT using the following equation:

$$\mathrm{DFT} = \mathrm{WFT} \times \%\mathrm{volume\ solid}/100$$

There are various kinds of DFT measuring equipment. Many of the DFT meters used to measure DFT on steel are based upon the magnetic flux principle. The attenuation of magnetic flux by an organic coating is calibrated in terms of its thickness. Other equipment is based upon the eddy current principle and can be used to measure thickness on ferrous and non-ferrous substrates.

4.11.2 Drying time

Once the paint is applied on a surface, there are various stages through which the paint dries and finally cures fully. Each of these stages indicates the rate of drying and is dependent upon the paint type, its composition and curing mechanisms (discussed in Chapter 1).

Factors on which drying time depends

- Drying time depends on resin chemistry.
- It can detect a wrong mixing ratio or improper mixing in the case of two-pack products.
- If longer than specified, it indicates slow curing and delayed or inadequate resistance properties.

4.12 Testing during the drying process [8]

4.12.1 Set-to-touch

1. Lightly touch the paint film with the tip of a clean finger.
2. Immediately place the fingertip against a piece of clean glass.
3. A film is set-to-touch when no coating is transferred to the glass plate.

4.12.2 Dust-free

1. Cotton fibers are dropped on the paint film from a height of 1 inch.
2. The film is considered dust-free when a gentle current of air removes the fiber from the surface.

This has great significance. For example, if painting is being carried out in the open, until the paint is dust-free it must be covered, otherwise there will be dust pick-up which will spoil the coating.

4.12.3 Tack-free

1. Tack is the ability of a coating to hold an object.
2. Test paper is placed on the paint film.
3. A steel cylinder (2 inch dia meter, 2.85 kg) is placed on the paper.
4. After 5 s, remove the weight and invert the test specimen.
5. If the paper falls within 10 s, the paint is said to be tack-free.

4.12.4 Dry hard

1. Involves pressing the paint film with thumb.
2. If no noticeable mark is seen after the paint film is lightly rubbed with a soft cloth, the coating is said to be hard dry.

4.12.5 Dry through

1. Involves pressing the paint film with thumb and turning the thumb through an angle of 90°.

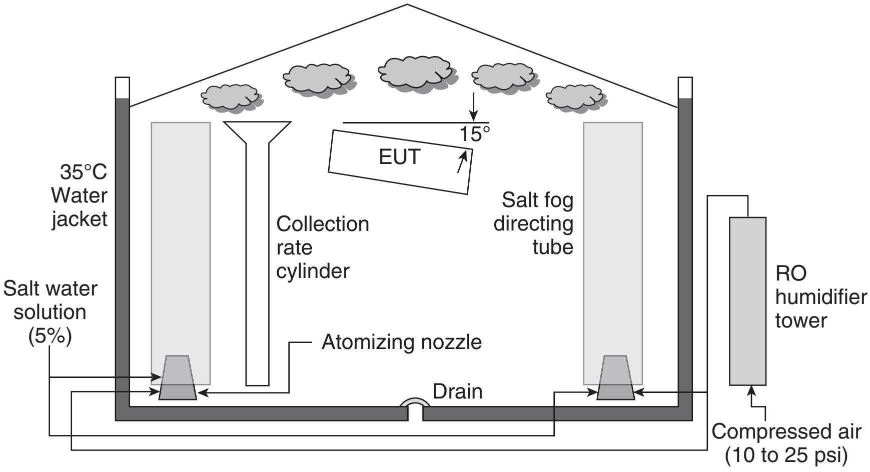
2. If no loosening, detachment or wrinkling is noticed, the paint is said to be dry through.

4.13 Corrosion resistance tests

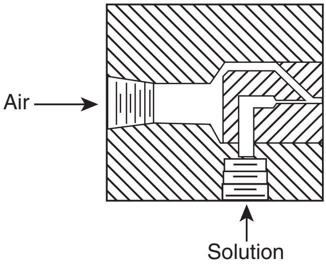
The purpose of an accelerated corrosion test is to cause corrosion, degradation or failure in a shorter time period than under normal conditions without change in failure mechanism(s). Accelerated corrosion testing is achieved by subjecting the test components to conditions that are more severe than normal service conditions. This results in shorter lives than would be normally observed. This can be accomplished using cabinet tests, simulated service tests, electrochemical corrosion testing, immersion tests and atmospheric corrosion tests. The main accelerated testing conditions are described below.

4.13.1 Salt spray test

The salt fog test, also known as the salt spray test, is an important test in evaluating corrosion resistance of coatings under atmospheric conditions. The specification of the test is given in ASTM B117 standard [9]. It provides accelerated corrosion conditions useful in evaluating performance under long-term exposure. The test is carried out in an enclosed, temperature-controlled tank. In the tank, the test sample is placed using a support. The other components of the tank are a salt solution reservoir, an atomizing nozzle (or nozzles), and a source of compressed air. Figure 4.4 shows a cross-sectional schematic drawing of the chamber, and a cross-section of



4.4 Principle of salt spray testing.



4.5 Typical spray nozzle.

an atomizing nozzle for converting the solution to an aerosol is shown in Fig 4.5.

The first part of the test is the creation of the salt solution. ASTM B117 allows for concentrations of 3.5% to 20% by weight; the most commonly used concentration is 5%, which is approximately equivalent to the salinity of salt water. The solution is mixed until the salt dissolves, and the salinity is checked by measuring the solution's specific gravity. The solution is then heated to 35°C and its pH is measured. The desired range is approximate neutrality (range of pH 6.2 to 7.2). Acid or alkali can be added for pH adjustment.

Then the salt solution is atomized by mixing it with humid pressurized air in the nozzle, and delivered to the salt fog chamber. The maximal humidity (i.e., using saturated air) of the chamber should be maintained within 95% to 98% range, and for that it may be necessary to preheat the incoming air to avoid a reduction in saturation due to heat loss during vaporization. A typical nozzle pressure would be 12 psi. A pipe is used to circulate the atomized spray from the top of the chamber to the bottom. At the bottom, a drain collects the solution. Normally, the collected solution is not recirculated; instead, if the test is long enough, the salt solution tank is replenished with fresh solution during the course of the test. The chamber is sealed and maintained at 35°C for the duration of the test. One suitable method of controlling the temperature is by use of a heated water jacket surrounding the test chamber; however, many commercial equipments use a heater and controller to maintain the temperature of 35°C. For most test protocols, the exposure is continuous for the specified period.

Although there is no direct correlation of the salt spray test duration with that of performance in a natural environments, there are still some rules of thumb which are usually practiced. A paint coating which passes just 500 h salt spray test is usually not recommended for more than six months in an industrial or coastal environment. In the same fashion, a 1000 h salt spray test is considered suitable for one year in a natural environment and a 2000 h test corresponds to two years of exposure. For a life expectancy longer than two years from a paint coating, a long-duration test from 3000 h to 5000 h is usually recommended.

4.13.2 Humidity test

Humidity is the most necessary condition for the deterioration of paint coatings, leading to the corrosion of the substrate. When a coating is exposed to a humid environment, moisture condensing from the environment slowly permeates through the coating, reaches the steel substrate and causes corrosion, leading initially to blister formation and cracks and finally to delamination of the paint coating. A humid environment can have a relative humidity (RH) of 60% to 100%. Coastal environments have an average humidity of around 60% throughout the year and above 60% during the wet or monsoon season. Thus highly impermeable paint coatings are required for coastal environments.

Humidity testing is carried out using an ASTM D 2247 standard [10]. The equipment consists of a closed chamber containing a heated, saturated mixture of air and water vapor, using a wet and dry bulb principle. The larger is the difference between the dry and wet bulb temperatures, the lower is the RH. Water used in a test chamber is kept usually at a temperature of 55°C, and relative humidity of 100% is maintained throughout. At 100% relative humidity, a very small temperature difference between the specimen and the surrounding vapor causes the formation of condensation on the specimen. Droplets of condensation appear evenly on the specimen.

Specimens, usually of a standard size, are exposed for various durations from 100 h to 3000–5000 h. The temperature of the chamber is usually maintained at 36–39°C and the humidity is raised to a value chosen as appropriate to the material under test. The temperature is generally cycled, so that the specimen is exposed to alternating humid air and condensation.

In addition to pure water, variations of this test also employ water with 5% sodium chloride, or acetic acid to reduce the pH to a range of 3.1 to 3.3, as well as copper(II) chloride dihydrate. These methods are described in ASTM G 85 [11]. At the end of the test, panels are removed from the booth and examined for various properties such as degree of blistering, change in gloss, etc. After examination, panels are allowed to dry at ambient temperature so that they may be subjected to other tests as desired, such as adhesive failure, etc.

Blistering is commonly assessed by using photographic standards published in ASTM Standard D 714 [12]. Loss of gloss is also estimated. Whenever significant blistering has taken place, it is not practicable to do this instrumentally, so that gloss is estimated to a normal scale in comparison with a control that has not been subject to test. Measurement of gloss is given in a later section of this chapter.

4.13.3 Prohesion test

This method is a modified form of the salt spray test. In this method, test materials are placed against the walls, where heaters are built in. The test materials are then subjected to a salt spray of 0.35% ammonium sulphate and 0.05% sodium chloride at 35°C for one hour and then allowed to dry at 40°C for one hour [13]. This is one cycle. The test procedure then continues for many cycles as required.

Apart from the above test procedures which are widely used to evaluate the corrosion resistance performance of coating systems, the following test procedure gives a fair idea of the weathering resistance properties of paint systems.

4.13.4 QUV accelerated weathering

This test reproduces the damage caused by sunlight, rain and dew. The QUV tests materials by exposing them to alternating cycles of light and moisture at controlled, elevated temperatures. The QUV simulates the effect of sunlight with fluorescent ultraviolet lamps. The test simulates dew and rain with condensing humidity and water sprays. Exposure conditions can be varied to simulate various end-use environments. The QUV can reproduce damage that occurs over months or years outdoors in only a few weeks. Although there is a 'standard cycle', customization is possible and includes temperature during UV exposure, temperature during condensing humidity exposure, type of UV exposure (UV-A (UVA-340 nm), UV-B (UVB-313 nm), or UV-C (UVC-254 nm)), amount of UV exposure, and amount of condensing humidity exposure. A standard procedure given by ASTM G 53 consists of exposing samples to a cycle consisting of 4 h UV, followed by 4 h of condensation at 60°C. Ten such cycles make one test exposure [14]. Accelerated UV tests are carried out from a minimum of 100 h to 4000 h. The latter is equivalent to 10 years of outdoor exposure.

Three types of information can be obtained from accelerated UV exposure: gloss change or gloss retention (ASTM D 523) [15], colour change (△E) (ASTM D 2244) [16] and chalking resistance (ASTM D 4214) [17]. The procedure for measuring these parameters is indicated in a later section in this chapter.

4.14 Evaluation of physical properties

Evaluation of physical properties is carried out after proper curing of the paint coating systems or after exposure of cured coating panels to accelerated or natural weathering conditions. The main physical properties that are of prime importance to the coating industries are described in the following section.

4.14.1 Adhesion

Adhesion testing has two roles: it helps to find out whether the coating has been adequately adhered to the substrate, and it may be a quality control requirement. Many factors can influence the adhesive strength of a coating: the thickness of the applied coating, climatic conditions during coating, cure times and temperatures, type of substrate and moisture contents, inadequate surface preparation methods, surface contamination, coating formulation, preparation and mixing parameters. Some of the common methods used for adhesion testing are the tape, knife, pull-off and scratch adhesion tests.

Tape adhesion test

The two test methods described below are based on ASTM D 3359 [18]. They involve the use of pressure sensitive tests.

- Method A: An X-cut is made in the coating, followed by application of a specific adhesive tape. Upon removal of the tape, the amount of coating removed is quantitatively evaluated and rated on a scale of 0–5.
- Method B: A lattice pattern with either six or eleven cuts in each direction is made in the film to the substrate, pressure sensitive tape is applied over the lattice and then removed, and adhesion is evaluated by comparison with descriptions and illustrations.

Knife adhesion test

In this method, a sharp knife is used to cut through to the substrate, making two cuts crossing at right angles. Then the knife is used to pry up the coating from the substrate and the various layers of coats from each other at the intersection of the two cuts. The amount able to be removed is used to rate adhesion.

Pull-off adhesion test

Pull-off adhesion testing is a measure of the resistance of a coating to separation from a substrate when a perpendicular tensile force is applied. All types of coated samples, metals, alloy, plastic or concrete can be tested for their pull-off strength. The principle of the method is to apply a properly designed aluminum dolly on the coated surface using a suitable glue (e.g. Araldite) and allow it to dry for more than 24 h. After assuring complete drying of the dolly to the substrate, the aluminum dolly is fixed into a jack and is then pulled up using a hydraulic pump [19].

The dial indicator is set to read zero prior to the start of the pull. The hand wheel of the instrument is tightened until the dolly is pulled from the substrate or the maximum tension is applied. The tension required to remove the dolly should then be read directly from the scale in either pounds per square inch or kilograms per square centimeter, as indicated at the bottom of the dial indicator. Observations of the removed test dollies are reported as percentage of adhesive, cohesive or adhesion failure. These types of failures can occur individually in any combination.

An alternative pull-off adhesion test is carried out as per Standard BS 4624 [20]. In this case the dolly consists of a 30 mm diameter round specimen on which the coating is applied according to the application procedure. This dolly is then fixed to the two ends of a long specimen holder using a glue (e.g. Araldite) and kept for drying for 24 h. The composite tensile specimen so formed is then fixed in a standard tensile testing machine and the strength is measured at which the dolly gets separated from the specimen holder.

Scratch adhesion test

This test is carried out as per British Standard BS 3900 [21]. A balanced beam is used to apply weight to a stylus which is dragged over the coated sample. The amount of weight needed to scratch completely through the coating, to create a holiday, is measured. The increase in weight is carried out stepwise, starting with 1 kg. If there is no scratch, which is indicated by the lighting of a indicator bulb and/or an acoustic signal, then the process is repeated at a different place with 2 kg weight and so on, until a scratch touching the substrate is obtained. The corresponding weight applied is called the scratch hardness of a coating.

4.14.2 Abrasion resistance

Abrasion resistance is an important mechanical property used to determine how much physical abuse the coating can handle. It is usually performed with a Taber Abrader (ASTM D 4060) [22]. Panels are rotated under abrasive wheels of a specific hardness at specific weights, and loss of coating is measured. For a standard abrasion test, usually a load of 1 kg is applied and the weight loss of the coating is measured in mg in 1000 cycles. Different kinds of wheels differing in terms of their surface hardness are used for specific purposes as given in Table 4.4.

Falling abrasive method (ASTM D 968) [23]

This test method covers the determination of the resistance of organic coatings to abrasion produced by abrasive falling onto coatings applied to a plain, rigid surface, such as a metal or glass panel. A fixed amount of sand is allowed to fall from a hopper through a straight tube on the sample sup-

Table 4.4 Abrasive wheels for different types of coating

Coating type to be tested	Type of wheel
Coatings of all types including those resistant to general handling	CS 10
Floor coatings resistant to pedestrian traffic	CS 17
Floor coatings resistant to vehicle traffic	H 22

ported on a frame at 45° to the stream of the sand. The Visual observation is made to decide the extent of coating failure.

4.14.3 Hardness

Hardness is the resistance of a coating to a mechanical force, such as pressure, rubbing or scratching. The hardness test of painted surfaces is one of the most important parameter in evaluating the quality of paint film. Depending on the requirements, there are various methods for testing hardness. These include pendulum, scratching, and indentation measuring methods.

Pendulum hardness

This method evaluates hardness by measuring the damping time of an oscillating pendulum. The pendulum rests with two stainless steel balls on the coating surface. A physical relation exists between oscillation time, amplitude and the geometric dimensions of the pendulum. The viscoelastic behavior of the coating determines its hardness. There are two types of apparatus defined in this test:

- The Konig pendulum
- The Persoz pendulum.

Both pendulums have spherical balls which rest on the coating under test and form the fulcrum. Both employ the same principle, i.e. the softer the coating, the more the pendulum oscillations are damped and the shorter the time needed for the amplitude of oscillation to be reduced by a specified amount. The two pendulums differ in shape, mass and oscillation time and there is no general relationship between the results obtained using the two pieces of equipment. The test simply involves noting the time in seconds for the amplitude of swing to decrease from either 6° to 3° (Konig pendulum) or 12° to 4° (Persoz pendulum) [24].

Indentation hardness

This method is suitable for coatings with plastic deformation behavior. ASTM D 1474 is used for testing the indentation hardness of organic coatings

[25]. The apparatus used in this test is known as the Buchholz indenter. It consists of a sharp-edged wheel (made of hardened tool steel) which is mounted in a rectangular block of metal fitted with two feet. When this apparatus rests on a horizontal surface, the effective load on the indenter is 500 g.

The test involves placing the indenter on the coating and leaving it for 30 seconds. A high magnification microscope fitted with an eyepiece graticule is then used, together with a light source, to measure the length in millimeters of the shadow cast by the indentation. The value obtained when 100 is divided by this length is known as the Buchholz indentation resistance of the coating.

$$\text{Buchholz indentation resistance} = \frac{100\text{mm}}{\text{indentation length}}$$

Coatings with elastic deformation behavior should not be evaluated with this test method, because after removal of the intrument an elastic coating will show no or very little indentation.

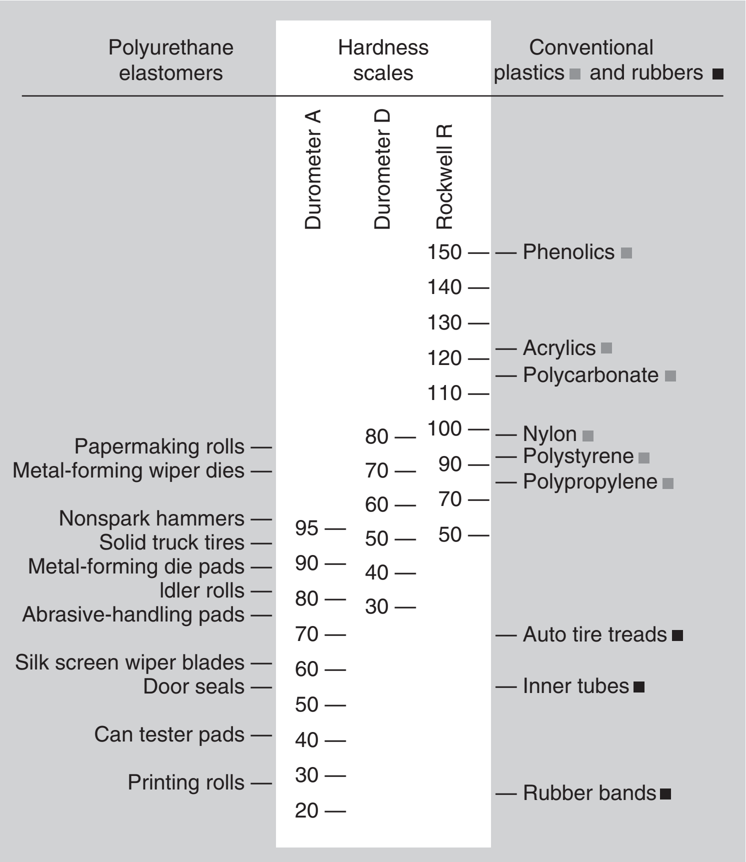
Shore hardness

This is a simple indentation technique in which a sharp indenter is allowed to penetrate the coating. Depending upon the softness or hardness of the coating, the indenter penetrates or resists penetration. This is read directly from an analog or digital reading. There are two kinds of Shore hardness scale, A and D. For paint coatings usually Shore D is used, while for soft rubber coatings Shore A is used. There is a relationship between Shore A and Shore D hardness, as given in Fig. 4.6, which gives a nomograph scale between Shore A and Shore D along with Rockwell hardness [26].

Pencil hardness tester

This test method measures the film hardness of an organic coating on a substrate in terms of drawing leads or pencil leads as per ASTM Standard D 3363 [27]. The pencil hardness test is one of the simplest forms of hardness test. Although some people may consider it to be ‘low tech’, using pencils to test hardness is still a method used by many coating manufacturers and some finishing shops. The test uses special pencils with different degrees of hardness to scratch the coating, which then determines its hardness. This test procedure is quite easy to do but still gives reliable and reproducible results as it depends mainly on the pencil specifications.

A complete set of pencils will have the following gradings, starting with the hardest: 9H, 8H, 7H, 6H, 5H, 4H, 3H, 2H, F, HB, B, 2B, 3B, 4B, 5B, 6B, 7B, 8B and 9B (the 9B is the softest pencil; it contains the most graphite and the least amount of clay). The ‘H’ stands for ‘hardness’ and the ‘B’



4.6 Relationship between Shore A and Shore D hardness along with Rockwell hardness [26].

stands for ‘blackness’, which comes from the amount of graphite used in the softer pencils. Artists’ pencils are made with leads that range in hardness from 9H (very hard) to 9B (very soft). A holder is provided with pencil sets which allows a pencil to be held at a 45° angle, while being pushed firmly across the surface of the coating under test. Pencils are pushed into the sample and the coating hardness is identified by the trace generated. The test procedure starts with the hardest pencil and continues using progressively softer pencils until the hardest pencil that does not mark the coating has been established. This is termed the ‘pencil hardness’ of the coating. The standard defines ‘marking’ of the coating as:

- a permanent indentation of the surface of the coating, *and/or*
- a scratch or rupture of the surface of the coating.

4.14.4 Impact resistance

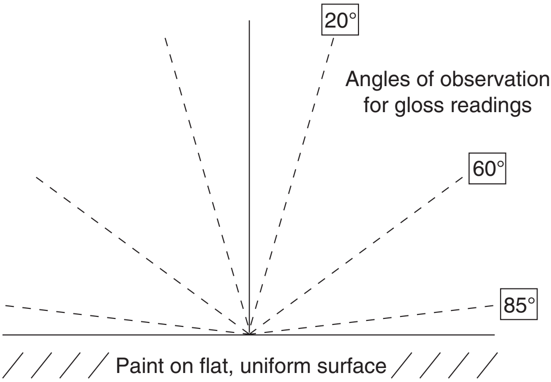
It is very important for many paints to know the effect of impact of a falling object. ASTM D 2794 provides a falling weight test [28]. Here a falling weight of 4.26 kg is allowed to fall on the coating from a height of 50 cm. If the impact area does not show any crack, the coating passes the test.

4.14.5 Flexibility of coating (ASTM D 522)

Flexibility of the coating is measured using a conical mandrel test [29]. A steel specimen of thickness less than 1 mm is coated and fixed vertically in the conical mandrel. The mandrel is then rotated, which turns the coating into several angles ranging from 0 to 360°. The coating is considered flexible if it does not show any crack on its surface.

4.14.6 Gloss

Gloss is often described as the attribute responsible for the shiny or lustrous appearance of a coating. Gloss measurement is essential where an esthetic appearance of the coating finish is required. Gloss is a measurement of the light reflectance of a paint surface. Gloss is determined using a gloss meter which directs a light (that has a similar wavelength range to that of the human eye) at a specific angle to the test surface and measures the amount of reflection. The percentage of the beam that is reflected at the same angle is measured by a photocell. Completely specular light reflection (perfect gloss) would be 100% whereas completely diffuse light reflection (matt or dead flat) would be 0% (Fig. 4.7).



4.7 Schematic representation of measurement of gloss of coated sample.

Table 4.5 Gloss ranges for various paints with different gloss measuring devices

Type of paint	20° Gloss	60° Gloss	85° Gloss (sheen)
Gloss	20–90	70–95+	–
Semigloss	5–45	25–75	–
Satin	–	5–25	10–40
Eggshell	–	2–15	5–25
Flat	–	0–10	0–15

The classification of paints according to gloss ratings depends on the ability of the surface to bounce back varying amounts of light beamed on it, and these readings show the relative reflectivity of the coated surface as compared with a smooth, flat mirror. The gloss reading at 20° serves to describe the 'depth of gloss' and is used to describe gloss and semigloss paints. The reading at 60° is the measurement of gloss referred to most often, and is used with all but dead-flat paints. The 85° reading describes the 'sheen' of flat, eggshell and satin paints. Paints described as flat, satin, semigloss and gloss will have sheen and gloss values falling into the ranges shown in Table 4.5. The gloss level of a coating is based on the pigment level in the paint. Pigment reduces the shininess or gloss of the binder.

One of the most important properties of coatings is gloss retention. A coating that has maximum gloss retention will remain unchanged for a long duration. PVDF coatings have very long gloss retention. It has been found that the gloss retention for PVDF coatings is more than 85% after 10 years (outdoor exposures) or 4000 h (accelerated weathering).

Another important property of coatings is the color change. This defines the fading in color or the tendency to change to some other color. A portable spectrophotometer is the most suitable system to measure both the gloss retention and the color change ($\triangle E$) in a single analysis. The lower is the value of $\triangle E$, the better is the color retention of the coating.

4.14.7 Holiday test

Holidays are nothing but very small regions on the coated surface where the paint failed to adhere. Their dimensions range from fractions of millimeters to a few millimeters. They are caused by several means:

- Air and solvent entrapment that results in the formation of voids or bubbles in the film.
- Pinholes caused by air or solvent migration through the films as the coating or lining dries.

- Poor application and drying conditions are usually responsible for excessive air bubble and pinholes. Sharp irregularities and unevenness in the surface, such as edges, corners and rough or porous welds, may also produce thin spots or porosity in the coatings.
- Physical damage after application, such as that caused by nicks and scrapes from equipment and personnel, is also a frequent cause of holidays.

It is very important to measure these holidays before the coated component is passed for actual use. A pinhole can be the easy path for the environment to penetrate the coating, reach the substrate and cause corrosion. These, therefore, must be detected first and must be plugged before the coated material is sent for use.

A usual way of testing for pinholes is by subjecting the coated surface to a high voltage between the substrate and a scanning electrode (in the form of a brush, broom, ring, etc.). When the electrode scans over the coated surface, it creates a spark at a place where there is a break (holiday). The voltage applied is not arbitrary; it varies with the thickness of the coating. The relationship between the applied voltage and the coating thickness as per ASTM D 5162 [30] is given by the following:

- If the coating thickness is less than 1.016 mm then the test voltage V is given by

$$V = M(T_c)^{\frac{1}{2}}$$

where T_c is the coating thickness and $M = 3294$ if T_c is in mm.

- If the coating thickness is more than 1.016 mm then the test voltage V is given by

$$V = K(T_c)^{\frac{1}{2}}$$

where $K = 7843$ if T_c is in mm.

Table 4.6 gives the test voltage for coatings of various thicknesses.

The electrical potential of low-voltage holiday detectors is usually under 90 volts and they are normally used for testing non-conductive films up to 20 mils in thickness applied over steel substrates. High voltages are available from 900 V up to 45 000 V for testing coatings or linings applied over both steel and concrete substrates from 20 mils to over 100 mils thickness. Voltage output can be adjusted to the requirements established for various types of coatings and linings and their recommended thickness. Most high-voltage holiday detectors operate on the pulse principle in which a short-duration pulse of high-voltage electricity is applied to the coating.

The surface of the coating to be inspected should be dry and free of oil, grease, dirt or other contaminants. Prior to holiday detection, the protective

Table 4.6 Test voltage for holiday detection for coatings of various thicknesses

Thickness (mil)	Thickness (mm)	Inspection voltage (KV)
8–12	0.20–0.31	1.5
13–18	0.32–0.46	2.0
19–30	0.47–0.77	2.5
31–40	0.78–1.03	4.0
41–60	1.04–1.54	5.0
61–80	1.55–2.04	7.5
81–100	2.05–2.55	10.0
101–125	2.56–3.19	12.0
126–160	3.20–4.07	15.0
161–200	4.08–5.09	20.0
201–250	5.10–6.35	25.0

coating should be dried or cured in accordance with the manufacturer's printed instructions, the project specifications, or the procedure permitted by the buyers.

The ground wire should be firmly attached to the substrate to be tested. If no uncoated area is available to ground to on the coated side of the substrate, the ground wire should be attached to the uncoated side of the metal substrate. The ground wire should be held to the substrate by adhesive tape, clip or other suitable means. Where a test coating is applied to a concrete substrate, the ground wire should be attached to the reinforcing steel. The concrete surface must be damp or otherwise conductive in order to complete the circuit.

The sensor electrode should be pressed flat against the surface of the coating and moved across the surface at a suitable speed. During holiday testing, complete surface contact between the electrode and the coated surface must be achieved. Activation of an audible signal implies the presence of holidays, pinholes or voids; when using a high-voltage detector, a spark will also be seen when a holiday, pinhole or void is detected. Various kinds of electrodes are used to scan the coated surface. The ring type is used to scan a big pipe in the shortest possible time (less than a minute).

After the detection of a holiday, the holiday should be marked by circling the spot with grease-free chalk. If several holidays are detected in one general area, a circle should be made around the whole areas. Spot areas should be touched up and larger areas recoated in accordance with the specifications and the manufacturer's instructions. After the repair is fully cured, it should be retested. In extreme cases of pinholes, in the coating or lining should be removed and reapplied.

However, precautions should be taken that the voltage should not be too high, otherwise holes would likely be burnt through the coating or linings to the metal, and the coating would have to be repaired. This would be expensive and time consuming and could cause serious delays.

4.14.8 Cathodic disbondment test (as per ASTM G8)

A cathodic disbondment test estimates the extent of disbondment around an already damaged coating [31]. The test is carried out at room temperature or at 65°C for a period of 28 days. The coated test sample is made to be the cathode, and platinum is used for the anode. A suitable current is passed into the cell so that there is a constant voltage of –1.5 V between a reference calomel electrode and the cathode. To start with, an intentional hole of 3–5 mm is made on the coated sample, which is dipped into a solution of 3.5% NaCl. After 28 days, the test is stopped and the coating next to the intentional hole is physically removed. The corroded area around the intentional hole (called the disbonded area) is measured and converted into millimeters radius.

4.14.9 Water permeability test

One of the most important properties of coatings is their permeability for water vapor [32]. Deterioration of a coating takes place when water vapor or moisture from the environment enters the coating, diffuses into the coating and finally reaches the substrate. Once the moisture reaches the substrate, the corrosion process begins and deterioration of the coating starts. Thus water permeation basically measures the life of a coating. ASTM D 1653 is used to determine water permeability.

In this method, free film of the coating is prepared, which is kept as a lid on a specially fabricated aluminum cup filled with water up to three-quarters of its height. It is then weighed and kept in a desiccator which is filled with a moisture absorbant such as anhydrous calcium chloride or phosphorus pentaoxide. The desiccant initially absorbs all the moisture in the desiccator. Now in order to establish equilibrium between the desiccator environment and the aluminum cup, water from the cup migrates out through the free film of the coating. This results in weight loss of the cup, which is measured after every 24 h. The experiment continues for 5–7 days or more till a constant weight loss value is reached. This value is the permeability of the coating expressed in $mg/m^2/24$ h.

4.15 Summary

This chapter has discussed the most important aspects of paint coatings, characterization, evaluation and various testing procedures. It covers topics such as coverage calculation, which is important not only for the paint applicator and supervisor to account for inventory, but also for the user for ordering the correct quantity of paint to be used for a job. Although there are many testing and evaluation methods and procedures based on different national and international standards, those most commonly used are covered in this chapter. The idea of this chapter is to appraise the first-time reader, paint applicator, supervisor and user to know the basic principles of various testing procedures.

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5

Selecting an appropriate organic paint coating

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5.1 Introduction

The study of paint coatings ultimately boils down to the coating selection for a particular application. What are the various criteria that govern the coating selection for a particular job? How are these guidelines chosen? How can it be assured that the paint coating will be durable for the life predicted? These are a few of the tasks that every user must know, every applicator must practice and every supervisor and coating inspector must understand.

Using a very simple logic, the following can be the most systematic steps in coating selection:

1. Detailed knowledge of the location of the object to be coated.
2. Basic properties one is expecting from the coated surface:
   - Mechanical properties such as hardness, impact, scratch resistance, abrasion, adherence, etc.
   - Chemical resistance.
3. Resistance to UV light
4. Ease of application
5. Surface preparation
6. Economic application.

Location is first and foremost in selecting a coating. Locations are classified on the basis of the severity of the environment. For a dry and rural environment, a cheaper paint such as alkyd paint is sufficient. As the environment becomes more aggressive, either better coating chemistry, such as chlorinated rubber to epoxies, or a combination of zinc-based primers with top coats, is required. For highly aggressive environments, such as offshore and other severe environments, it is essential to strengthen the coatings with strengthening or barrier pigments such as glassflakes or mica. The presence of glassflakes not only strengthens the paint matrix but also increases the mechanisms responsible for enhancing the life of the coating.

Table 5.1 Corrosivity of environments as per ISO 12944-2

Category	Description	Example
C1	Rural areas with low pollution and humidity, interior of buildings (dry)	Residential and commercial buildings
C2	Rural areas with low pollution and humidity with possible condensation	Communication towers, road signs, etc.
C3	Urban and industrial areas with moderate SO_2 pollution, coastal salinity, interior areas with high humidity and air pollution	Water foundries, metal fabrication factories, airport terminals
C4	Industrial and coastal areas, chemical processing plants	Seaport equipment, fertilizer plants, drumming terminals, marine jetty topside structures, etc.
C5-I	Industrial zones with high humidity and aggressive atmosphere	Power plants, bridges, pulp and paper mills, petrochemical plants, oil refineries, etc.
C5-M	Marine offshore, coastal with high salinity	Marine piles, jack-up rigs, buoys, semi-submersible rigs, Floating Production Storage Offloading (FPSO), etc.
C5-Im1	Fresh water	River installation, hydroelectric power plant
C5-Im2	Sea and brackish water	Harbour areas with structures like sluice gates, locks, jetties, offshore structures
C5-Im3	Soil	Buried tanks, steel piles, steel pipes

Table 5.1 describes the classification of various environments on the basis of the severity of the location.

A user must be clear what kind of mechanical properties he is looking for in the coating. Coating formulations change accordingly depending upon whether one needs a hard and rigid, or a soft and stretchable, coating. Strong impact resistance and erosion resistance will require an alternative coating. In the same way, the coating requirement may depend upon the extent of chemical resistance one is looking for. Chemical resistance can be in terms of salt spray resistance, immersion resistance in various solvents or resistance to strong acids and alkalis or various organic solvents.

If the coating is to be exposed to an open environment, it is very important that it must have strong resistance to ultraviolet (UV) radiation. Color fading, loss of gloss or chalking are the usual defects that appear when many coatings are exposed to outdoor exposure. Again depending upon the life of UV resistance, one can choose different coatings. For example, polyurethane coatings can resist UV radiation for 3–5 years and polysiloxanes for 10–15 years, while PVDF coatings are affected very little even after 20 years' exposure.

Ease of application is one of the most important criteria of many coatings to be selected for a particular site. If the coating can be applied by brush or roller, the cost of application is almost negligible; however, if the coating is to be applied by air spray or airless spray, the cost of application includes the cost of spraying machines also. Again, though the cost of an airless spray gun is small compared to that of an airless spray system, many sophisticated coatings such as elastomeric polyurethanes and polyurea require very sophisticated machines that have an exorbitantly high cost. Further, it must be kept in mind that sometimes in order to achieve strong protective properties, as well as to complete a large volume of surface, the use of spray machines is the only alternative.

Another factor on which the selection of coating depends is surface preparation requirements. It is well known that surface preparation is perhaps the most important factor in deciding paint coating life as well as in saving it from coating failure. However, sophisticated methods of blasting and hydroblasting are not only costly, they require several safety precautions. Hence, many users prefer paint coatings which can be applied on as-received surfaces with minimal cleaning. It is well known that several paint formulations now exist that can be applied on the as-received surface with simple degreasing and wire brush cleaning. Surface tolerant coatings are in great use today for many maintenance applications, where shot blasting is a safety hazard. However, in order to get a long paint life and in order to clean a very big surface, it is not possible to avoid blasting techniques.

Economy in paint coatings is perhaps an individual's decision. It basically depends upon the available project cost and the share of the project cost on paint coating application for corrosion protection. Systems are available in which cheaper paint coatings can be applied, but these will give a shorter coating life. In order to get a long coating life one has to spend more to achieve the desired properties, as discussed above. Thus for a new plant whose expected life is more than 20–30 years, it is not good practice to count the immediate expenditure on coating; life cycle cost calculation is a better option. A cheaper coating will require frequent replenishment and plant shutdown. Hence it is advisable to use a good coating system if long and uninterrupted plant life is the main aim.

5.2 The decision-making process

Having discussed the basics of coating selection in the section above, it is time to make a decision. The question is whether your decision will result from critical analysis based on the facts discussed above, or whether you will follow a conventional decision making process as given below:

- Continue using the product that we have been using up to now.
- Follow what others are doing (always be second).
- Use what is being used globally.
- Use what suppliers and manufacturers suggest.
- Use low cost coatings.
- Change only if you know about failures in existing coatings from other users.

There is a better way. Although the selection process can be very complex and tedious, using very simple logic it can be made useful for our job. One should look for placing one's requirements on some scale and calibrating them. Calibration means a lot – gathering information from other users, getting information from appointed consultants, carrying out a few laboratory tests to ascertain the truth about suppliers' recommendations.

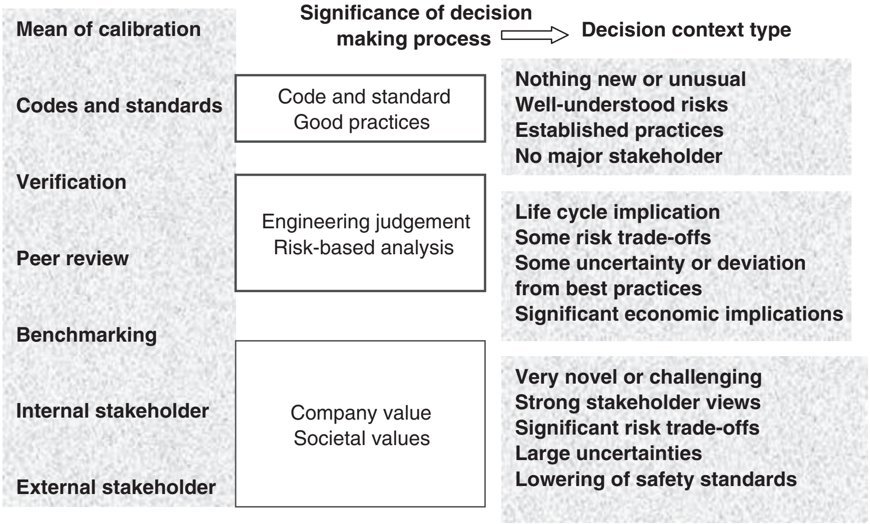
One way to judge the necessary level of complexity is to consider the context of the decision, which may run from the mundane to extremely challenging, or from one where there are no major stakeholder implications to one where society itself has a stake in the outcome. Obviously the level of validation and calibration required of any coating decision needs to be matched to the context of the decision. Whereas a simple comparison with existing codes and standards may be acceptable for a few low-level decisions, those that involve high levels of uncertainty, trade-offs of risk or possible safety implications may include reviews and benchmarking or consultation with external stakeholders (government regulators, etc.).

The UK Offshore Operator Association (UKOOA) came out with a very simplified but quite exhaustive way of carrying out the decision making process. This is given in Fig. 5.1. Everybody wants to 'make good decisions'. Understanding decision making processes and characteristics of good decisions will prove to be a valuable tool when selecting coatings.

5.3 Key steps in the decision-making process

The decision making process requires a consistent and well-defined approach:

1. Clearly define the objectives after carefully analyzing the problem.
2. Identify relevant criteria and define prerequisites.
3. Identify all available candidates that meet all prerequisites.



5.1 Decision making process as per UK Offshore Operator Association (UKOOA).

4. Collect information on candidates and identify additional criteria.
5. Rank candidates.
6. Take action.
7. Review results.

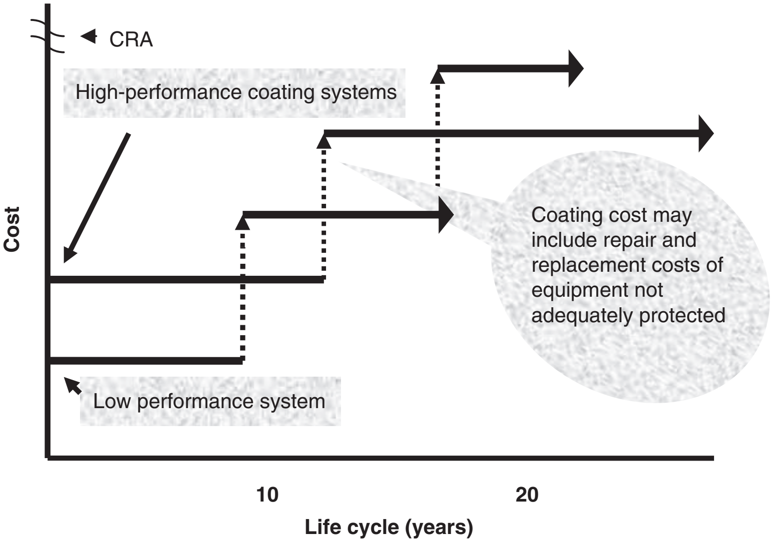
Good decisions are:

- made with an objective in mind
- based as much as possible on relevant criteria and factual information about candidates
- flexible – subject to change based upon better quality information or new criteria
- aligned with applicable laws, regulations and policies
- made with the informed consent of stakeholders.

Some of the criteria which can help in making the right decisions while selecting coatings can be:

- The coating meets the basic objectives of the job.
- Coating formulator/manufacturer track record
- Recommendations from existing users
- The application procedure suits the location.
- Life cycle cost.

Many users are confused about the difference between instant cost and life cycle cost. It must be noted that a good coating system will cost initially



5.2 Hypothetical coating cost versus life cycle.

more; however, because of its high performance and long durability, it will last longer before it needs replenishment. A low performance coating may initially be cheap but will require quick replenishment and hence cost more every time and may hamper the normal plant functioning. Figure 5.2 depicts the life cycle cost of two paint systems.

Let us now take a specific example of coating selection for an offshore platform. There can be a number of prerequisites for selecting offshore coatings. The most trivial consideration would be to use a coating system recommended by the supplier, taking into account the ease of application provided by the supplier and the application contractor and other assurances such as number of years of life and length of recoating intervals.

5.4 Coating selection criteria for offshore structures

- The obligatory criteria that affect the coating
- Compatibility with the substrate and surface preparation
- Compatibility with the available surface preparation
- Compatibility with cathodic protection – wherever applicable.

Other factors which must meet the project requirements can be:

- Low cost or lower life cycle cost
- Duration of effective protection.

5.5 Service environment

Various service environments and any future changes must be considered. These variables include:

- Extreme temperature and thermal cycling
- Relative humidity
- Immersion, alternate wet/dry or dry conditions
- pH limits
- UV exposure
- Damage resistance from mechanical impact or abrasion
- Protection against marine organisms.

5.6 Regulatory requirements

Regulatory requirements include the amount of volatile organic compounds (VOCs) that may be emitted to the atmosphere during application and curing. These regulations vary from country to country. Low VOC coatings are becoming more available and are perhaps not suitable for various applications, hence their performance is still a question in many high-performance applications such as offshore structures. Another restriction is on hazardous air pollutants (HAPs) for which the relevant regulations must be followed.

5.7 Substrate compatibility

Coating selection for new construction and maintenance must be compatible with the substrate. Whether it can be applied as such with or without blasting is an essential consideration. If the structure is already coated, one must find out whether it can be applied on the existing coating after degreasing and cleaning with water, or needs to be cleaned as per St2 and St3 surface preparation. Hydroblasting surfaces require special paint systems to take care of flash rusting; thus it must be made clear whether the chosen coating can be applicable on the hydroblasted surface or not.

5.8 Application alternatives

It is important to select a coating with the knowledge whether or not equipment such as airless spray can possibly be used on offshore platforms, otherwise coatings will need to be chosen that can be applied by brush and roller. However, if high-performance solventless coatings are chosen that are usually applied at a greater thickness (~1000 µm) per coat, high-value airless spray guns are a must. Since these coatings are two-component with a very short working pot life, arrangements must be made to apply them within the prescribed time to avoid any curing of coating within the gun and hoses. The availability of trained operatives who have no water-phobia and can work with a steady hand on the specially made scaffolding is one of the main requirements.

5.9 Cost of painting

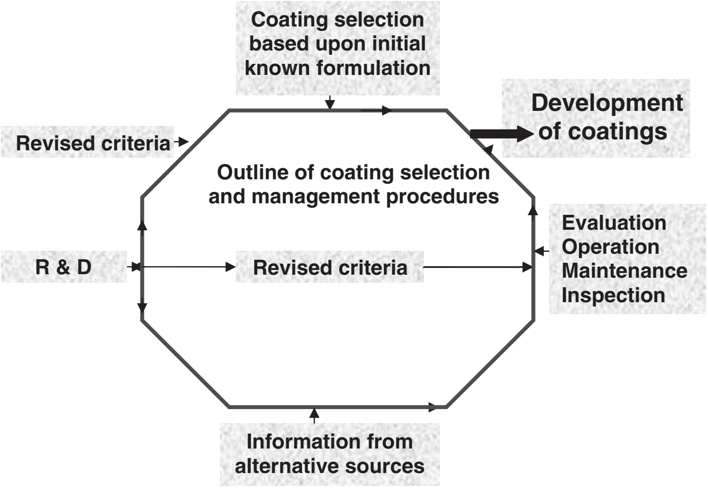
Offshore coatings differ greatly from onshore and other coatings. Here the cost of the coating material is small compared to the downtime costs. Coating offshore structures requires hiring barges, special scaffolding, and divers who can coat under water and in the splash zone. Hence, a single-coat coating is not the only requirement; management of its proper application is also needed. Any mistake during coating can be very expensive, as recoating, additional barge time and scaffolding would be required, which is a costly proposition.

This also implies that for such highly aggressive environments, best quality coating with quick application and the lowest number of coats (preferably only one) is the prime requirement. There is no place for multiple coats that are applied one after another after drying of previous coats. This not only involves more downtime, but also results in incorporation of moisture and salts within intermediate coats. Further, the life cycle cost has great importance here. Any repairs on offshore structures will be immensely costlier, hence choosing paint with long life is again a prime requirement.

Like any other part of a construction or maintenance project, coating application jobs must be managed not only within a material and corrosion management program but also within the entire organization. With today's many reorganizations, we have seen not only the reduction of manpower but also reduced overall awareness and understanding of the coating process.

Thus selection of the coating process can be taken as a continuous improvement process (Fig. 5.3) in which the performance of the coating that was initially selected by a perhaps imperfect procedure is judged. Any drawbacks, limitations, or any kind of failures observed need critical analysis, followed by reformulation, additional information from other sources, and sustained R & D. The new information can now lead to revised procedures for surface preparation, coating application or other modifications in the coating formulation.

Thus in the end, it can be said that coating selection is a complicated process, which needs basic knowledge of paint chemistry to assess the role of resin in corrosion protection, a fair knowledge of surface preparation methods, thorough experience of application techniques, the effect of environmental parameters and a clear understanding of the requirements of



5.3 Coating selection – continuous development program.

protecting the substrate, and finally a good skill to analyze the results to achieve the best performance at lower cost.

5.10 Summary

This chapter sets out and discusses guidelines for selecting coating systems for the various applications and environments listed in Table 5.1. Recommendations involving some of the most common paint systems used in industry are tabulated for various environments described by ISO 12944-2 in Table 5.2.

Table 5.2 Some recommendations of using various coating systems for different environments

Environment category as per ISO-12944-2	Surface preparation required as per ISO 8501	Coating system	No. of coats	DFT (μm)
C 3 Non-immersion medium corrosion (temperature up to 120°C)	St 2	*Medium durability*		
		Primer: MIO-based alkyd	1	50
		Top coat: Modified alkyd (with urethane)	1	50
		Long durability		
		Primer: Epoxy mastic	1	50
		Top coat: 2-pack aliphatic PUR	1	100
	Sa 2.5	*Medium durability*		
		2 coats of alkyd	2	150
		Long durability		
		Primer: Zn-rich	1	50
		Top coat: 2-pack aliphatic PUR	1	80
C 4 Non-immersion high corrosion	Sa 2.5	*Medium durability*		
		Primer: Zn-rich epoxy	1	50
		Intermediate: Epoxy MIO	1	60
		Top coat: 2-pack aliphatic PUR	1	50
		Long durability		
		Primer: Inorganic Zn silicate	1	50
		Intermediate: Epoxy MIO	2	150
		Top coat: 2-pack aliphatic PUR	1	50

C 5 Non-immersion very high corrosion (temperature up to 120°C)	Sa 2.5	*Medium durability*		
		Primer: Inorganic Zn silicate Intermediate:	1	50
		Epoxy MIO	2	150 (2 × 75)
		Top coat: 2-pack aliphatic PUR	1	50
		Long durability		
		Primer: Inorganic Zn silicate	1	50
		Intermediate: High-build epoxy MIO	2	160 (2 × 80)
		Top coat: 2-pack aliphatic PUR	1	50
C 3 Non-immersion medium corrosion (temperature up to 400°C)	Sa 2.5	*Medium durability*		
		Aluminum coating	2	250
		Long durability		
		Primer: Inorganic Zn silicate	1	50
		Top coat: Silicon-based coating	2	200
C 3 Non-immersion medium corrosion (temperature up to 600°C)	Sa 2.5	*Medium durability*		
		Primer: Silicon-based	1	50
		Top coat: Polysiloxane	2	250
Immersion service: tanks for fuel, oil, crude, chemicals and process water	Sa 2.5	Solventless epoxies	1	500
Immersion service: sewage lines, water treatment facilities	Sa 2.5	Glassflake epoxies or Combination of glassflake and reinforced epoxies	1 or 2	1000 or more

(*Continued*)

Table 5.2 Continued

Environment category as per ISO-12944-2	Surface preparation required as per ISO 8501	Coating system	No. of coats	DFT (μm)
Immersion service: splash zone in sea water	Sa 2.5	Polyester glassflake	1	1000
Underwater	HA 2	Water-repellent epoxies	2	2 × 400
Immersion service: water jetties, sea water	Sa 2.5	Glassflake epoxy or Novolac epoxy	1 or 2	1500–2000
Immersion service: freshwater treatment facilities, locks and gates	Sa 2.5	Solventless epoxies	1	1000
Underground structures: gas pipelines, water pipelines	Sa 2.5	External oil and gas		
		3-layer PE (FBE primer, adhesive and PE)		2000–3000
		Water pipelines	3	3000–5000
		Coal tar or tar epoxy, tar-urethane		
		Liquid epoxy, elastomeric PU	1	700–1000

7

Mechanical degradation of organic paint coatings

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7.1 Introduction: paint damage produced by mechanical action

The use of organic coatings is one of the most common methods for corrosion protection of industrial components. In the past few years, demand for better protective performance and coating integrity has increased. In addition, the protective properties against corrosion, in many applications, require several other properties including aesthetic aspects, resistance to solar exposure, etc. In other applications, good resistance to abrasion and particulate impacts is required. This is particularly important for the automotive industry, naval applications, military and agricultural uses, and all those applications that involve the possibility of abrasion due to the friction between the coated component and other components, or in case of the presence of dust, sand or grains of hard materials.The effect of the impact of stones or damage due to abrasion is of primary importance in the optimization of paint. In fact, mechanical damage can locally result in reduction of the protective properties, hence the need to restore the integrity of the paint. In the case of limited damage without a reduction of corrosion protection properties, it is possible to have a detrimental effect on the aesthetic aspect of the paint, with gloss or colour modification. Considering that the second reason for the application of an organic coating is aesthetic appearance, it is also very important to understand this damage phenomenon, as well as to evaluate with accuracy the resistance to abrasion of the coating system to obtain information about the service life of the protection system.

In the case of the surface of two components that are in contact, reciprocal action produces a damage wear phenomenon. There are four wear mechanisms but only two are of interest in paint applications. Adhesive wear is present when two bodies are in contact and there is plastic deformation and adhesion phenomena between the surfaces. It is possible to obtain the formation of junctions and the resulting breakage causes the damage.

This phenomenon is characteristic of the interaction of two components made of the same material. Considering the paints this aspect could be present when both components are protected with an organic coating.

Considering that the contact of two painted components is not very frequent and that the damage is limited due to the similar surface hardness, the second damage method is more important. Abrasion wear is observed when the abrasion action is produced by the roughness of one body or, in case of the presence of three bodies, by the action of a third body entrapped between the other two surfaces. Considering the ductile materials the abrasion wear could be observed in the case of one surface having more hardness (20–30%) than the second one. In case of a coupling of a painted component with a brittle material, such as a ceramic material, the damage could be produced by the ceramic. The third body could be produced during wear action or could be present just at the beginning. The last case is the presence of sand or abrasive ceramic particles present in the environment with a natural or artificial origin. Presence of abrasive sand can come from masonry ash, mineral handling, seashores or deserts. The effect of winds, tornadoes and desert storms can move great quantities of abrasive sands. Moreover, winds can transport the lightest sands to areas very distant from the origin. These phenomena can cause abrasion of organic coatings, due to the direct action of transported sand, or to cases of deposited sands, which act as third bodies.

In the case of abrasive particles, the dimension of particles, their geometry and hardness are very important. In cases where the abrasive particles are transported by the air or by a fluid it is possible to call the damage phenomenon erosion. Quite frequently there is only the painted component present, without contact with another part. The damage effect is produced by the action of free abrasives. Considering the organic coating systems there are two types of mechanical damage of a paint. Mar is damage which occurs within a few microns of the surface. In this case the corrosion protection properties remain and only a change in appearance is seen. The second type of damage produces a reduction or loss of protection properties. This phenomenon is more dangerous. In this case a removal of organic matter from the paint surface is present with a decrease in protection properties.

The abrasion resistance is connected with the hardness of the coating and with the friction coefficient, nevertheless this relation is not obvious. In the first instance, the higher hardness and lower friction coefficient gives better abrasion behaviour. A material with elastic deformation properties that recover normally shows a good abrasion resistance; materials which show a lower tearing resistance present a lower abrasion resistance.

In the evaluation of mechanical damage of paints there are several critical aspects. The first important point is how possible it is to simulate mechanical damage. In fact, it is not easy to reproduce actual damage phenomena in the laboratory because of the presence of several different parameters which have an influence on degradation. Logically, to evaluate the degradation behaviour it is very important to obtain useful information in a short time. Nevertheless it is not easy to carry out an accelerated test, with results representative of the actual damage process.

The evaluation of the damage produced during laboratory tests is the other critical point. The following shows some parameters that are considered representative of the damage produced but in many cases some methodologies appear doubtful.

Finally, it is very important that the chosen laboratory test presents high reproducibility to allow comparison of the data obtained in different laboratories. Nevertheless, there does not exist an experimental test that allows assessments of protective properties to be made in an exhaustive way. This has caused the automotive industry to create a variety of tests with the intention of simulating the abrasive damage during the service life of the components [1, 2]. All these tests have some limitations, and they do not determine a precise value of the protective capacity and only allow us to perform comparative tests among the different coating systems, giving rise to limited concepts of the abrasion behaviour [3]. Similarly, several standards are created to simulate the abrasion and erosion conditions of the components during service life. Nevertheless there is no generally accepted test method for quantitative analysis of the abrasion or erosion resistance.

7.2 Mar degradation

As previously introduced, mar resistance is the ability of a coating to resist permanent deformation or fracture, resulting from the application of a dynamic mechanical force. Physical damage that affects appearance is produced. The major contribution of mar damage is micro-scale scratches caused by light abrasion. In this damage process there is the production of micro-scale scratches which change the pattern of reflected light and reduce gloss. Considering this aspect to obtain useful information about the mar phenomenon it is important to choose a test which produces minimal damage which could influence the aspect of the paint without modification of the protection properties. To evaluate the experimental data it is necessary to consider a property directly related to the aesthetic aspect.

The standard ASTM D6037 (Standard Test Methods for Dry Abrasion Mar Resistance of High Gloss Coatings) considers the use of the Taber test apparatus [4–6] to characterize the mar behaviour of paint systems. Two abrasive wheels are rotated due to the rotation action of the samples. Other details about this test will be introduced in the following part about abrasion resistance evaluation. In the case of mar degradation the CS10 abrasive

7.1 Taber test apparatus.

wheels or wheels fitted with abrasive paper are frequently used to simulate a low damage action. To evaluate the produced damage, the level of gloss is measured. With the same test apparatus other authors have produced more intense damage by using a more abrasive means as the CS17 wheels [7]. Figure 7.1 shows the Taber test apparatus.

Another possibility to produce surface damage is the ASTM D2486 standard (Standard Test Methods for Scrub Resistance of Wall Paints). This standard is not dedicated to the study of mar damage of paint but nevertheless could be interesting because light surface damage is produced. In this case, the abrasion apparatus consists of an abrasive brush. By using different hardness and abrasive effects of the brushes it is possible to obtain different levels of damage. Also from the literature it is possible to consider different tests. A very good review of mar damage testing was made by Osterhold and Wagner [8].

Several methods to produce aesthetic damage on paints are considered. The most important test simulates the car wash action in the laboratory. A brush with sprayed water and quartz powder is used on the coated panel. A similar test is obtained using the Rota-Hub-Scratch-Tester where a rotating disc with the scratching medium produces the damage. A similar test uses abrasive particles contained in the 'Scotch Brite' sponge [9, 10]. The Crockmeter produces linear damage using a rubber finger with and without the presence of abrasive powder. Also, micro-indentation hardness is frequently used to evaluate the hardness of the paints to find a correlation between the paint and abrasion resistance. Nevertheless, no clear correlation has been highlighted. Other authors consider the micro- and nano-scratch experiments [11–15]. In this case it is not easy to correlate the experimental data with the mar phenomenon. Nevertheless, considering that the mar damage is produced by a very superficial and low action, these techniques appear interesting. Considering the previously cited test methods

7.2 Glossmeter for measurement of gloss of a surface.

it is possible to conclude that no one test is considered completely suitable to simulate the mar damage phenomenon.

The system to evaluate the damage obtained in the laboratory is easier to derive. During damage action, a modification of the surface increasing the roughness is present. The physical modifications could be easily checked using AFM technology or a roughness meter. Although a good mapping of the surface state is obtained in this way, no direct correlation with the aesthetic appearance is easily obtained. For this, the measurement of a characteristic that can be directly correlated with the optical nature appears more interesting. The gloss measurement is then the most suitable technique. The measurements, carried out at a 60° angle, appear the most indicative because it is an intermediate angle between a 20° angle, for which the effect of wear is dominant, and an 85° angle, for which the effect of the morphological texture is dominant on the gloss of the polymer coatings. Figure 7.2 shows the glossmeter for the measurement of the gloss of a surface.

7.3 Reduction of protection properties due to mechanical damage

Mechanical damage can significantly decrease the protection properties. This type of damage is more dangerous because not only the aesthetic aspect is lost but there is the possibility of corrosion attack on the substrate. There are two different phenomena present in this case: erosive wear, where the velocity of abrasive in air or in solution is important; and abrasive wear, where a material comes into contact with rugged or abrasive particles. When the abrasive material abrades the softer material, two-body abrasive wear geometry is present; when loose abrasive particles remove the softer material, three-body abrasive wear geometry is present.

7.3.1 Erosive wear

Erosive wear is a very important damage phenomenon for the automobile industry which currently lacks quantitative tests for assessing the durability of paint systems under conditions of both impact and abrasion by hard particles.

Some test methodologies are used [1, 16–22]. Frequently the erodent particles are accelerated along a nozzle in a flowing stream of gas, usually air, or a centrifugal accelerator is used. Other different types of apparatus to accelerate the abrasive materials are being developed [1]. Different abrasion material is used: natural abrasion sands and artificial abrasives, such as Al_2O_3 [23, 24]. Normally, the damage produced is evaluated by optical and microscopic observation or by considering the volume of paint removed per gram of impacted sand. Another possibility is measuring the decrease in thickness. However, in all cases, no direct indication concerning the protection property loss is collected. This aspect will be considered.

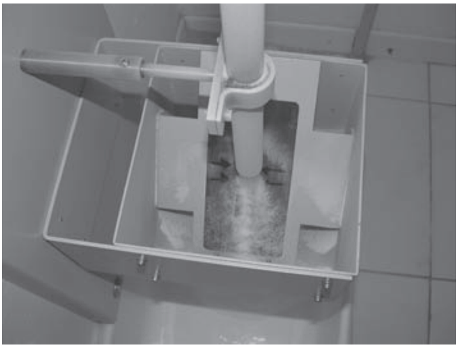
The most used test is the methodology presented in the ASTM D968 standard (Standard Test Methods for Abrasion Resistance of Organic Coatings by Falling Abrasive). Abrasive sand falls due to gravity through a transparent glass tube on the painted panel which is placed at a 45° inclination. Figure 7.3 (a and b) shows the test apparatus.

Two abrasion means are considered in the standard: siliceous sand with round grains, called Ottawa sand, and silicon carbide abrasive with edge grains. Nevertheless it is possible to use the same test geometry with different types of abrasive, to assess the quality of the tested paint and the service life of painted components. Two litres of abrasive fall on the painted samples, producing an elliptical damage area (25 mm × 30 mm), as reported in Fig. 7.4. It is important to note that this area is not uniformly damaged with differing reduction of protection properties. Following the standard, the test ends when a 4 mm diameter area of substrate without paint is produced. The abrasion resistance is obtained in litre/mil (0.001 inch) by dividing the used abrasive volume (in litres) by the thickness of coating (in mil). As an alternative, the abrasion resistance could be obtained by calculating the weight of used abrasive (kg) against the thickness of coating (in mil). The gloss measurement after a fixed quantity of falling abrasive could give information about the change of the surface aspect. By comparing this test with those where the abrasive is transported by a stream of gas or air it is possible to observe that, in this case, the damage is less intense [25].

7.3.2 Abrasive wear

Several tests have been introduced to simulate the actual behaviour of paint systems to abrasive wear. One test gives a variable tribological intensity and

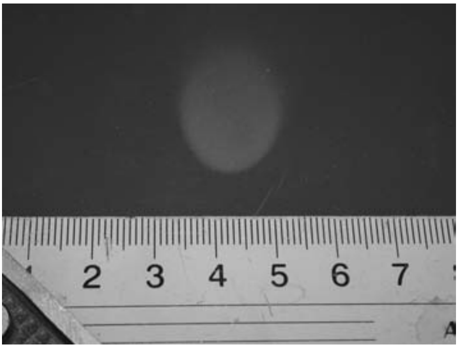
(a)



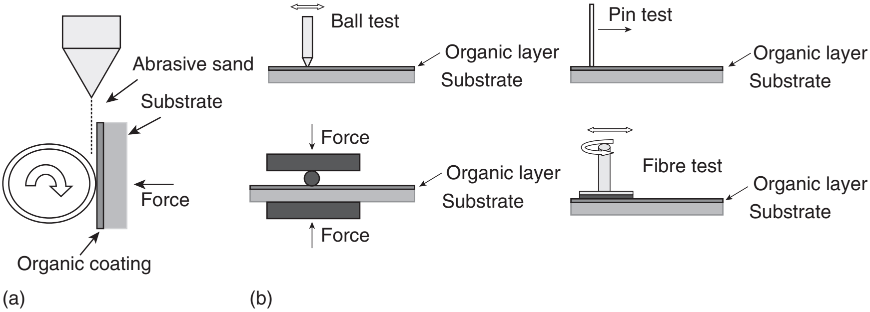
(b)

7.3 Apparatus for falling abrasive test: (a) complete apparatus; (b) particulars of the abrasion process.

a variable abraded area during testing. Considering this aspect, the most frequently used test is outlined in the ASTM G 65 standard (Standard Test Method for Measuring Abrasion Using the Dry Sand/Rubber Wheel Apparatus) [26–30]. A rubber-rimmed wheel slides against the surface of a plane test sample in the presence of abrasive particles (Fig. 7.5a). During abrasion the area of contact increases. As in previous tests the damage produced is evaluated by measuring the mass or volume loss. Abrasive wear is also tested by using a scrubbing brush that moves backwards and



7.4 Typical morphology of damage produce by falling abrasive test.

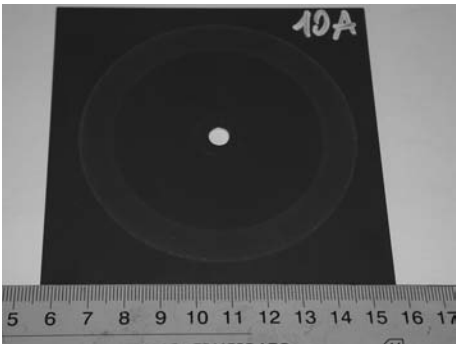


7.5 Test geometry of (a) dry sand rubber wheel and (b) scratch tests.

forwards at a constant rate and force over a substrate [31]. In this case, the damage is evaluated by measuring the weight loss or by the analysis of the sample surface.

Other authors use the scratch test [17, 31–37]. The abrasive mechanism consists of a cylindrical (or half-cylindrical) tool or a pin, a ball or a fibre tool. This tool is in sliding contact with the painted flat sheet under a varying normal load. Different materials are used to produce the abrasion action: steel, diamond, carbide (Fig. 7.5b). In the case of fibre test, a circle of scouring cloth composed of nylon fibres, which was rotated at 60 rpm and moved back and forth over the sample, is used. The damage produced is evaluated by analysing the scratched surface using a profilometer or using optical and microscopical techniques. In some cases, the friction coefficient is considered. All these tests show an increase in the dimensions of the damaged area with the consequent modification of the test parameters over time. In this case, tests that produce damage on a constant area with nominally constant tribological intensity could be interesting.

The most important test is the Taber test shown in the ASTM D4060 standard (Standard Test Method for Abrasion Resistance of Organic



7.6 Typical morphology of damage area produced by Taber test.

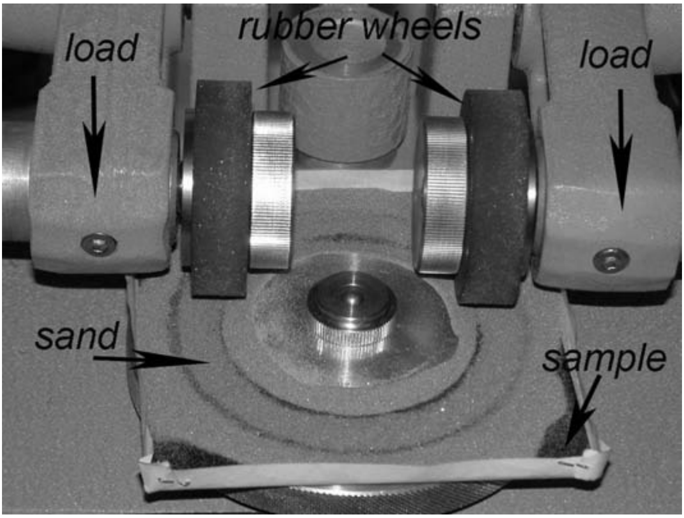
Coatings by the Taber Abraser). This test was developed to evaluate the resistance of organic coatings [4, 5], but it is also quite widely applied to other coated systems, such as hard layers produced by PVD [38–40] or those produced by sol-gel techniques [31, 41, 42] or coated polymeric materials [1, 2, 5, 6, 23, 24, 43–46]. The coated sample rotates (60 rpm) and induces rotation of two abrading grinders, causing mechanical degradation of the protective layers [2, 23, 24] as shown in Fig. 7.1. To increase the action of the grinders, a weight in the range 250–1000 g is imposed. The damaged area consists of an annulus (Fig. 7.6). The abrasion resistance is evaluated by considering the mass decrease (ΔW, in mg) after, usually, 1000 cycles. From this value it is possible to obtain the wear (or Taber) index:

$$\mathrm{TI} = \Delta W \times 1000 / c$$

where c is the number of cycles.

To evaluate the resistance of organic coatings, abrading grinders CS10 and CS17 are usually used. These are wheels (50 mm in diameter and 12 mm thick) made of a rubber matrix with tungsten carbide and other unspecified materials as abrading parts [23, 24]. The abrasion wheels simulate the effect of abrasive particles during the service life of components. Nevertheless the abrasion produced using the Taber abrasimeter results in more uniform and constant damage than that produced by free abrasive methods. The wheels reduce uniformly the thickness of paints. During the test the abrasion efficiency decreases and to maintain a constant abrasive action it is necessary to grind the wheels using an abrasive paper each 500–1000 cycles.

To produce more realistic damage some authors undertake the test using rubber wheels instead of abrasive wheels [47–49]. Between the painted sample and the wheels, different abrasive means with different characteristics (granulometry, form and hardness of grains) are introduced. The need to confine the abrasive on the tested area requires a modification to the testing apparatus as shown in Fig. 7.7 [47, 48].

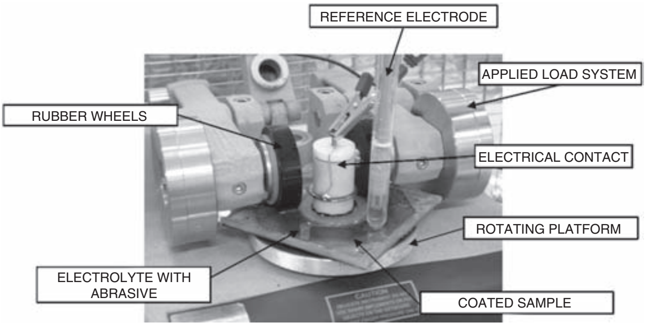


7.7 Modification of Taber test geometry to study abrasion effect of free abrasive [47].

7.3.3 Abrasive wear in presence of solution

In some cases the painted components are damaged by the action of a solution which contains the abrasive slurry. Several applications could be cited, including marine environment, chemical plants and car washing machines. In cases where the abrasive is contained in a solution, the abrasive effect changes totally. The solution could act like lubricant, reducing the damage action. Nevertheless the presence of water can produce damage in the paint due to water uptake with adhesion loss, blister formation and swelling of the paint. If the solution has an aggressive action against the organic coating or the metallic substrate, a significant influence on mechanical–chemical degradation could be observed.

In the literature there are studies of the characterization of the abrasive effect of an abrasive neutral slurry using a particular test method. Some authors use a scrubbing brush that moves backwards and forwards at a constant rate and force over a substrate. A scrub paste consisting of water, thickener, sand and detergent is used to simulate the car washing process [50, 51]. Other authors use a ball rotating in a slurry of small silicon carbide abrasive particles [17]. The ASTM G 105 standard (Standard Test Method for Conducting Wet Sand/Rubber Wheel Abrasion Tests) works by abrading a specimen with a slurry containing grit. The abrasive is introduced between the test specimen and a rotating wheel with a neoprene rubber tyre. The test specimen is pressed against the rotating wheel at a specified force. Other authors have modified the Taber test abrasimeter to produce an



7.8 Modification of Taber test geometry to study effect of abrasive slurry and to enable electrochemical measurements without moving sample from Taber platform [48, 49].

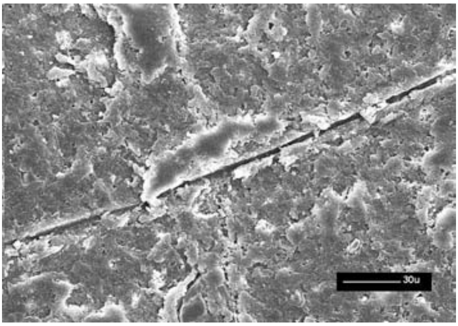
action that contains the electrolyte and the abrasion types (Fig. 7.8) [48, 49].

7.3.4 Limitations of test methodology and measurement of the damage

Some test methodologies present deficiencies. The reproducibility of tests is not optimal, particularly when the results are obtained in different laboratories [23]. Considering the Taber test, the variability in the properties of the abrasive wheels during use, weathering effect and influence of the wear debris, is transferred to some extent to the wheel surface, despite measures to remove it continually from the specimen. The use of a rubber wheels and free abrasive could reduce this problem [47].

Some research has investigated whether it is possible to establish a correlation between the data obtained with different test methods. Only Chisholm *et al*. [24] compare the Taber test with the jet abrasion test (JAT) using a stream of Al_2O_3 particles. He finds a good correlation between the Taber and the JAT, suggesting that the mechanisms of abrasion for the two processes give similar results. Moreover, the great problem using the Taber test, as with the other abrasion test methods, relates to the evaluation of the damage and to checking the decrease in the protection properties. The evaluation of damage is made only through mass loss measurements, without considering the form of the damage, and the consequent influence on corrosion protection performances. This fact is very important because a sample could present a good Taber index (low mass loss), but its corrosion protection properties could be notably decreased due to formation of defects.

Figure 7.9 shows an epoxy polyester powder coating after 1000 cycles of Taber test using CS17 abrasive wheels and 1000 g of imposed load. It clearly

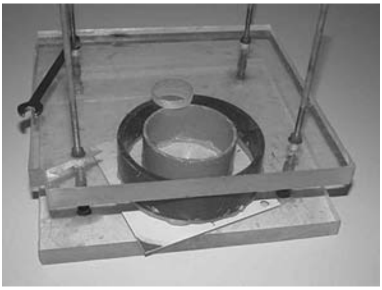


7.9 Damaged surface of powder coating using Taber test (after 1000 cycles of abrasion using 1000 g weight and CS17 grinders) [5].

shows the presence of a deep defect, probably produced by a third body, which reduces the protection properties of the coating. Nevertheless the mass loss value is low. Considering only the mass loss or thickness decrease, this painted sample presents very good abrasion resistance. On the contrary, the protection properties are lost locally due the presence of this defect.

Considering this aspect, the only possibility is to use a method that allows us to highlight the decrease in protection properties as a function of the abrasion time. The electrochemical measurements and, in particular, electrochemical impedance spectroscopy (EIS) are widely used to check the protection performance of organic coatings [52]. This approach permits us to obtain information without the necessity of knowing the reduction of mass or the decrease of thickness. In particular this technique is very sensitive to the presence of defects which reduce the protection performance of an organic coating [52].

Ramamurthy *et al.* [3, 17] introduced the use of electrochemical measurements to estimate the corrosion connected with the damage produced by the impact test. Rossi *et al.* [5, 6, 47] introduced the use of EIS measurements widely to check the damage produced by abrasion action in particular using the Taber test. By using this electrochemical method it is possible to evaluate the damage trend with information about the decrease in protection properties (resistance of coating) and the thickness decrease trend (capacity of coating). The influence of the type of abrasion wheels and imposed weights is easily highlighted. Using EIS measurements and considering the coating resistance as representative of the protection properties of the paint system, to obtain results it is necessary to calculate a threshold value to determine how protective the coating is. Frequently, for normal organic layers, the values of the coating resistance equal to 10^6 Ω cm^2 could be considered as the limit of the protection properties [53]. Using this approach, it is important to introduce the possibility of using the

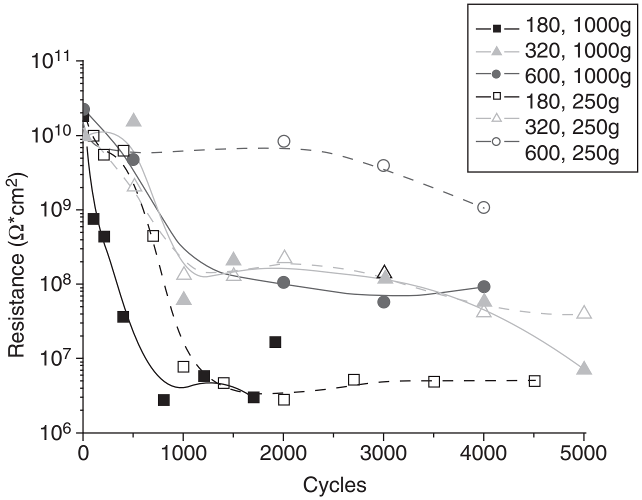


7.10 System to make electrochemical measurement step-by-step in abrasion test.

electrochemical measurements after each abrasion step to obtain useful data about the reduction of the protection properties of the layer as a function of the abrasion test parameters. For this goal it is necessary to formulate a test methodology to make the electrochemical measurements at each abrasion step; after the electrochemical measurement it must be easy to continue in the abrasion action. A new electrochemical cell could be introduced like that shown in Fig. 7.10. Step-by-step the sample is taken from the platform of the Taber test apparatus to carry out electrochemical measurements. It is important that the electrochemical measurements and the contact with the electrolyte do not produce additional damage or modification in the tested paints. It was demonstrated that the EIS measurement results did not influence the damage when a non-aggressive electrolyte is used (Na_2SO_4 for example). In addition, a thermal treatment at low temperature could eliminate the eventuality of water uptake effects [47, 54]. After the evaluation of the damage the sample could be replaced on the Taber apparatus for the following abrasion step.

With this approach, considering the coating resistance, it is easy to obtain information about the damage level of the coating. For example, using rubber wheels and free abrasive it is possible to evaluate the influence of the form of the grains and dimension, the hardness of the abrasives and the imposed weights on the decrease of protection, as shown in Fig. 7.11. More interesting could be the possibility of checking the damage produced continuously during the abrasive action. Nevertheless, it is not possible to obtain good electrochemical data because of the noise produced by the abrasion action during damage steps [49].

Nevertheless, the modification of the Taber test configuration and the use of an abrasive slurry permit us to carry out EIS measurements without moving the coated samples from the abrasion apparatus. There is the possibility of carrying out electrochemical tests more frequently without introducing noise factors. For this purpose it necessary to use a slurry (water and

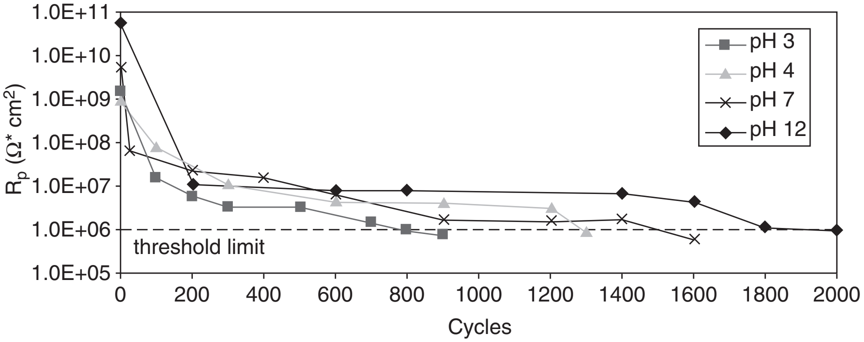


7.11 Coating resistance trend as function of cycles using abrasive means with different dimension of grains (180 320 and 600 mesh) and imposed weight (250 and 1000 g) [47].

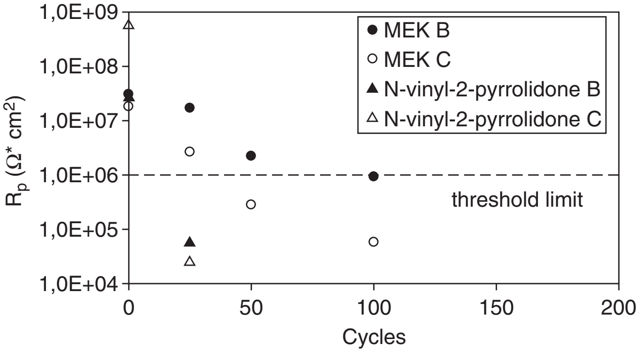
abrasive sand) to allow the electrochemical measurements to be made. A non-aggressive solution such as Na_2SO_4 is indicated. This method allows us to evaluate the abrasion effect of slurry with the presence of different abrasives (natural sands and artificial abrasives) [48,49]. Using this approach it is possible also to consider whether the presence of an aggressive solution (for coating or for metallic substrate) could have an influence on mechanical–chemical degradation phenomena. Considering different slurry solutions, it is possible to check the influence of the pH, the presence of aggressive ions in the substrate, such as chloride ions, or the action of organic solvents that could interact with the coating's organic matrix [55]. For example, Figs 7.12 and 7.13 show the influence on the protection properties of a polyester paint of the pH of the slurry and the effect of different organic solvents (methyl-ethyl-ketone and *N*-vinyl-2-pyrrolidone) on the decrease of properties of the paint.

7.4 Understanding damage morphology

In the abrasion tests the analysis of the damaged surface could provide useful information that is complementary to the electrochemical test data. The damaged area could be investigated using optical and scanning electronic microscopes. The environmental scanning electron microscope is very useful, because it is possible to observe the damaged paint surface without the sample preparation necessary using traditional SEM to create a conductive surface.



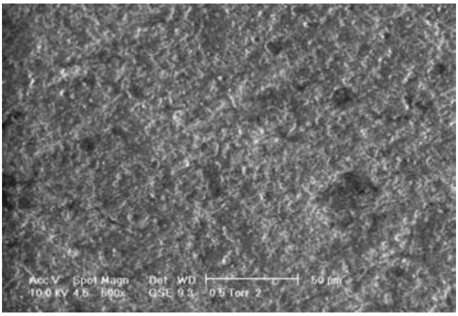
7.12 Trend of coating resistance as function of abrasion cycling for abrasion test using aggressive slurry with different pH [55].



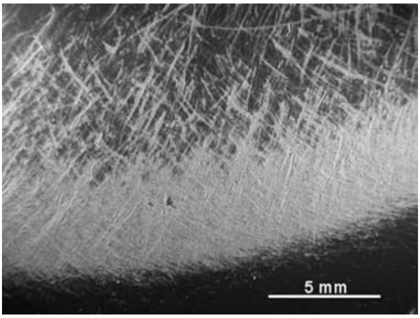
7.13 Trend of coating resistance as function of abrasion cycling for abrasion test using organic ketones [55].

Logically the damage morphology depends on the abrasive system used and the characteristics of the organic coatings tested. Nevertheless it is possible to introduce the same considerations. Using the standard abrasive wheels of the Taber test apparatus a, uniform reduction of the thickness after the first abrasion cycle is produced. Then, after about 1000–2000 cycles an increase of roughness of the sample surface is shown (Fig. 7.14). Frequently at this time the presence of localized defects and scratches is observed, which could reduce considerably the protection properties of the paint. The action of the wheels produces a typical track orientation. In some cases after several cycles it is possible to observe the formation of debris coming from the consumption of the wheels and from the damage to the paint [5]. Finally the consumption of the total thickness of the organic layer is produced in some areas, uncovering the metallic substrate.

The use of abrasive sands or particles produces a different morphology in terms of function of dimension and geometry of the grains. The hardness of



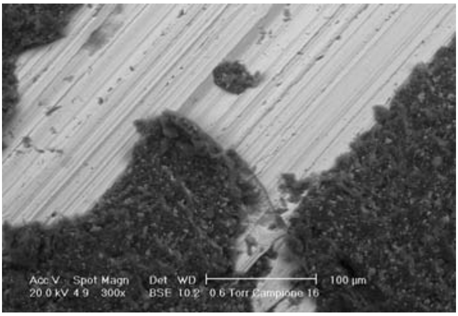
7.14 Abraded surface after 1000 cycles of Taber test (CS17, 1000 g of imposed weight) [5].



7.15 Optical micrograph of abraded sample surface using imposed load of 500 g, after 1100 cycles obtained by modified Taber test using abrasive slurry [49].

sands could be shown to influence the intensity of the damage. Thin sands with round grains produce uniform damage with a constant reduction of thickness. The damage morphology appears similar to those produced using Taber wheels. Increasing the dimension of the grains and using abrasives with sharp edges gives localized damage with the formation of cut and scratches.

This type of wear mechanism, together with the growth of defects, is the main cause of the loss of protection properties of the system. The grains of sand are able to cut and snatch the paint, creating defects in the coating. The resulting abrasion area is not uniform on all surface samples. A small portion of the external zone of the damage produced by artificial sand is uniformly abraded; on the contrary, the internal zone was not uniformly abraded, as clearly shown in Fig. 7.15. The internal zone is the result of the superimposition of grooves with an 'X' shape, caused by the action of the two wheels correlated to the difference of the relative speed between the external and the internal faces of a wheel and the platform. Possibly,



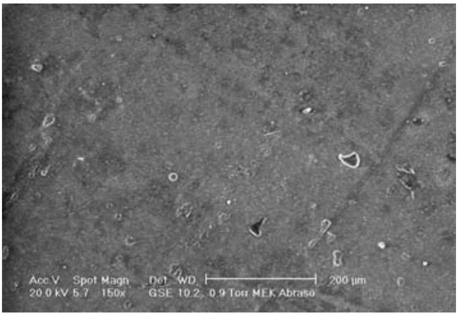
7.16 SEM micrograph of abraded sample surface using imposed load of 500 g, after 1100 cycles obtained by modified Taber test using abrasive slurry [49].

the difference in the damage morphology and extent is due to the different amount of grains of sand in the two zones. In fact, the grains of sand could roll towards the external zone because of the rotation of the platform. Also the effect of the abrasive slurry produces a damage morphology very similar to those produced by the use of abrasive without solution. The thickness of the coating appeared not to be uniform on the abraded track. The bare metal substrate is revealed where the coating is detached by the action of the grains and also the metal substrate was heavily abraded by the sand (Fig. 7.16) [49].

The use of an aggressive abrasive slurry could modify totally the damage morphology. In cases where the solution is aggressive for the substrate, considering the short time of the test, only an acceleration of the protection properties is produced. No change in the damage morphology is evident. Totally different is the case of an aggressive slurry for the organic matrix. This is the case in the use of organic solvents like alcohols or ketones. In this last case the effect on the protection system depends on the chemical interaction between the solution and the organic materials. In some cases it is possible to observe the formation of cracks in the paints, blistering and swelling morphology or localized defects that produce uncovering of the metallic substrate (Fig. 7.17) [55].

7.5 Conclusions

At the end of this chapter it is important to highlight some points about the effects of abrasion action on a protective organic coating system. Mechanical damage on paint could reduce the aesthetic aspect (mar) and the corrosion protection properties. In the literature, several testing methods are introduced and discussed. Besides, it is not easy to compare the experimental data obtained using different tests.



7.17 Abraded surface of samples using organic slurry (MEK) after 50 cycles [55].

The abrasion effect with the loss of protection properties is the most important phenomenon. In the tests used to study the effect of mechanical damage, considering thickness and mass loss, and analysis of the damaged surface, it is not possible to evaluate completely the damage and the loss of protection properties. It is necessary to formulate other methods to correlate the damage with the decrease in protection properties. Using electrochemical measurements and particularly electrochemical impedance spectroscopy, it is possible to highlight the actual damage produced by abrasive action and the decrease of protection properties of the organic coatings. It is possible to evaluate the influence of characteristics of abrasive means (form, granulometry, chemical composition and hardness). In many cases it is necessary to modify the testing apparatus to enable the electrochemical measurements to be made with more accuracy, avoiding noise problems.

Finally, the use of neutral slurry, abrasive means in a solution, or an aggressive slurry for the metal substrate or for organic matter allows us to evaluate the mechanical–chemical degradation phenomenon.

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Part II

Types of organic coating

8

High-performance epoxies and solvent-less epoxies for corrosion protection

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8.1 Introduction

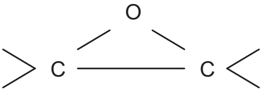
The word epoxy has become synonymous with anti-corrosion in today's industrial environment. Epoxy resin was invented by Dr Castan and Dr Greenlee in 1936 and commercialized in 1948. Since then, every decade has seen the evolution of new applications for epoxy resin, thereby keeping epoxy on a continuous growth path for more than half a century. The reasons for the success of epoxy resin lie in the unique combination of properties that epoxies possess. In the following pages we will look in more detail at the various properties and performance-related attributes of epoxy resin.

8.2 Epoxy basics

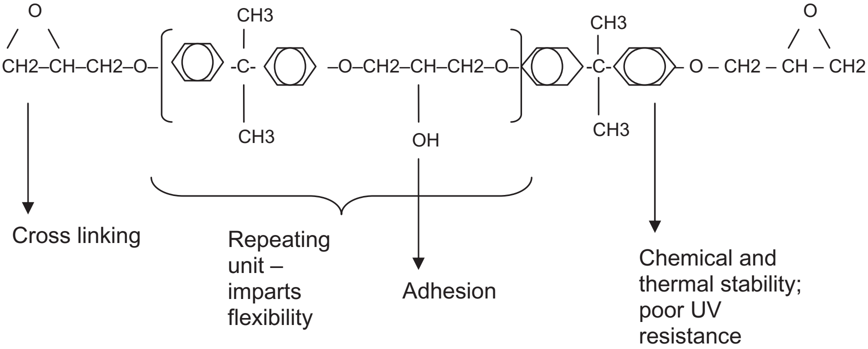
8.2.1 Structure of epoxy resin

Epoxy resin refers broadly to the polymer that contains an epoxide ring (a three-membered ring containing oxygen and carbon, also called an oxirane ring and shown in Fig. 8.1). The three-membered ring requires that the bond angle within the ring be about 60°, which is far from the normal single bond angle of about 109°. These distortions from the preferred bond angle raise the energy of the molecule and also bring the three-membered ring under strain. The strain and the energy together make the oxirane ring very active and cause it to undergo often exothermic reactions with a number of functional groups.

There are a number of curing agents available to react with the epoxide group. The most common of them are amines, mercaptans, amides, phenols, isocyanates, anhydrides, acids, etc. Many of these curing agents start reacting immediately as soon as they are mixed with the epoxy resin and the reaction proceeds rapidly even at room temperature.



8.1 Epoxide ring.



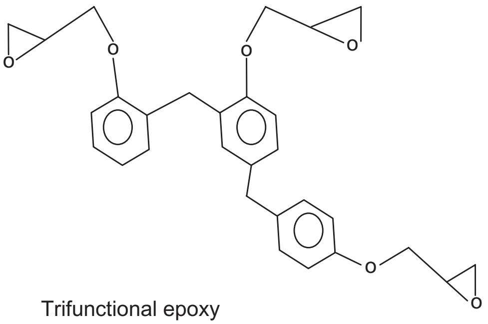
8.2 Basic structure of DGEBA.

The most commercially important liquid epoxy resin is diglycidyl ether of bisphenol-A (DGEBA). It is prepared by reaction of epichlorohydrin (ECH) with bisphenol-A (BPA) using base catalyst. Figure 8.2 gives the basic structure of DGEBA. In basic liquid epoxy resin ideally the value of repeating unit '*n*' should be zero. In practice it is observed that the basic liquid resin is a mix of predominantly monomer with $n = 0.15$ indicating the presence of some proportion of dimer and trimer in the basic liquid resin.

The higher molecular weight BPA based epoxy resins are made by oligomerizing DGEBA with an additional quantity of BPA using a catalyst such as triphenyl phosphine. This process is also called the advancement process. Above epoxy equivalent weight (EEW) of about 230 the product becomes semi-solid and at about 400 the product turns to low molecular weight solid.

The resins discussed above are essentially bifunctional. It is possible to make multifunctional epoxy resin, which has its own advantages over standard BPA based resins. To make these multifunctional resins ECH is reacted with phenol-novolacs to give epoxy phenol novolac resin. These resins tend to be highly viscous and are employed when high chemical resistance of an ambient cured coating is required. Figure 8.3 gives the representative structure of trifunctional epoxy resin.

Many other modified epoxides are made by using different chemistries and find use in various applications including UV cured coatings, UV resistant coatings, insulating coatings, anti-corrosive coatings, underwater coatings, castings, encapsulants, fire resistance, high thermal resistance, laminates, etc.



8.3 Trifunctional epoxy resin structure.

8.2.2 Characteristics of epoxy resin

The reasons for the widespread use of epoxy resin lie in the following attributes:

- *Easy cure*. Epoxies can be cured quickly and easily at practically any temperature between 10°C and 200°C depending upon the choice of curing agent.
- *Low shrinkage*. One of the most advantageous property of epoxy resin is their low shrinkage during cure. No by-products are generated and no water is evolved and hence very little molecular rearrangement is involved during curing.
- *High adhesion*. Due to the presence of polar hydroxyl group and ether linkages, epoxy resins are excellent adhesives. The low shrinkage during curing also helps to minimize the distortion of the surface contacts.
- *Thermal stability*. In general the presence of aromatic groups in the cured resin network tends to increase the thermal stability, the cyclic structure being most stable, the linear next and the branched the least stable of all in terms of weight loss. The ether links and ester links are relatively good in terms of thermal stability.
- *Good chemical resistance*. Those factors tending to promote thermal stability also tend to improve chemical resistance. The ether linkages are fairly stable; the aromatic structure improves further the chemical resistance. In general most epoxy resins possess extremely high resistance to caustic and good to excellent resistance to inorganic acids and fair to good resistance to organic acids. Outstanding chemical resistance can be obtained by selective choice of materials.
- *Versatility*. Epoxy can be modified in different ways to alter and improve certain properties just by blending or by chemically modifying.

Apart from the above, the epoxies also possess other properties like high mechanical strength, good electrical insulation, water resistance, serviceability at wide temperature range, and ease of handling and processing.

The epoxy resins, first successfully commercialized in the late 1940s, were based mainly on bisphenol-A. Today, although the majority of successful epoxy coatings are still based on the bisphenol-A resins, many improvements have been made by chemically modifying the basic resin and by the use of new curing agent and coreacting resins.

8.2.3 Types of epoxy resin

There are various types of epoxies. The major types are:

- Bisphenol-A based epoxy resin
- Bisphenol-F based epoxy resin
- Multifunctional epoxies:
  - Epoxy phenol novolac
  - Epoxy cresol novolac
  - Epoxy bisphenol novolac
- Cycloaliphatic epoxy resin:
  - Hydrogenated BPA based epoxy resin
  - Hexahydrophthalic anhydride based epoxy resin
  - Cyclohexane based epoxy resin
- Fire retardant epoxies:
  - Halogenated (brominated) epoxy resin
  - Halogen-free epoxy resin
- Modified epoxy resin:
  - Dimer acid modified epoxy resin
  - CTBN modified epoxy resin
  - Silicone modified epoxy resin.

The epoxy resins, being thermoset in nature, cannot be used alone. They require what is called a hardener to effect the curing of the coating and conversion of the coating into a useful protective yet aesthetically appealing film.

8.3 Curing agents

Curing agents form another important part of any epoxy based coatings. As seen earlier, the bonds in the epoxide ring are under constant strain and make an epoxide ring very active. This gives a wide choice of curing agents for curing the epoxy resin.

8.3.1 Types of curing agents

Some of the common curing agents are:

- Base curing agents:
  - Lewis bases (R3N:), e.g. pyridine, triethylamine
  - Inorganic bases, e.g. caustic soda
  - Aliphatic amines, e.g. diethylene triamine
  - Amides, e.g. polyamide 115, polyamide 125
  - Cycloaliphatic amines, e.g. isophorone diamine
  - Aromatic amines, e.g. diamino diphenyl methane
- Acid curing agents:
  - Lewis acids, e.g. BF3 etherate
  - Phenols, e.g. bis-phenol
  - Organic acid, e.g. salicylic acid
  - Anhydrides, e.g. phthalic anhydride
- Coreacting resins:
  - Phenol-formaldehyde resin
  - Urea-formaldehyde resin
  - Acrylic oligomers, etc.

8.3.2 Characteristics of some of the curing agents

Phenol formaldehyde (PF) resin

PF curing agents provide the maximum in chemical and abrasion resistance obtainable with DGEBA coatings and superior elevated temperature performance but with discoloration. They are used mostly in corrosion resistance for piping, wire coating, electrical varnishes, collapsible tube coatings, lining for drums, can coatings, etc. PF resins are somewhat sluggish in reactivity and need a catalyst or an increase in cure temperature to attain the full cure of the system with acceptable reaction rate.

Amino resin

The amino resin epoxy coating is used in the appliance and automobile industries, drum linings with UF/epoxy systems giving the best color and MF/epoxy systems providing excellent toughness. These are well suited to fulfill the stringent requirements for metal can and drum linings and chemically resistant tank linings. The amino resins provide finishes with outstanding detergent resistance. High MW epoxy resins are used to provide the exceptional flexibility and solvent resistance needed in these coatings.

Epoxy ester

The properties of epoxy esters depend upon the molecular weight of fatty acid, the type of modifying acids, and the degree of esterification of the epoxy and hydroxyl groups in the epoxy resin. The important epoxy esters are almost always based on the solid type of epoxy resin. The versatility of esters makes them suitable for a wide variety of end uses. These are employed as metal primers, floor coatings, air dry maintenance finishes and appliance enamels. These resins show overall good performance in terms of gloss, adhesion, toughness, flexibility and durability, but not in terms of alkali resistance.

Polyamide

The fatty polyamides are generally considered to offer several advantages over the primary aliphatic polyamines, including higher flexibility and impact resistance even after aging. Additionally, fatty polyamides render the films to adhere well on wet and tightly rusted surface. Humidity and surface preparation are thus somewhat less critical. Other advantages over amines include improved moisture resistance, better blush resistance and very low or no irritation. On the other hand, polyamides show somewhat reduced solvent, fuel and alkali resistance compared to amines.

Polyamine

Polyamines are preferred over amides when chemical or solvent resistance is sought. Unless proper stoichiometry is used, they provide films with poor resistance to water and tend to be sensitive to high humidity during cure and produce rather brittle and inadequately cured films at lower ambient temperatures. Full room temperature cure will be obtained in about 7 days at 25°C or above.

Aliphatic polyamines are irritating and can cause sensitization by skin contact. They are also prone to blush by reaction with moisture and carbon dioxide in the air during curing and give finishes with reduced gloss in humid conditions. Aliphatic polyamines are good for solvent and chemical resistance. To overcome the drawbacks of aliphatic polyamines, amine adducts were developed. These adducts have more convenient mixing ratios. They are also low in irritation and gives improved compatibility with epoxy resin and hence better blush resistance.

Another class of amines is aromatic amines. These are normally considered suitable for curing at elevated temperature but by catalyzing with suitable catalyst it can be made to react at ambient temperature. However, the films tend to be darker in color and with reduced flexibility. Certain aromatic amines have acquired a bad name in the market due to health hazards associated with their use.

Generally little excess of amine curing agent over the stoichiometry amount is used. At below the stoichiometric amount poor solvent resistance and flexibility are obtained.

8.4 Epoxy reactive diluents

An epoxy system cannot become complete unless this very important part is considered. Epoxy, being viscous in nature, needs to be diluted further, not only for ease of processing, but also for ease of application. The simplest way to dilute an epoxy resin is to add solvent in the composition. This is one of the easiest ways to reduce the viscosity of epoxy resin. Its drawback is that it increases the volatile organic content of a composition and hence it is not a preferred choice nowadays. Another way to reduce the viscosity is by the addition of diluents.

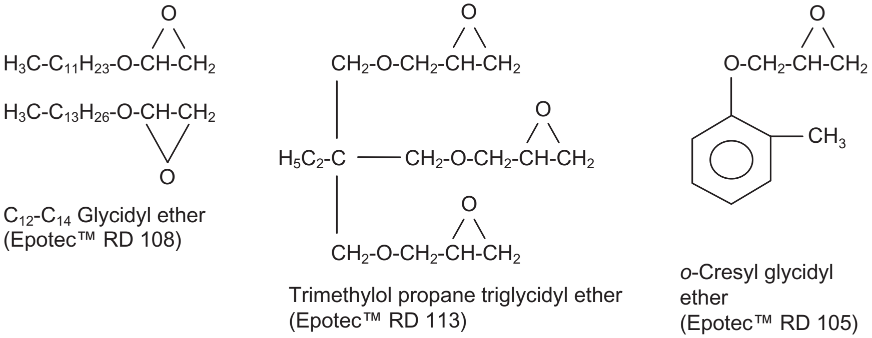
Diluents are low molecular weight, low viscosity, high boiling entities. Diluents, especially non-reactive diluents, are similar to solvents but do not have volatility similar to solvents. There are two main types of diluents:

- Non-reactive diluents
- Reactive diluents.

As the name indicates, non-reactive diluents are those without any functionality. They reduce the viscosity due to their own low viscosity and impart flexibility to a certain extent. They have high boiling points and do not evaporate easily. In most cases over a period of time these non-reactive diluents migrate slowly to the surface and are lost from the coated film, thereby rendering the film brittle. Examples of this type of non-reactive diluents are benzyl alcohol, dibutyl phthalate, dioctyl phthalate, etc.

Unlike non-reactive diluents, the epoxy reactive diluents contain functional group(s) like epoxy resin. These diluents are produced by epoxidation of alcohols and polyols. They react in a similar way to epoxy resin with the curing agent used in the composition and become an integral part of the cured film. The advantage of this type of diluent is that the flexibility they offer is permanent, so that once incorporated they remain in the cured film throughout its life. Figure 8.4 shows some of the common epoxy reactive diluents used in coatings.

The viscosity reduction efficiency of different reactive diluents is different. Some reactive diluents, such as butyl glycidyl ether (BGE), are very effective in cutting the viscosity, but they also tend to alter the solvent and chemical resistance properties and T_g, on the downside when used beyond a limit; on the other hand some reactive diluents, such as trimethylol propane triglycidyl ether (TMPTGE), though not as effective in reducing



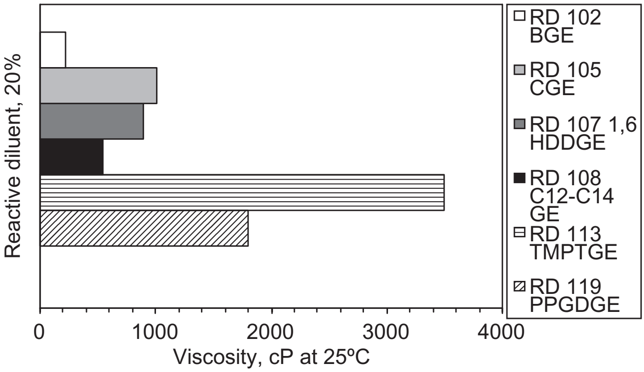
C_{12}-C_{14} Glycidyl ether (Epotec™ RD 108)

Trimethylol propane triglycidyl ether (Epotec™ RD 113)

o-Cresyl glycidyl ether (Epotec™ RD 105)

Epotec™ is a trade mark of Aditya Birla Chemicals (Thailand) Ltd.

8.4 Common epoxy reactive diluents.



Viscosity at 25°C (77°F) – Epotec™ resin YD 128 + 20% Epotec™ reactive diluent
Epotec™ is a trade mark of Aditya Birla Chemicals (Thailand) Ltd.

8.5 Effect of epoxy reactive diluents on viscosity of epoxy resin.

the viscosity as BGE, tend to offer better crosslink density and minimal reduction in T_g with better overall resistance properties.

Figure 8.5 gives a representative comparison of viscosity reduction of DGEBA by some common reactive diluents. These data have been collected from the study report generated by Thai Epoxy and Allied Products Co. Ltd.

8.5 Corrosion

All corrosion of metals, with the exception of direct chemical attack, is caused by the formation of local galvanic cells. To prevent corrosion it is therefore necessary to prevent the formation of these cells. This can be achieved in the following ways:

- by avoiding differences in the potential in the metal by removing mill scale and other foreign matter;
- by avoiding the formation of electrolyte by protecting the metal with a tough, durable and chemically resistant coating having the highest electrolytic resistance and lowest permeability;
- by avoiding reaction on the anode or cathode by incorporating rust-inhibiting compounds.

In coatings clear varnishes based on DGEBA type epoxy resins are seldom used for corrosion resistance because their outdoor durability is limited. Clear, water white systems can be developed but these systems discolor and show chalking, fading and gloss reduction tendency when exposed to UV radiation. Therefore, most of the epoxy coatings, except for electrical varnishes and wire coatings and some special coatings, are pigmented. In addition to improving stability against UV, the pigments also provide hiding, color, abrasion resistance and anti-corrosion properties.

Two package epoxy coatings are known to give long-term protection to a variety of substrates even when exposed to aggressive environments. This high performance is obtainable only when proper surface preparation is done.

8.6 High-performance coatings

8.6.1 General purpose maintenance paint

Adhesion of general maintenance coatings on steel over mill scale or a smooth surface is inferior. Hence commercial blast cleaning is advised as a surface preparation. For highly corrosive environments or in immersion service, blast cleaning to white metal is always recommended. Table 8.1 gives guidelines for the formulation of general purpose maintenance coatings.

8.6.2 High solids/high build epoxy coating

Organic coatings in solvents have attractive features in dry film properties. They are also simple to manufacture and can be applied with standard equipment with relative ease. Solvents also offer a versatile tool in the hands of a formulator.

The ever-increasing pressure to reduce the volatile organic content in a coating has led formulators to develop high solids coatings. Though no concrete definition exists, most term a coating as high solids when the volume solids in the composition are more than 70%. The basic approach to high solids coatings is to use epoxy resin of lowest possible viscosity meeting the quality parameters. The better option for this could be

Table 8.1 General maintenance paint formulation

Material	Pbw
Base resin Part A	
Epotec™ YD 011X75*	180
TiO_2	50
$BaSO_4$	50
Phthalo. Blue	1
Methyl ethyl ketone	18
Xylene	32
Ethoxy ethanol	45
Leveling agent	1
Curing agent Part B	
Polyamide 115	40
Xylene	40
Properties	
% Non-volatiles	59
Pigment : binder ratio	0.47
PVC	14

* Product of Aditya Birla Chemicals (Thailand) Ltd.

bisphenol-F based low molecular weight epoxy resin as it has half the viscosity of comparable bisphenol-A based resin, but cost prevents the wide use of this resin. The viscosity in solution of standard bisphenol-A epoxy resin can be substantially reduced by modifying the bisphenol-A diepoxide resin with dimer acids. In theory two molecules of diepoxide resin can be joined with one molecule of dimer acid. The product so formed gives excellent flexibility. Automotive primers can be made from this resin by combining with thermosetting acrylics. Table 8.2 gives guidelines for the formulation of high solids primer coatings.

Thermosetting acrylic resin oligomer with molecular weight 1000–1500 and with pending carboxylic groups can be crosslinked with liquid epoxy resin. The products are generally formulated and applied at much higher solids level, about 70–90%, than normal.

The amine cured epoxy coatings are designed to give dry film thickness of 2–3 mils without sagging. To obtain higher build maintenance coatings with dry film thickness in the range of 8–10 mils it is common practice to increase both the extender level and the thixotrope additive level. Alternatively another route to improve the anti-sagging behavior at higher thickness is by replacing part of the liquid epoxy or low molecular weight solid epoxy binder with higher molecular weight epoxy resin; this change also hastens the dust-free time of a coating.

Table 8.2 High solids coating formulation

Material	Pbw
Base resin Part A	
Epotec^{TM} YD 274MX-90*	100
TiO_2	30
$BaSO_4$	90
Curing agent Part B	
Epotec^{TM} TH 7555*	35
Xylene	17
Properties	
% Mass solids	90
% Volume solids	83
PVC	17
VOC	170 g/l

*Product of Aditya Birla Chemicals (Thailand) Ltd.

High solids compositions based on cycloaliphatic epoxy resin can also be made. In cycloaliphatic epoxy resins the good flexibility, adhesion to various substrates, chemical resistance qualities, etc., of bisphenol-A epoxy resin are retained. Additionally the drawbacks associated with bisphenol-A based epoxy resin of poor gloss retention, severe chalking, cracking and yellowing tendency or color instability of the film upon exposure to weather, especially sunlight, have almost been overcome. This change was made possible by the presence of the cyclohexane ring, instead of the unsaturated aromatic ring of bisphenol-A, in the cycloaliphatic epoxy resin. Another advantage claimed for cycloaliphatic epoxy resin is that the resin has better solubility in solvents, which allows increased solid contents in a coating composition.

8.6.3 Marine coatings

Coatings used in the shipping industry arguably face some of the harshest conditions a coating manufacturer can imagine. The coating here is not only required to protect the base metal, i.e. mild steel, which remains the material of choice to build the vessels, but it also has to withstand abuse from handling container cargo, spillage of chemicals and other crude minerals, the weather – sun, rain and temperature fluctuations – salty and oily water splash, etc. Epoxy coatings have become the industry standard in this segment owing to their excellent resistance to chemicals, corrosion protection and adhesion qualities. Epoxies are widely used in this segment for primers and undercoats as well as maintenance coats.

Table 8.3 Coal-tar epoxy formulation

Material	Pbw
Base resin Part A	
Epotec^{TM} YD 128*	50
Curing agent Part B	
Coal-tar	50
Polyamide 140	30
Xylene	48
Magnesium silicate	95
Ethanol (95%)	5
Bentonite (10% in xylene)	6
Properties	
% Non-volatile	84
Pigment : binder ratio	0.54
PVC	16

* Product of Aditya Birla Chemicals (Thailand) Ltd.

Coal-tar epoxy coating is an example of a high-build heavy-duty epoxy coating. The tar and bitumen derivatives have long been used for the protection of steel and wood, especially when the structures are submerged or buried. Normally the harder versions of tars are preferred over the softer grades to get optimum hardness and scratch resistance. These systems are applied in two layers to get a final thickness of around 350–400 microns. They are widely used for offshore and marine maintenance where resistance to fresh as well as salt water and mineral acids is important. These coatings find use as internal linings for crude oil storage tanks, tanks for untreated water as well as sea water, ballast tanks of ships, underwater hulls of ships, etc. Coal-tar epoxy coatings also find extensive use on sewage water lines and industrial effluent treatment facilities. These coatings find limited usage where solvent/fuel resistance is required, since the solvent/fuel can attack and dissolve part of the coating, making it unsuitable for use. Table 8.3 gives tar-based epoxy coating formulations.

Offshore coatings are similar to marine coatings except that unlike shipping vessels the offshore platforms, once fixed to the sea bed, will not return to the shore for dry docking and maintenance. Hence in these cases special high-build epoxy coats are used.

8.6.4 Baking-type epoxy coatings

Thermally (heat) cured coatings of excellent quality can be made from blends of epoxy resin with phenolic or amino co-curing resins. These coat-

Table 8.4 Epoxy-phenolic resin coating formulation

Material	Pbw
Base resin Part A	
Epotec™ YD 019*	110
Butyl cellosolve	90
Xylene	90
Curing agent Part B	
Phenolic resin (80% in *n*-butanol)	45
Silicone-based leveling agent	2.5
Ethoxy ethyl acetate	25
Xylene	25
Phosphoric acid (85%)	2.6
n-Butanol	25
Properties	
% Non-volatile	35
Epoxy : phenolic ratio	75 : 25
Curing schedule	200°C pmt for 10–15 min

* Product of Aditya Birla Chemicals (Thailand) Ltd.

ings give high resistance to solvents, chemicals and temperature and high flexibility. Generally, phenolic resins are said to give maximum resistance to chemicals. The coatings made with these resins are tough but tend to be yellow-brown in color. On the other hand amino resin will give coatings with excellent flexibility and clarity. Table 8.4 gives details of baking-type epoxy-phenolic coatings for drum lining.

Thermoplastic epoxy resins of very high molecular weight can also be made. These resins are termed phenoxy resins and are generally available in solution form. They require no curing agent to give useful films. Coatings based on these resins dry solely by solvent evaporation. These resins have molecular weights ranging from 25 000 to 300 000 or more. These resins when used as primer or base coat can be overcoated with two-pack epoxy top coat without loss of adhesion. The thermoplastic epoxy resins are especially suitable for primers of the zinc-rich type. These primers are generally used in maintenance systems, marine applications, automotive coatings and shop primers for structural steel before fabrication. Table 8.5 gives details of zinc-rich epoxy primers.

8.7 Solventless epoxy systems

Solvent in a formulation is required to facilitate processing and application. It has been proved that by using low molecular weight resin entities it is

Table 8.5 Zinc-rich epoxy primer formulation

Material	Pbw
Base resin Part A	
Zinc dust	730
Epotec™ XYD 66 (50% NV)*	165
Bentone	5
Butyl cellosolve	60
Aromatic solvent	40
Properties	
% Non-volatile	80
Pigment : binder ratio	8.9

* Product of Aditya Birla Chemicals (Thailand) Ltd.

possible to formulate a system free of solvent. This absence of solvent means that much higher film thickness can be applied without worrying about solvent entrapment. On the other hand removal of solvents altogether increases the concentration of reactive ingredients and reduces the pot life. In practice these systems are restricted to flooring and other civil engineering applications.

Epoxy resins can provide a tough, wear-resistant top covering for concrete flooring. One can get the advantage of dust proofness, high gloss, wear resistance, chemical resistance, ease of cleaning, oil resistance, etc., in addition to choice of colors and choice of gloss. Another advantage of epoxy flooring that appeals most to the pharmaceuticals processing and food processing industries is its ability to form seamless floors. The elimination of seams that are normally present when a floor is made from tiles has rendered the floor hygienic by avoiding accumulation of dirt, dust and growth of micro-organisms on the surface.

The thick epoxy floor coatings provide excellent resistance to wear and obliterate and fill surface imperfections, cracks and dents, making the floor smooth and giving a pleasing appearance. They also give better performance compared to concrete in terms of fast cure, toughness, chemical resistance, etc.

8.7.1 Self-leveling epoxy flooring

Seamless self-leveling floors are based on liquid epoxy resin reduced in viscosity by addition of diluents, especially reactive epoxy diluents. The common hardeners for this application are polyamide resin, aliphatic/cycloaliphatic amine or amine adducts. They may be used at a thickness of 0.5

Table 8.6 Self-leveling epoxy flooring formulation

Material	Pbw
Base resin Part A	
Epotec™ YD 515*	100
Color paste (epoxy based)	5
Quartz sand	300
Air release agent	2.5
Leveling agent	3.5
Curing agent Part B	
Epotec™ TH 7301*	58
Properties	
% Non-volatile	100
Application thickness	1–3 mm
Thin film set time	4 h
Pot life	40 min
Hard dry	Overnight
Full cure	7 days at 25°C
Hardness (Shore D)	80

* Product of Aditya Birla Chemicals (Thailand) Ltd.

to 3 mm and give excellent adhesion to varied substrates like concrete, brick, stone and metal. Table 8.6 gives the starting formulation for self-leveling flooring.

8.7.2 Heavy duty epoxy mortar

In addition to the properties discussed earlier, industrial epoxy floors are required to give high compressive strength, wear resistance and chemical resistance too. Industrial epoxy floors, sometimes also called epoxy concrete, are filled heavily. The selection of silica size is very important to get maximum compressive strength and optimum trowelability. Generally a mix of different size silica is used to reduce the voids and increase the compressive strength. The systems are viscous and are usually applied by troweling. They can be applied at high thickness and there is absolutely no shrinkage; at the same time good adhesion and service are obtained for many years. Table 8.7 gives guidelines for the formulation of the mortar coat.

8.7.3 Anti-static epoxy flooring

Electrostatically conductive or electrostatic dissipative floors are used in specific applications where discharge of static energy may create a

Table 8.7 Industrial epoxy mortar coat formulation

Material	Pbw
Base resin Part A	
Epotec^{TM} YD 522*	100
Quartz sand (depending upon sand size)	600–900
Air release agent	3.5
Leveling agent	3.5
Curing agent Part B	
Epotec^{TM} TH 7905*	40
Properties	
% Non-volatile	100
Pot life	20
Hard dry	4 h
Full cure	7 days at 25°C
Hardness	83
Compressive strength	800 kg/cm^2

* Product of Aditya Birla Chemicals (Thailand) Ltd.

dangerous situation. These systems are generally used in the electronics industry and electronic goods assembly lines. They are made by using conductive filler such as coarse carbon black, copper powder, aluminum flakes, etc. The proportion of conductive filler is adjusted in such a way that the conductive particles remain in contact with each other and can discharge the charge, if generated, to the earth.

8.7.4 Radiation cure coatings

Radiation cure is the newest technology used for curing epoxy coatings. Epoxy resin can be radiation cured in two different ways:

- by photoinitiated cationic polymerization
- by a free radical mechanism.

Radiation cure provides benefits in terms of super-fast cure rate, energy savings, zero volatile organic content, cost efficiency in mass production, productivity, etc. On the other hand this technology has certain limitations. Being a new technology, it requires special curing equipment whose initial cost is higher. There are also restrictions on the usage level of colorants and fillers. For UV curing the film thickness and the pigmentation level must be low.

In free radical polymerization, epoxy diacrylate resin produced by reacting liquid epoxy resin with acrylic acid is used. This resin has fast cure speed

Table 8.8 Overprint varnish formulation

Material	Pbw
Base resin Part A	
Epotec^{TM} TAC 1261-20*	44
Epotec^{TM} TAC HDDA*	31
Epotec^{TM} TAC TMPTA*	4
Benzophenone	6
CN 386	10
Bentone	0.5
Properties	
Viscosity	730 cP
Thickness	5 μm
Cure speed	50 m/min
Appearance	Glossy

* Product of Aditya Birla Chemicals (Thailand) Ltd.

and gives films with excellent resistance to acids and solvents. It is used to produce materials such as UV curable printing inks, screen inks, wood coating, overprint varnishes for paper coating, coatings for flexible PCB and electronic components. These systems are required to add photoinitiators, which absorb the UV light, generate the free radical and initiate the cure of the coating. Though the free radical initiates the curing reaction, the propagation of the reaction occurs only in a limited area. Not only does this limitation make the coating composition use extra quantities of photoinitiator, but it also becomes essential that the entire coating area sees UV light. Any coated area not exposed to UV light may remain uncured. Table 8.8 gives the indicative formulation for OPV coating.

In cationic coatings, cationic photoinitiators such as diazonium salts, iodonium salts and sulphonium salts are used to effect the curing. Cationic coatings do not show the air inhibition during curing that is generally shown by free radical curing systems. The curing in cationic coatings once initiated continues even in the dark. Almost all types of epoxy resins can be cured cationically but cycloaliphatic epoxies show faster curing rates and hence are preferred.

In the electron beam (EB) curing technique the high energy electron beam generates free radicals which then propagate the reaction. These systems do not require additional photoinitiators to effect the curing. This is a very versatile technique and can cure any coating system irrespective of thickness, pigmentation level, temperature, substrate, etc.

8.7.5 Powder coating

Powder coating could be another important type of 100% solids coating. It is well known that solid epoxy resins, especially type 3 and type 4 resins, are used extensively to make decorative as well as functional powder coatings. Many things could be written on this exotic type of coating but it is beyond the scope of this chapter.

8.8 Epoxy waterborne coatings

After initial setbacks due to inferior performance of waterborne coatings, this technology has now acquired some ground and is showing promise as a coating of the future. This change has occurred due to the developments that have taken place in this technology to improve the performance to meet the expectations of customers and to make epoxy waterborne coatings comparable to solvent-based coatings. This has taken place partly also due to the sustained pressure from various government bodies and policies to reduce the volatile organic content.

The so-called fourth generation products now available give excellent salt spray resistance, adhesion and mechanical properties, with drying comparable to solvent-based coatings but at the same time having sufficiently longer working times. These are used nowadays to make anti-corrosive coatings, industrial maintenance paints and marine coatings. They are also used to make thick self-leveling/trowelable floor toppings, especially for floors that need water vapor permeability to avoid developing water vapor pressure beneath the coating layer. These special systems are called breathable coatings by some and also can be used on green concrete without loss of adhesion. Table 8.9 gives the water-based epoxy flooring composition.

Another very successful use of waterborne epoxies for coatings is to make electrodeposition (ED) paints. These are a special type of paint used as a first/primer coat on each and every automobile body coming out of the original equipment manufacturer's shop floor. These coatings are known to give excellent corrosion resistance but are relatively soft and cannot be built beyond a certain thickness due to application technique. Thus they need to be further coated with hard primer coats. The cathodic ED paints have now replaced the anodic ED paints, owing to their better throwing power and superior corrosion resistance. The cathodic ED coatings also do not attack the metal and avoid discoloration problems.

8.9 Summary

The basic epoxy resin technology has now become a matured technology. It has evolved over the last six decades and has developed a variety of

Table 8.9 Water-borne self-leveling epoxy flooring formulation

Material	Pbw
Base resin Part A	
Epotec™ THW 4501*	11.5
TiO_2 rutile	6
$CaCO_3$	15
Silica floor M10	15
Silica sand M32	35
De-foam agent	1
Air release	1
Water	10
Curing agent Part B	
Epotec™ YD 128*	10
Water	7.7
Properties	
% Water	15
Pigment : binder ratio	4.2 : 1
Hardness (Shore D)	75
Appearance	Matt finish

* Product of Aditya Birla Chemicals (Thailand) Ltd.

epoxidized materials from oils, glycols, alcohols, phenols, dimer acids, etc. Starting with a small volume of a few thousand tons, the production of epoxy has today reached 1.8 million MT and is growing. Its applications have also diversified from dental filling material to coatings, composites, electrical insulation, adhesives and civil engineering applications, the latest being waterborne and radiation cure applications. Epoxies offer great versatility in formulating and curing and can be formulated with a wide choice of curing agents.

Epoxies have adapted to the changing industry norms, especially in terms of VOC and other regulations, thereby giving formulators a free hand in formulating either solvent-based or high solids or even solvent-free high performance compositions. Epoxies have also been developed to meet the needs of waterborne and acrylated materials, as well as for coatings that come into contact with food and potable water. It will be interesting to see the impact of the new EU regulation for Registration, Evaluation, Authorisation and Regulation of Chemicals (REACH) that came into force in mid-2007.

Nanotechnology is yet another area where the technological advantages and advancements in material sciences can be combined and put to use in enhancing and enriching the characteristics and performance of epoxy resin. Undoubtedly, epoxies are here to stay and are expected to grow in the coming years both in current applications and also by exploring and entering into newer end uses.

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9

Polyester coatings for corrosion protection

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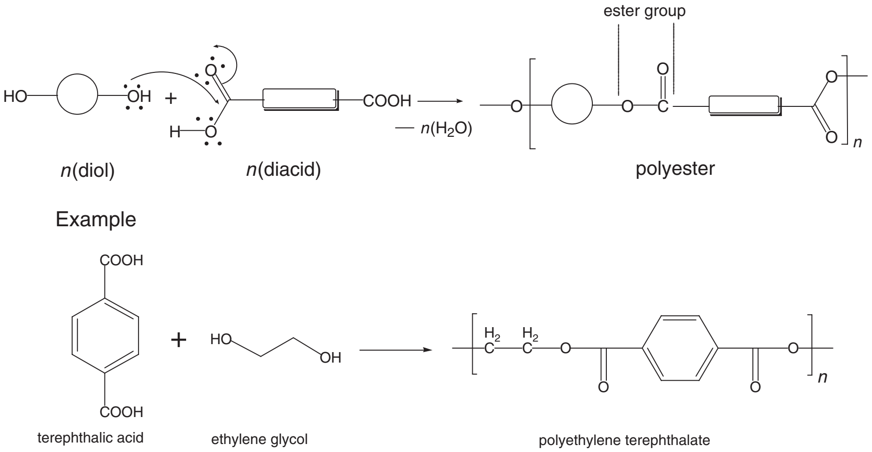
9.1 Introduction

Paints are industrial products mainly used for the protection of objects from destructive external attacks and for decoration. The basic components of paints are vehicle (binder), solvents, pigments and additives. Among different binder systems used in coatings, saturated polyester resin is one of the most widely used. The design of macromolecular architecture using unique combinations of monomers is an important and challenging topic that is being explored by many researchers for the development of coatings with improved mechanical properties. The overall intent of this chapter is to provide information on different saturated polyester coatings used for high performance applications.

9.2 Polyester resin

The term polyester is typically reserved for acid and hydroxyl functional polyester resins that are relatively free of oil moieties. These resins are mainly prepared from the reaction products of polyhydric alcohols with dibasic or tribasic acids or anhydrides (Fig. 9.1). Condensation reaction produces an ester functional group in its main chain. Therefore, the family of polyesters comprises all polymers with ester functional groups in the polymer backbone. With the number of hydroxyl and carboxyl groups on each molecule and possible lengths of these molecules, a great deal of diversity is possible. Condensation polymerization, a form of step-growth polymerization, is a process by which two molecules join together, with the loss of a water molecule (no loss of water with anhydrides) [1]. The type of end product resulting from a condensation polymerization, as well as their stereochemical arrangement in 3D space, is dependent on the type of monomers and number of functional end groups of the monomer used in the preparation of polyester. Therefore, the chemistry of the structural units connecting the ester groups can be varied over an immensely broad



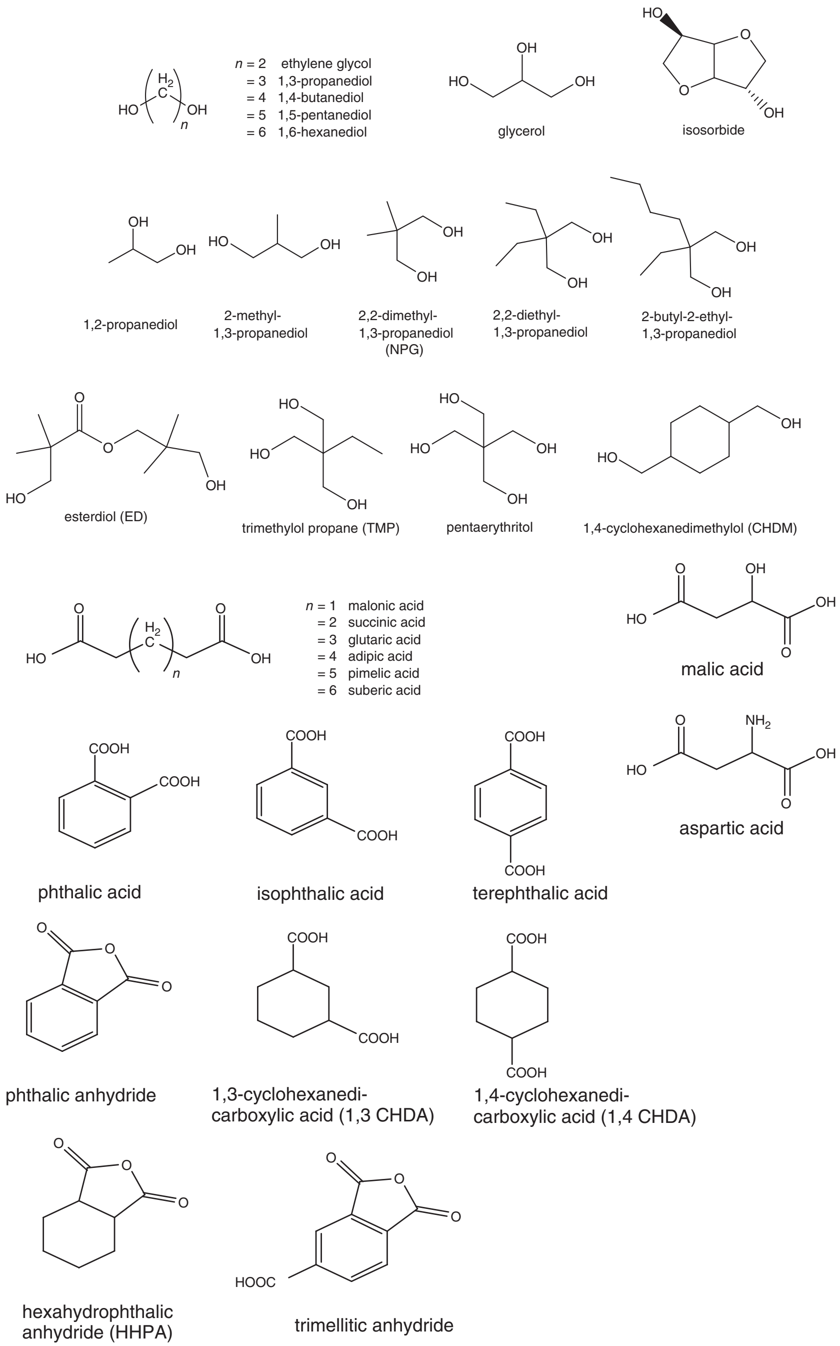
9.1 Synthesis of polyester resin.

range, making the polyesters a diverse group for coating applications. Synthesis of aliphatic polyesters by polycondensation of diols with dicarboxylic acids traces back to Carothers' work in the 1930s. However, the low melting points inherent to aliphatic polyesters, together with the difficulty in obtaining high molecular weight polymers, had prevented wide usage of aliphatic polyesters as polymeric materials for a long time [2, 3]. Later on, with the advent of new monomers and synthetic protocols, the synthesis of tailor-made polyester resins and their application span in coatings increased.

9.3 Raw materials and reactions

The structure of the polyester can be varied by the ratio of di-, tri- and tetra-functional monomers and degree of conversion. The polyester is either acid-functional or hydroxy-functional depending on the mole ratio of the ingredients used. The composition of the di/tri-functional monomers can be varied perpetually, allowing the structure and properties of the resulting polyesters to span over a very broad range [1, 4]. Diacids and diols used for the preparation of polyester resins are far too plentiful to be mentioned here. Nevertheless, some structurally relatively simple diacids, diols, tri- and tetra-functional monomers widely used in the coatings industry are shown in Fig. 9.2.

Some of the most common glycols or polyols used for polyester preparation are ethylene glycol, 1,3-propanediol, 1,3-butanediol, 1,4-butanediol, 1,2-propylene glycol, 1,6-hexanediol, 1,5-hexylene glycol, isosorbide, esterdiol, styrene glycol, bisphenol A, oligo(ethylene glycol)s, neopentyl glycol



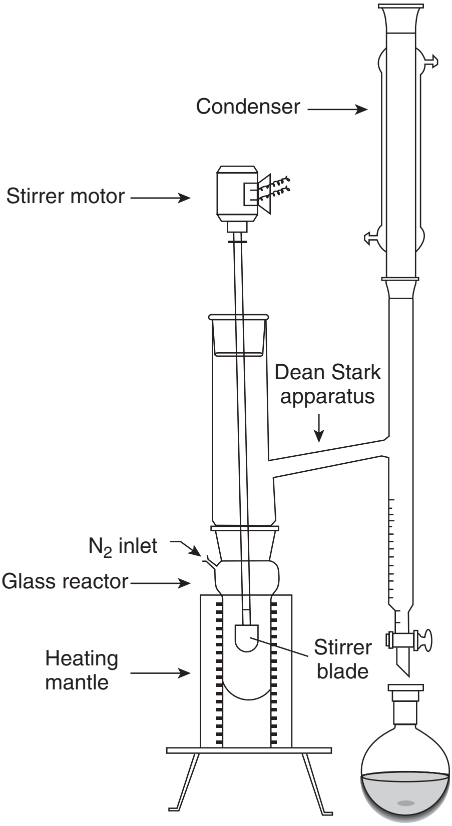
9.2 Different di-, tri- and tetra-functional monomers widely used in the preparation of polyester resin for coating applications [1].

(NPG), trimethylol propane (TMP), di-trimethylol propane (diTMP), mono-pentaerythritol (MPE), di-pentaerythritol (diPE), glycerol, 1,4-cyclohexanedimethanol (CHDM), etc. Widely used diacids are malonic acid, succinic acid, glutaric acid, adipic acid, pimetic acid, suberic acid, azelaic acid, sebacic acid, isophthalic acid (IPA), phthalic acid, terephthalic acid (TPA), fumaric acid, oxalic acid, aspartic acid, malic acid, etc. Trimellitic anhydride, phthalic anhydride, hexahydrophthalic anhydride (HHPA), etc., as dianhydride are widely used to prepare polyester coatings.

The most straightforward route to improve mechanical properties and to minimize hydrolytic instability is the introduction of aromatic units into the polyester main chain. The aromatic diacid compounds are used to increase the glass transition temperature (T_g), hardness, and chemical resistance. This is why TPA is such a tremendously important building block in commercial thermoplastic polyesters. In conventional systems, TPA usually provides chain rigidity and thus sufficiently high T_g. On the other hand, replacement of TPA by IPA, an isomer of TPA in the polyester backbone, significantly increases the weathering resistance of coatings [5]. However, aromatic monomers have the disadvantage that they are more susceptible to photo-oxidation, leading to yellowing of the coating with time [6–8]. In the early 1990s, cyclohexyl dibasic acids were proposed as replacements for the aromatic dibasic acids. The cyclohexane isomeric diacid monomers which are typically used in the preparation of polyesters are hexahydrophthalic anhydride (HHPA), 1,3-cyclohexanedicarboxylic acid (1,3-CHDA), and 1,4-cyclohexanedicarboxylic acid (1,4-CHDA). The cycloaliphatic structure gives the intermediate physical properties between that of aromatic and linear aliphatic polyesters except the yellowing resistance, which is better with linear diacids. Relative to aromatic polyesters, T_g of cycloaliphatic polyester is lower, but is higher compared to linear aliphatic polyesters. The flexibility of cycloaliphatic polyester is also intermediate between the aromatic and linear aliphatic polyesters due to the presence of cyclic structure in the monomer that can absorb energy through the interconversion of chair and boat conformations [9, 10].

9.3.1 Reaction setup

Usually two processes are used in the preparation of saturated polyesters, i.e., the melt process and the solvent process. In the solvent process, an azeotropic solvent such as toluene or xylene is used to take out the water formed during the polycondensation reaction. The basic raw materials are charged in the reactor and reaction is carried out in general at around 200–240°C. The reaction is monitored by following the acid value periodically [11] and stops when the acid value comes down below 5. A laboratory-scale reaction setup for polyester preparation is shown in Fig. 9.3.



9.3 Laboratory-scale reaction setup for polyester preparation [12].

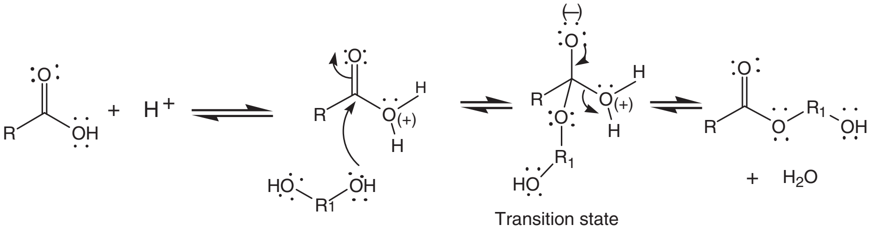
9.4 Polymerization methods

9.4.1 Direct esterification

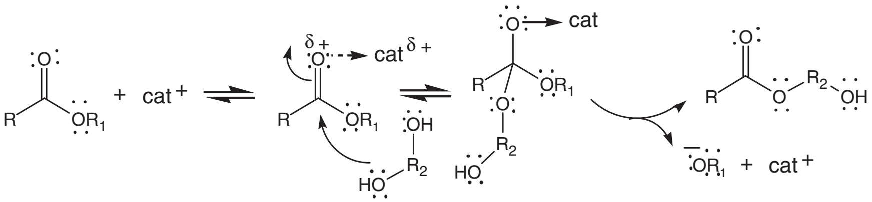
The monomers for the polyesterification reaction are di-/polyacids and di-/polyols. The mixture of monomers should be charged to the reaction kettle and the reaction takes place after melting of the reactants with the elimination of water molecules (Fig. 9.4). When dianhydrides are used instead of diacids, no water removal takes place from the system.

9.4.2 Transesterification

In transesterification, the methyl or ethyl ester of the diacid is reacted with di-/polyols. During this reaction, methanol or ethanol (depending on the acid ester used) is generally collected into a graduated receiver as a



9.4 Mechanism of direct esterification reaction.



9.5 Mechanism of transesterification reaction.

by-product to allow estimation of the extent of conversion. The electrophilic mechanism for metallic catalysis of the transesterification reaction is shown in Fig. 9.5 [13, 14].

9.4.3 Effect of catalysts

Many researchers have studied the effects of various catalysts for both the transesterification and polycondensation reactions. Tin-based esterification catalysts such as dibutyltin oxide, dibutyltin dilaurate, titanium tetrabutoxide, titanium (IV) *n*-butoxide, *p*-toluene sulfonic acid (*p*-TSA), etc., are widely used as esterification catalyst. Different results show that titanium-based catalyst is more active than antimony- and tin-based catalysts. The activity of the polycondensation catalysts follows the order Ti > Sn > Sb > Mn > Pb [14]. However, titanium-based catalysts have the disadvantage of imparting a yellow color to the polyester [15].

9.5 Determination of hydroxyl value and acid value

The hydroxyl value is defined as the number of milligrams of potassium hydroxide (KOH) equivalent to the hydroxyl content of one gram of the sample. Hydroxyl value is estimated by following the method set out in the ASTM standard [16]. The acid value is defined as the number of milligrams of potassium hydroxide required to neutralize the free carboxylic acid present in one gram of the polyester. The acid value of the resin is estimated as in the ASTM D 1639–70 method [17] by titration of the sample with standardized KOH or NaOH solution. The solvent in the sample must be removed and the sample in solid basis must be weighed. Then the sample is dissolved in isopropyl alcohol and toluene. Phenolphthalein is used as indicator and a pink coloration indicates the end point. The acid number is calculated from the following equation:

$$\text{Acid number} = \frac{V_{\text{KOH}} \times N_{\text{KOH}} \times Mw_{\text{KOH}}}{m_{\text{sample}}}$$

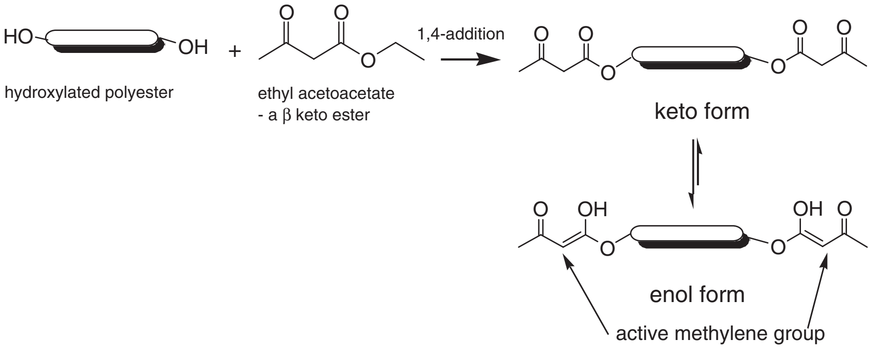
where V is the volume of potassium hydroxide solution consumed in mL, N is the normality of the solution, and m is the weight of the sample in grams (solid basis).

9.5.1 Effect of hydroxyl and acid number

In general, the synthesized hydroxyl or carboxyl terminated polyester resins are crosslinked with different crosslinkers in thermoset coatings to obtain desired properties. Therefore an increase in hydroxyl or acid number in the polyester backbone results in an increase in the crosslinking density of the final thermoset coatings.

9.6 Backbone modification of polyester resin for high solid coatings

In general an increase in the hydroxyl number of polyester resin produces thermoset coatings with better chemical resistance and mechanical properties. This is due to the increase in the crosslink density of the coatings. However, an increase in the hydroxyl number in the resin produces increased intermolecular hydrogen bonding, which increases the viscosity of the system. Therefore it is essential to modify the resin structure to give low viscosity and good crosslink density with the crosslinker. This can be achieved by partial replacement of the available hydroxyl groups in hydroxylated polyester with the less polar acetoacetate groups, which leads to an increase in solid content at the application viscosity as well as increase in adhesion due to the chelate effect (Fig. 9.6). Acetoacetylated or β-ketoester incorporated polymers offer a versatile crosslinking mechanism. This versatility results from the presence of two sites available for crosslinking reactions. These sites are the active methylene group and the ketone carbonyl group. β-ketoester groups are amphoteric and can participate in a variety of chemical transformations, which might be used to modify or crosslink polymers. There are several routes by which acetoacetylated materials can be prepared, of which the transesterification route is preferred for coating applications [18–21]. The crosslinking reaction of the



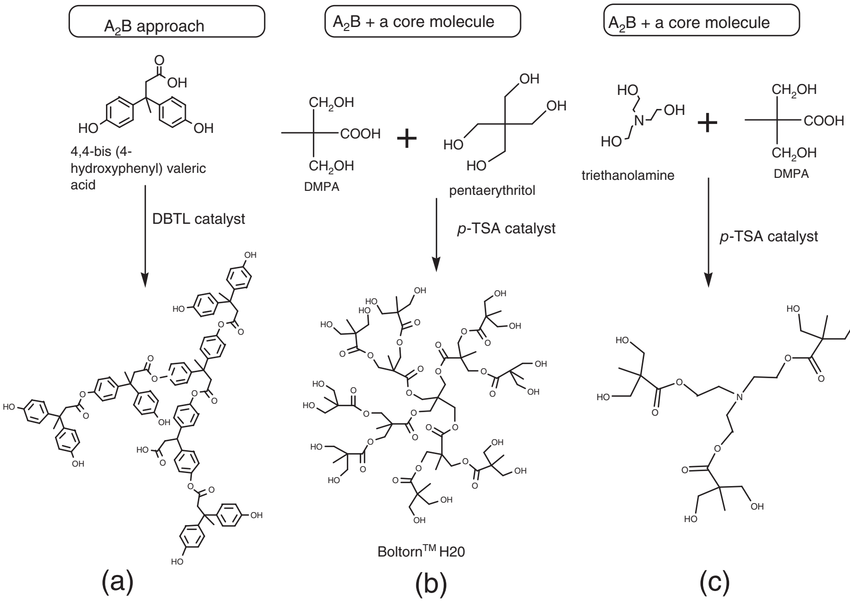
9.6 Backbone modification of hydroxylated polyester by Michael addition reaction.

active methylene group in acetoacetylated polyols with diisocyanate produces additional crosslink density with superior properties and weathering stability [22–25].

9.6.1 Functional branched polyesters for coating application

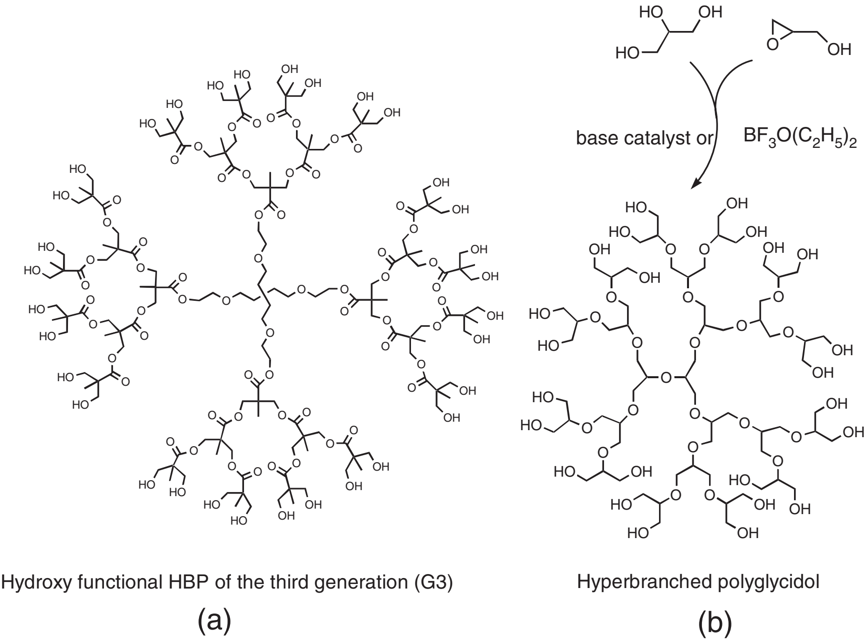
The ability to synthesize new polymers with predetermined and controlled structures is important when new materials are to be created with desired physical and chemical properties. Hyperbranched polymers (HBPs) have been extensively studied as part of recent research efforts aiming at tailoring the properties of polymeric materials by variation in the molecular architecture. HBPs are highly branched structures based on AB_x or A_xB monomers ($x \geq 2$ and A and B are hydroxyl and carboxylic acid moieties, respectively), which introduces potential branching points in every repeating unit as well as at the end-groups. The large number of end-groups and branching points gives HBPs different properties compared to their linear analogs. For instance, HBPs have low melt and solution viscosity and high solubility, and are easy to modify to obtain tailored properties [26]. The lower solution viscosity of HBPs compared with linear polymers is due to the lack of entanglements, which result from their packed structure. They also often possess very high solubility compared to those of linear polymers, as a result of the large number of peripheral terminal functional groups available per macromolecule. Therefore, the use of HB polyesters as specific crosslinking agents for coatings seems a very promising way of synthesizing new three-dimensional networks with controlled architecture [27].

Recently, different methodologies for constructing HB polyester polyols from AB_x monomers have been explored. The routes involve thermally driven homo-polycondensation or activation of either A or B functional-



9.7 Different synthetic approaches for the preparation of hyperbranched polyols [59].

ities. Thermally driven polycondensation of AB_2 monomers uses *p*-TSA or an organometallic catalyst. Huybrechts and Dusek [28] reported that the properties of low volatile organic component (VOC) coating formulations containing HB polyol are superior to those of linear polyols. In Sweden, a systematic investigation of HB polyesters as curing agents was developed [29, 30]. At present, several dendritic/HB polyester polyols are commercially available from Perstorp Polyols, Inc., Perstorp AB, Sweden, with the trade name 'Boltorn', and are easy to synthesize [31]. For instance, HB aliphatic polyester prepared from 2, 2-bis(methylol) propionic acid (DMPA) and 2-ethyl-2-(hydroxymethyl) 1,3-propanediol was used as crosslinking agent in coating formulation. Ziemer *et al.* [32] synthesized HBP using 4,4-bis(4-hydroxyphenyl) valeric acid as an A_2B type raw material (Fig. 9.7(a)). Researchers also proposed the polycondensation reaction of AB_2 monomer in the presence of a B_n core molecule as an improved method to control the condensation reaction [33]. Examples of such an AB_2-monomer/B_n-core approach include the preparation of HBPs from DMPA (an A_2B monomer) and pentaerythritol [34] (Fig. 9.7(b)), triethanol amine (Fig. 9.7(c)) and trimethylolpropane (TMP) [35, 36] as core molecules. Pavlova *et al.* [37] used HB polyester prepared from 4,4-bis-(4′-hydroxyphenyl)pentanoic acid and TMP as core molecule for coatings preparation. The commercially available (Perstorp Polyols, Inc.) hydroxyl-functional HB polyester of the third generation (G3) prepared from DMPA and ethoxylated



Hydroxy functional HBP of the third generation (G3)

(a)

Hyperbranched polyglycidol

(b)

9.8 A third-generation hyperbranched polyol (a) and hyperbranched polyglycidol (b).

pentaerythritol (a core molecule) is shown in Fig. 9.8(a). An $A_2 + B_3$ approach produces an AB_x molecule as an intermediate during the condensation reaction and is important due to the commercial availability of A_2 and B_3 type monomers. As an example, the synthesis of aliphatic HBP polyol from adipic acid and glycerol can be mentioned [38]. Recently, Frey and coworkers [39, 40] and Xinling and coworkers [41, 42] developed different synthetic routes that emerge from the combination of the multi-branching polymerization of glycidol with well-established epoxide polymerization techniques, leading to unprecedented polymer architectures. The synthesis of hyperbranched polyglycidol (HPG) involves the cationic ring-opening polymerization of glycidol, by glycerol in the presence of boron trifluoride diethyl etherate catalyst in chloroform. The reaction was carried out at 25°C for more than 3 h and in a nitrogen atmosphere (Fig. 9.8(b)).

9.7 Polyester-melamine coatings

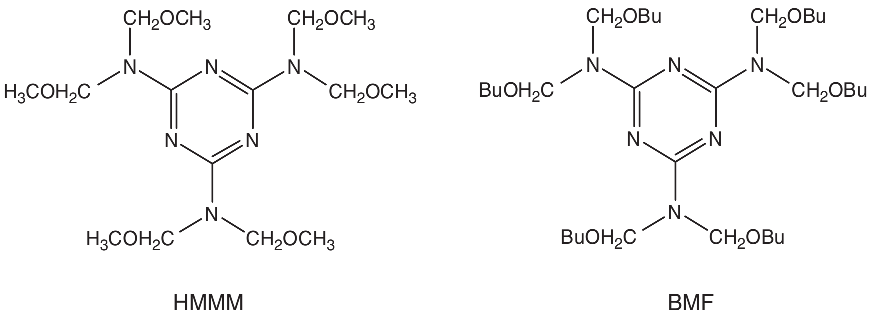
Melamine-formaldehyde (MF) resins are important components of thermosetting resin products. They are widely used in the coatings industry as binders and crosslinkers to produce highly durable coatings. Thermoset coatings based on the reaction of MF resins with hydroxyl functional polyester have long been used in the coatings industry. For instance, polyester resin crosslinked with hexamethoxymethyl melamine (HMMM) were developed in 1972. MF crosslinkers have been shown to give improved chemical, heat, wear and scratch resistance, improved hardness, and exterior durability to coatings. Typical applications include coatings use in household appliances, automotive OEM coatings, industrial coatings for coils and cans, agricultural and construction, etc. Because of their value, MF resins have been extensively studied in order to optimize the properties of the final coating. Such formulations are commonly cured by baking at temperatures above 100°C for 10 to 40 min in the presence of *p*-TSA catalyst. The wide acceptance of *p*-TSA is due to the compatibility of its molecular structure and hydrophobic nature with the paint components.

9.7.1 Melamine-formaldehyde resins

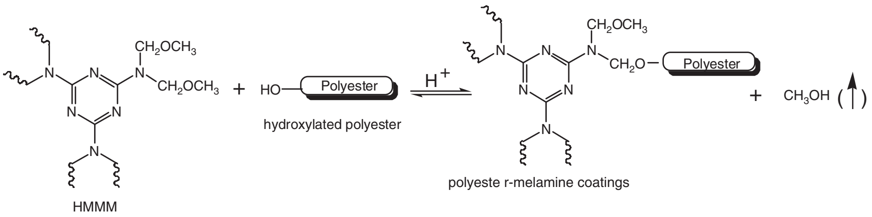
MF resins are mixtures of compounds with different degrees of substitutions [43]. The final form of the MF resin produced depends on the reaction temperature, pH of the medium, reactant ratio, and the degree of polymerization. HMMM resins are the reaction products of melamine (2,4,6-triamino-1,3,5-triazine) with formaldehyde to form methylol groups and converting these methylols to methoxymethyl groups using methanol. Up to six moles of formaldehyde can be combined with one mole of melamine to produce hexamethylol melamine. In the preparation of coating resins, usually 5–6 moles of formaldehyde are reacted with one mole of melamine. The degrees of methylation and methoxy-methylation are varied according to the intended end-use applications. HMMM resin may contain, besides pure HMMM, also dimers and trimers, and other end-groups than $–CH_2OCH_3$. The various functional groups influence the reaction mechanism and rate of reaction. Furthermore, during the crosslinking reaction self-condensation of HMMM can occur between the various functional groups. HMMA is a versatile crosslinking agent for a wide range of polymeric materials, both for solvent-borne high solids and for water-borne coatings. Butylated melamine resins (BMF) are widely used in industrial stoving primers and enamels, in acid-catalysed wood finishes and in force-cured coatings. They are widely used for interior applications, interior container coatings, and two-component solvent-based wood finishes. Figure 9.9 shows the structure of fully substituted methylated MF and butylated MF resin.

9.7.2 Reaction of polyester with melamine resin

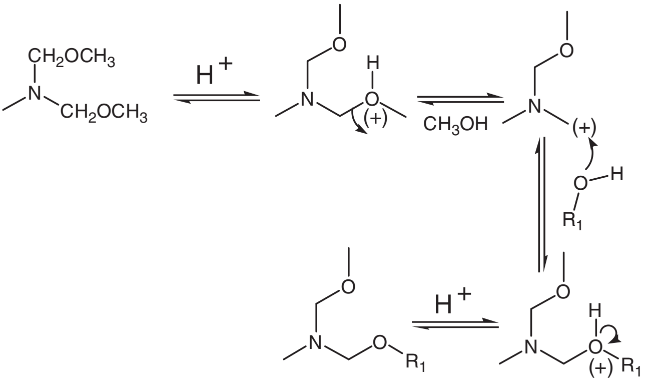
Hydroxylated polyester resins are generally crosslinked with BMF and HMMM in a ratio of 90/10 to 70/30. The curing reaction (Fig. 9.10) is catalyzed by a strong acid such as *p*-TSA. The catalyzing mechanism as



9.9 Structure of fully substituted methylated (HMMM) and butylated melamine (BMF) resin.



9.10 Crosslinking reaction of hydroxyl-terminated polyester with HMMM.



9.11 Catalyzing mechanism of the reaction of HMMM with polyols.

proposed by Blank [44] is described in Fig. 9.11. Besides protonation of the methylated methoxy group, also protonation of already formed crosslinks may take place and results in cleavage of the bond formed between polyester and melamine resin. Evaporation of the alcohol results in shifting the equilibrium towards the right-hand side and thereby a crosslinked network forms.

Previous studies have shown that, under acidic conditions, the primary reaction is the transetherification of the crosslinker with the hydroxyl groups on the polyester. Additionally, there can be a number of self-condensation reactions between reactive groups on two melamine rings [45–50]. The cure rate and reaction pathways are important variables and changes of these parameters result in coatings with alteration in properties. A number of reactions during the baking condition of polyester-melamine coatings make it difficult to sort out the pathways between different competing reactions that take place during cure.

9.7.3 Evaluation of curing condition

As already discussed, the cure reaction between HMMM and the hydroxy-functional polyester involves acid-catalyzed transetherification between the polyester hydroxyl groups and the crosslinker methoxy groups to create an ether bridge. Therefore, the film formation in such coatings is a complex process in which a liquid material transforms into a solid layer with simultaneous solvent evaporation and crosslinking. The speed of solvent evaporation and crosslinking depends on the baking conditions applied to such a system. It is therefore necessary to ensure that sufficient crosslinking of the system under investigation has taken place, otherwise premature failure of the coating may take place during exposure. In general, the cure condition can be evaluated using Dynamic Mechanical Analysis (DMA) or Differential Scanning Calorimeter (DSC) instruments, applying isothermal or dynamic heating rate and different evaluation time [22]. The mechanical properties, such as hardness, flexibility, impact resistance, appearance of the film surface, and chemical resistance of the cured film, may be affected by the degree of crosslinking during the curing process. It is demonstrated that the changes in cure condition and composition have a significant impact on the relative rates of co-condensation (between polyester and HMMM) and self-condensation (of HMMM) reactions, forming coating matrices with different chemical structures [51].

9.7.4 Properties of the cured coatings

Polyester-melamine cured systems can exhibit moisture resistance and good mechanical properties and can be extremely hard. The moisture resistance feature of melamine-based coatings, combined with their durability, may provide advantages for exterior applications. Crosslinked polyester-melamine coatings are colorless, chemically resistant and resilient. They provide a tough and durable finish to items that will be repeatedly exposed to harsh environments. There is a great deal of empirical knowledge relating crosslinking mechanisms and the effects of conditions on basic physical and mechanical properties of isothermally cured polyester-melamine coatings. The ultimate service properties of thermoset coatings are determined in part by the structure of the matrix and in part by the severity of the environmental factors to which the coating is exposed. Variations in the cure conditions and crosslinker concentrations can influence the properties of the coating by affecting the extent of crosslinking and, therefore, the structure of the matrix. Researchers have described the thermal characterization of polyester-melamine crosslinked matrices of various compositions and cure conditions [51], the effect of composition and cure conditions on the distribution of melamine during cure [52], etc.

Kojima *et al.* [53] studied the surface properties of melamine-polyester films using X-ray photoelectron spectroscopy (XPS) and showed that the nitrogen content at the air–film interface increased with an increasing amount of the acid catalyst used because of the increasing self-condensation nature of melamine with increasing catalyst amount. Kanai *et al.* [54] showed that amine-blocked acid catalyst enhances surface melamine content, whereas a non-blocked acid catalyst did not. Hirayama *et al.* [55] used attenuated total reflectance (ATR) and showed that melamine distribution at the surface of polyester-HMMM films was uniform unless the hydroxy content was low and the cure temperatures were relatively high. Researchers [54, 55] also reported that surface hardness and stain resistance could be improved in polyester-melamine films by allowing segregation of melamine towards the polymer/air interface.

The effect of polyester molecular weight on the surface properties of polyester-melamine films cured for a short time at high temperature was investigated by Yoshida *et al.* [56]. Their results showed that surface melamine content influences the surface properties of the cured resin such as water contact angle and adhesion. Kawanishi *et al.* [57] showed that the surface melamine had a negative influence on the adhesive properties and a positive influence on the stain resistance of coatings. The surface enrichment of melamine in polyester-melamine coatings was attributed to the difference in free energy between polyester and melamine components [24, 54]. For example, butylated melamine resin possesses lower surface free energy than polyester and hence a surface enrichment of BFM may take place in the cured film. On the other hand, methylol- and imino-substituted melamines, because of their higher surface free energy, segregate towards the bulk of the cured film and hardly exist on the surface. HMMA, having a moderate surface free energy, showed an intermediate result of surface segregation behavior. The effect of the polyester and HMMM mixing ratio also has a favorable influence on the surface segregation behavior, and below a certain value of this ratio there was no melamine enrichment at the surface, but a higher melamine concentration was observed in the bulk [58]. Gamage *et al.* [52] investigated the effects of the polyester-HMMM binder composition and cure conditions on the melamine distribution in model clear coats during a dynamic rapid cure experiment.

9.7.5 Parameters influencing polyester-melamine coating performance

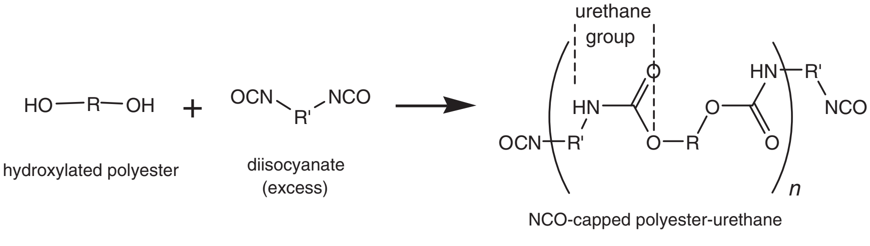
The following parameters influence the polyester-melamine coating performance:

- Type of acid and di-/polyols selected for making polyester resin
- Hydroxyl number of the polyester backbone
- Melamine concentration and type of melamine crosslinker, e.g. HMMM or BMMM
- Concentration and type of catalyst
- Curing conditions such as baking temperature and time
- Environment to which coating is exposed.

9.8 Polyester-urethane coatings

Demands for improved interior and exterior quietness as well as good weathering stability have risen over the years until it has now become one of the fundamental performance requirements of coatings. Polyester-urethane (PU) is a well-known coating material that produces good protection of the substrate on demand. The basic chemistry involved in its synthesis is the addition reaction of a polyester-polyol with a di-/polyisocyanate, where the hydroxyl group of the polyester acts as a neucleophile and isocyanate carbon (—N=C=O) acts as an electrophile (Fig. 9.12).

Different secondary reactions such as the formation of allophanates, biurets, dimerization (uretidione ring formation) or isocyanurate (trimer) may also take place depending on the reaction condition. Traditional approaches in enhancing performance are to select appropriate raw materials to produce polyester-urethane coatings, achieve a good trade-off in NCO/OH ratio, and control the side reactions. In order to prevent



9.12 Basic reaction scheme for polyester-urethane formation.

premature gelation of the coating composition, either the polyisocyanate must be kept separate from the resin in what is known as a two-package or two-component coating system, or the highly reactive isocyanate groups on the curing agent must be blocked (e.g., with an oxime or alcohol). Blocked polyisocyanates, however, require higher temperatures (e.g., 150°C or more) to unblock and begin the curing reaction. The volatile blocking agents released during cure can possibly adversely affect the coating properties, as well as increase the volatile organic content for the composition. In this part of the chapter, we will discuss fundamental aspects of polyester-urethane coatings [59].

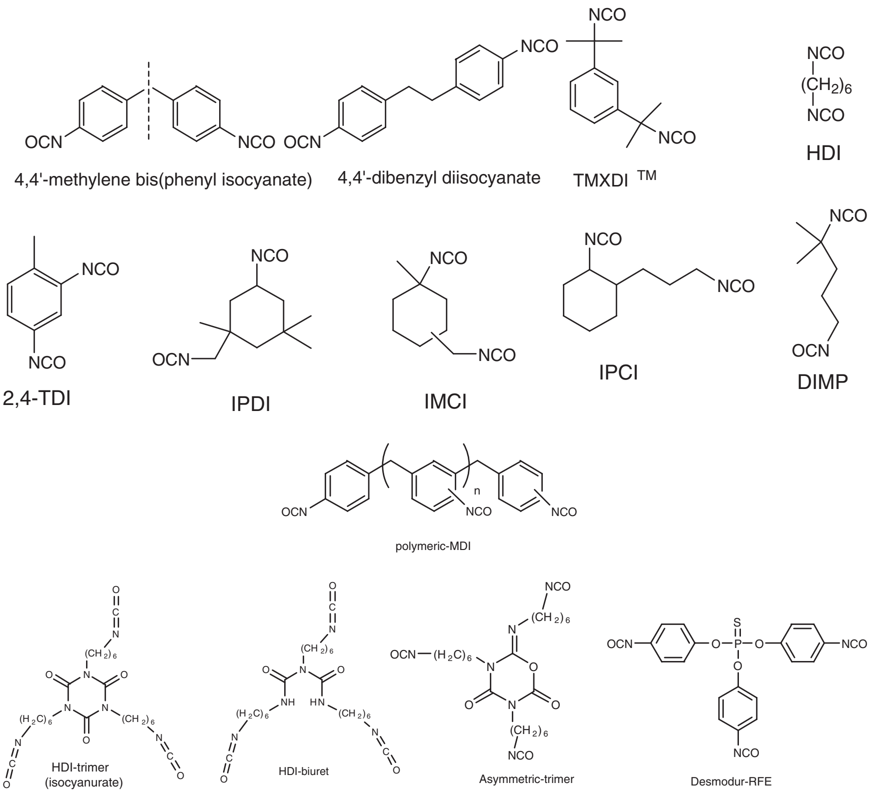
9.8.1 Structure of isocyanates

Isocyanates are highly reactive chemicals of low molecular weight containing the functional group —N═C═O. Isocyanates are classified based on the number of —N═C═O groups in the molecule into monoisocyanates (one NCOs), diisocyanate monomers (two NCOs), or polyisocyanates (multiple NCOs). Diisocyanate monomers are important because the two NCO groups allow them to undergo direct polymerization reactions with alcohols to form PUs. The self-condensation reaction of diisocyanates results in the formation of polyisocyanates. Isocyanates are also classified as aromatic (one or more aromatic rings) or saturated (aliphatic and alicyclic), the term aliphatic isocyanate referring to saturated isocyanates. Toluene diisocyanate (2,4- and 2,6-TDI), methylene diphenyl diisocyanate (4,4′-MDI), and their higher polymers are commercially the most important aromatic isocyanates, whereas hexamethylene diisocyanate (1,6-HDI), isophorone diisocyanate (IPDI), methylene dicyclohexyl diisocyanate (H_{12}MDI) and their higher polymers are the most important aliphatic isocyanates [59, 60].

Figure 9.13 lists the chemical structures of some major isocyanates of commercial importance. Aliphatic isocyanates such as those based on HDI are used mostly in external paints and coatings due to their excellent resistance to chemicals, good abrasion resistance, and superior weathering characteristics such as gloss and color retention. Aromatic isocyanates such as TDI and MDI are used where a fast curing rate is essential.

9.8.2 Reaction of polyester polyol with isocyanate

The discovery of the excellent catalytic effect of organometallic compounds as well as of the metal carboxylates on the reaction of hydroxyl compounds with isocyanates has been of great significance for the synthesis of PUs. For the reaction of an isocyanate with an alcohol, many effective urethane catalysts are available commercially. Those used most often are tertiary amines



9.13 Structure of different isocyanates widely used in the coatings industry.

and organotin compounds. Dibutyltin dilaurate, dibutyltin diacetate, dibutyltin dichloride, tributyltin chloride, butyltin trichloride, stannous octoate, stannic chloride, triethyltin chloride, trimethyltin bromide, tetraethyltin, dibutyltin difluoride, triethyltin fluoride, cobalt naphthenate, etc., as organotin compounds are widely used as catalysts. Of the many metals available, tin compounds like stannous octoate (SnOct) and dibutyltin dilaurate (DBTL) are the most popular. Organometallic catalysts act as Lewis acids, and are generally thought to function by interacting with basic sites in the isocyanate and polyol compounds. They form an intermediate complex with an isocyanate group and a hydroxyl group of the polyol. Researchers [61, 62] have suggested that the metal carboxylates as well as organometallic species catalyze the isocyanate–alcohol reaction by formation of a ternary complex. Robins [63] has elaborated this concept and suggested that the metal acts both to increase the electrophilic character of the isocyanate carbon through coordination with the isocyanate group and to

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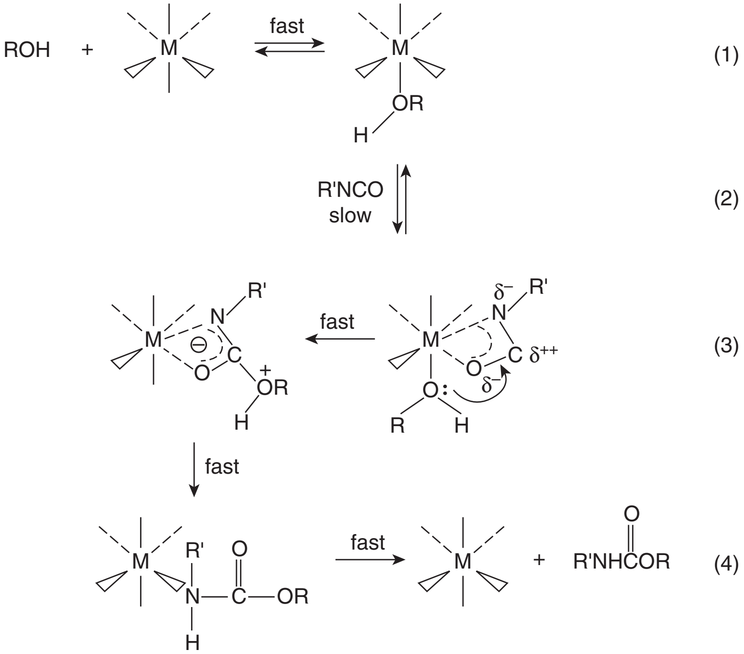
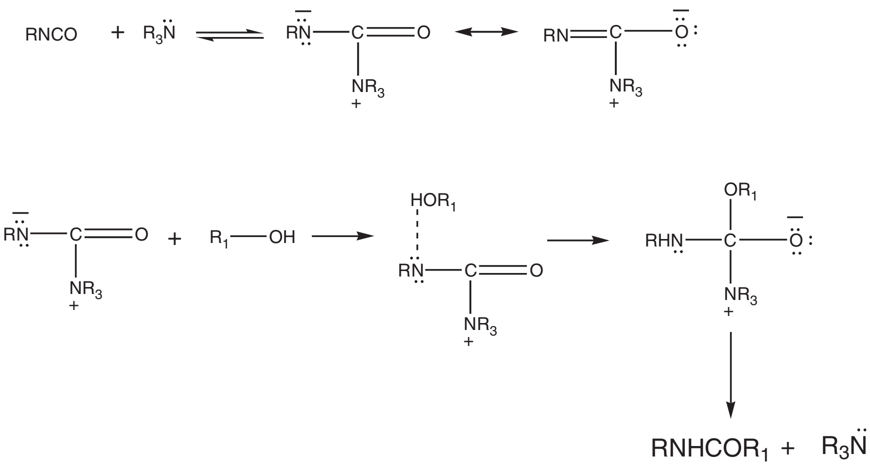


9.14 Mechanism of metal catalysis in urethane formation.

bring the reactants into close proximity through the formation of a ternary complex (Fig. 9.14(1,2,3,4)) [64, 65].

Some of the more commonly used tertiary amines are *N*,*N*-dimethylethanolamine (DMEA), diaminobicyclooctane (DABCO), triethyl amine (TEA), triethylene diamine (TEDA), bis(2-dimethylaminoethyl) ether (BDMAEE), *N*-ethylmorpholine, *N′N′*-dimethylpiperazine, *N*,*N*,*N′*,*N″*,*N″*-pentamethyl-diethylene-triamine (PMDETA), *N*,*N*-dimethylcyclohexylamine (DMCHA), *N*,*N*-dimethylbenzylamine (DMBA), *N*,*N*-dimethylethylamine, *N*,*N*,*N′*,*N″*,*N″*-pentamethyl dipropylene triamine (PMDPTA), etc. The efficiency of tertiary amine catalysts (Fig. 9.15) in isocyanate reactions depends upon their chemical structure. The basicity and steric hindrance of tertiary amine are considered the two main factors influencing the rate of isocyanate reactions. The catalytic activity of tertiary amines generally increases as the basicity of the amine increases and the steric shielding of the amine nitrogen decreases. In addition to these factors, the structure of the tertiary amine also has a profound effect on the promotion of different reactions [66–69].

The formation of biurets from the reaction of an isocyanate and an aromatic urea requires vigorous conditions in the absence of a catalyst. Under these conditions, where the temperature may be in the range of 100–150°C, side product formation also takes place [70].



9.15 Mechanism of tertiary amine catalysis in urethane formation [59, 61].

9.8.3 High-solids coatings

Solvent-borne one- and two-component coating materials, for the most part thermally curable, play an important role in industrial applications. However, the reduction or elimination of VOCs has been a main task of paint research for many years due to environmental requirements and regulatory pressure. Thus, the percentage of common solvents containing coating materials has been reduced despite their well-known and excellent properties [71]. However, in these systems, the molecular weight of the polymer is less and reactive functionality has been incorporated therein so that further polymerization and crosslinking can take place after the coating has been applied on the material. High-solids coatings (HSCs) currently used in different parts of the coatings industry are typically thermoset systems which derive most of their physical properties from the formation of highly crosslinked networks.

9.8.4 Waterborne polyester-urethane coatings

Waterborne polyester-urethane coatings (WBPUs), as a non-toxic, non-flammable and environment-friendly material, have gained considerable attention in the coatings sector. An aqueous polyurethane dispersion is a binary colloidal system in which the particles of PU are dispersed in a continuous phase, the water. The particle size tends to be of the order of 20–200 nm, and the particles have a high surface energy. This results in a strong driving force for film formation with the evaporation of water. PU ionomers usually contain a minor component carrying pedant acid (carboxylic acid or sulfonic acid) or tertiary nitrogen groups, i.e., tertiary amine groups (<10 mol%) that are completely or partially neutralized or quaternized, to form salts. Aqueous PU dispersions are of three types: (a) non-ionic: stabilized by hydrophilic polyether chains, (b) cationic: stabilized by tertiary nitrogen groups, and (c) anionic: stabilized by carboxylic or sulfonate groups depending upon the type of hydrophilic segments present in the PU backbone [72].

The preparation and description of aqueous PUDs is well known and described in a number of reviews [73, 74]. Routes available to prepare aqueous PUDs are the prepolymer mixing process [75, 76], the acetone or solution process [77], the ketamine/ketazine process [78] and the hot-melt process [79].

Crosslinking of PUDs can be used to improve physical properties such as tensile strength, toughness, thermal resistance, solvent resistance, etc. Different methods used for the crosslinking reaction of PUDs are as follows:

- Addition of aziridines or melamines to carboxylated PUDs [59, 80, 81]
- Introducing UV curable groups [82]
- Use of blocked isocyanates [81]
- Addition of functionalized silanes, etc.

Factors influencing properties of PUDs are as follows:

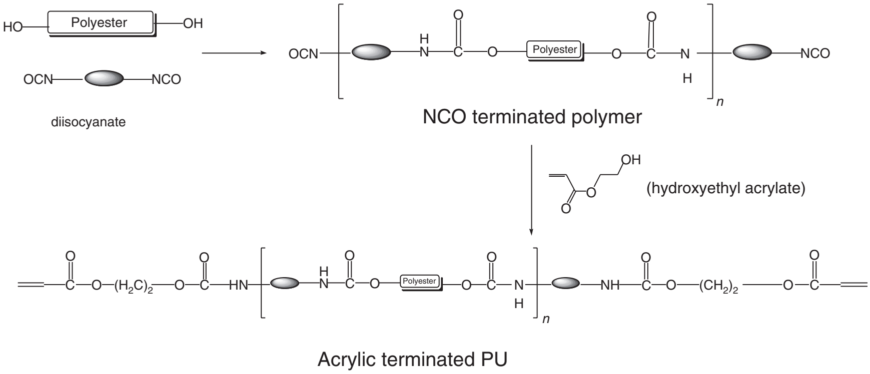
- Degree of neutralization [83, 84]
- Type of ionic moiety present [85]
- Neutralization agents [86]
- Counter ion used [59], etc.

The disadvantage of water-borne coatings is their application problems in the presence of high relative humidity in the atmosphere, which produces defects in the coating structure. These defects result from the fact that under conditions of high humidity, water evaporates more slowly than the organic co-solvents of the coalescing aid, which reduces the film formation capability as well as the film's physical properties. Poor gloss, poor uniformity and pinholes unfortunately often result. Additionally, water-borne coatings are not as resistant to corrosive environments, as we observe for conventional solvent-borne coatings [87].

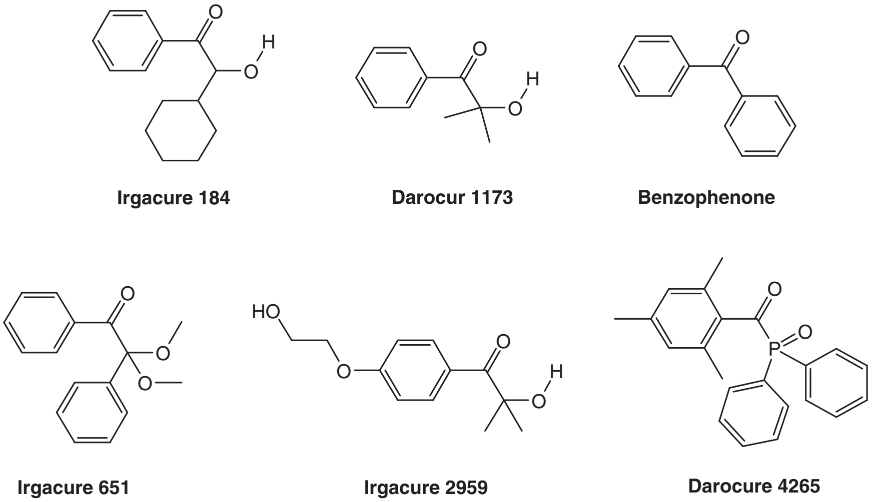
9.8.5 Photo- and thermal cure polyester-urethane-acrylate coatings

Polyester-urethane-acrylate represents a new class of PU coatings, which contains polyester soft segments as well as acrylic structural units. The relatively easy polymerization of liquid acrylic polyester-urethane oligomers by UV light represents another convincing proof of their technical and scientific interest in coating science. The UV-curing process is a very attractive alternative to conventional curing processes because it offers several distinct advantages over solvent-based processes or thermal-curing processes, such as high speed, operation at room temperature, lower energy consumption, and environmental compatibility. The liquid resin is transformed in a very short time into a solid polymer that is absolutely insoluble in organic solvents and has a high level of thermal and mechanical properties. UV light initiates free-radical polymerization with very low activation energy. This allows high polymerization rates at room temperature [88–90].

Polyester-urethane-acrylates are usually synthesized in a three-step process. In the first step, an excess molar concentration of a diisocyanate reacts with a polyester diol to form an isocyanate-terminated prepolymer in bulk or in the solvent. The prepolymer is then reacted with hydroxyethyl acrylate (HEMA) or methacrylate (HEA) to form unsaturated terminated polymer in the second step (Fig. 9.16), which later is self UV/thermal cured or UV/thermal cured in the presence of other unsaturated monomers or polymers (step III). Acrylated resins are preferred over methacrylated ones because of their higher cure rates at room temperature and their lower oxygen inhibition [91]. Parameters such as functionality of urethane acylate, type of isocyanate used, polyester polyol components and molecular weight influence the properties of the cured coatings. For instance, lower functionality in urethane acylate produces lower reactivity and viscosity but higher flexibility in the final cured coatings. On the other hand, a higher functional urethane acrylate results in improved reactivity, chemical resistance, hardness and scratch resistance. However, a higher functionality in the polymer



9.16 Preparation of acrylic terminated PU prepolymer for UV cure coatings [59].



Irgacure 184 **Darocur 1173** **Benzophenone**

Irgacure 651 **Irgacure 2959** **Darocure 4265**

9.17 Chemical structures of different photoinitiators used in the UV cure process.

possesses a higher viscosity and imparts brittleness in the final coating. The functionality of urethane acrylate resin, i.e., the degree of unsaturation, can be controlled by changing the parameters such as molecular weight of NCO-capped polyester urethane prepolymer and isocyanate content (the NCO/OH ratio). A high NCO/OH ratio during the synthesis of polyester urethane and its lower molecular weight increase the functionality of the urethane acrylate resin produced from it.

The structures of different photoinitiators used for the UV cure process are shown in Fig. 9.17. The absorption bands of the photoinitiators should overlap the emission spectra of the UV bulbs used to cure the resin. The choice and concentration of photoinitiator are determined by factors such as the radiation source, the wet film thickness, and the pigmentation amount, if any.

On the other hand, different thermal cure free-radical initiators widely used are benzoyl peroxide (BPO), *tert*-butyl hydroperoxide, 2,2′-azobis (2,4-dimethylpentanenitrile), 1,1′-azobis(cyclohexanecarbonitrile), 2,2′-azobisisobutyronitrile (AIBN), etc. Sometimes it is necessary to use oxygen scavengers, as oxygen inhibits the curing of acrylates by quenching the photo- or thermal initiator. The curing process in the presence of oxygen produces unreacted species with a less crosslinked structure that reduces the film properties. Five different methods of oxygen inhibition are use of a suitable oxygen scavenger, a nitrogen blanket, high-intensity UV lamps to speed up the cure, a high concentration of initiator, or wax.

9.8.6 Moisture cured polyester-urethane coatings

Isocyanate-functionalized PU prepolymers are used as one-component coatings. The curing is achieved in the presence of atmospheric moisture by permeation of water molecules from the surrounding environment into the prepolymers. The nucleophilic addition reaction of the water molecule with the isocyanate (NCO) group attached to the polymers used in the formulation results in film build and crosslinking. The cure reaction advances with time and increases the crosslinking density through the formation of urea bonds. Recently, different 2,2′-morpholino-containing substances such as dimorpholinodiethyl ether (DMDEE), as well as reactive amine catalysts, were used as catalysts to speed up the moisture cure reaction. The major drawback of moisture-cured formulation is the formation of side products during storage that reduce the pot stability and shelf-life of the coating. The formation of allophanate and isocyanurate as side-products adds branch points and increases the viscosity of the NCO-terminated prepolymer during storage. On the other hand, the advantage of moisture-cured formulations is in obtaining superior hardness, strength, stiffness and flexibility as well as good adhesion with different metals [59, 92–98].

9.8.7 Polyester-urethane-imide coatings

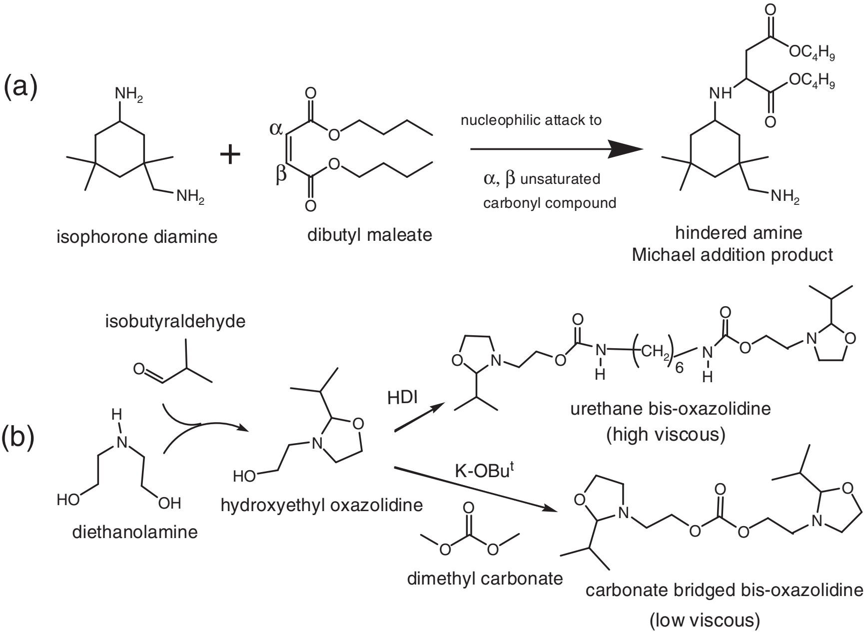
The drawback of PUs is their low thermal resistance, which limits their use as engineering materials in environments where high thermal stress is involved. The thermal stability of PU depends on the chemical structure of its backbone, which consists of various hard segments and soft segments. For example, PUs produced from monomers with different diisocyanate structures present different thermal stabilities. Extensive research effort on improving the thermal stability of PU has resulted in great progress in the field of its processing and application. Chemical modification of PU structures or introductions of chemical crosslinks are effective ways to improve the thermal stability of PUs. Chemical crosslinking results in hard and stiff network formation and reduces macromolecular degradation to a negligible amount, even up to 300°C. The other way of improving thermal stability or thermo-mechanical properties is to incorporate heterocyclic structures, such as an imide, into the PU backbone by a one-shot technique or via a sequential method. Different methods of incorporating imide structures into PUs are as follows [62]:

- Reaction of isocyanate capped PU prepolymer with acid dianhydride [99–103]. Pyromellitic dianhydride (PMDA), 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTDA) and 3,3′,4,4′-sulfonyldiphthalic anhydride (DSDA) are widely used, commercially available acid dianhydrides

- Reaction of acid dianhydride with aminoethonal to give a hydroxyl-terminated imide monomer that can be reacted with NCO-capped PU prepolymer
- Reaction of isocyanate-terminated PU prepolymer with aromatic diamines and dianhydride to prepare PU containing imide groups in the backbone
- Intermolecular Diels–Alder reaction of 4-methyl-1,3-phenylenebis(2-furanylcarbamate) with various bismaleimides [104, 105]
- Use of polyamide acid [106], diimide-dinaphthols [107], and imidization of blocked PU prepolymer [108, 109].

9.8.8 Polyurea coatings

Polyurea coatings are formed by the reaction of amine-functional reactants with isocyanate-functional compounds. The high cure speed of polyurea coatings results in short pot life. Wicks *et al.* [110, 111] developed a methodology to slow down or reduce the cure speed, which requires making the amines secondary rather than primary, sterically hindering them and generally making the molecule more bulky, thus reducing the reactivity [112]. This can be achieved by making a polyaspartic ester by means of the Michael addition reaction. The reaction is shown schematically in Fig. 9.18(a). The hindered amine species has a higher viscosity than the amine.



9.18 Preparation of hindered amine and oxazolidine derivative for polyurea coatings [59].

One way to reduce the viscosity is to utilize a low-viscosity oxazolidine. Oxazolidines are useful species that may be used in both one- and two-component PUs as moisture scavengers, reactive diluents and latent hardeners. Hydroxyethyl oxazolidine, shown in Fig. 9.18(b), can be converted to a urethane bis-oxazolidine (high viscous) or a carbonate-bridged low viscous product [113].

9.8.9 Parameters influencing polyester-urethane coating performance

The physical properties of polyester-urethane coatings depend on several factors such as the composition of repeating units, type of monomers used, flexibility of the chain, presence of polar groups, molecular mass, degree of branching or crosslinking, orientation, etc. Short-chain branches increase the crosslink density of coatings, while long-chain branches increase the flexibility of the coatings.

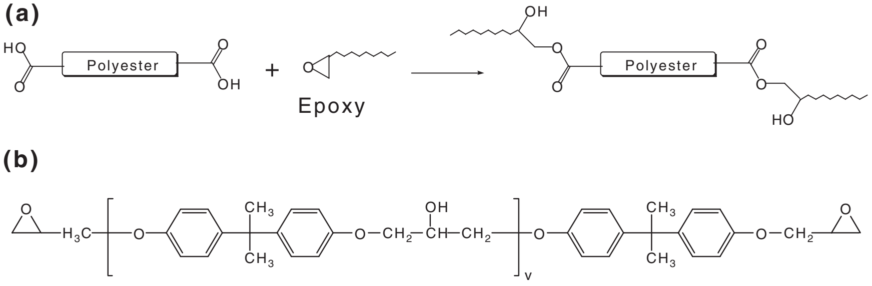
9.9 Other types of polyester coatings

9.9.1 Polyester-acrylate coatings

Polyester-acrylate coatings are generally prepared by the reaction of carboxyl-terminated polyester with HEA or HEMA. This reaction produces terminal unsaturation, and a polyester free-radical chain can form a crosslinked network through both intramolecular and intermolecular reactions in the presence of free-radical generators such as thermal or photoinitiators. Polyester acrylates vary in functionality, chemical backbone and molecular weight. Typically, the higher molecular weight produces a viscous resin with a highly flexible polymer after cure. A high molecular weight reduces the reactivity of the polymer. The mechanical properties of polyester-acrylate based coatings are greatly affected by the network structure of the crosslinked polymer. The chemical backbone has a large influence on properties such as reactivity, color stability, hardness, etc. The monomers and the functionality of the polyesters play an important role in the reactivity of the pendant double bonds [114–116]. Kim and Seo [88] studied the UV-curing behavior and mechanical properties of a UV-curable polyester acrylate resin system containing different photoinitiators and reactive diluents at various levels of contents.

9.9.2 Polyester-epoxy coatings

Many commercially available epoxy resin powder coatings contain solid polyester polyols which are crosslinked with epoxy resins. These coating



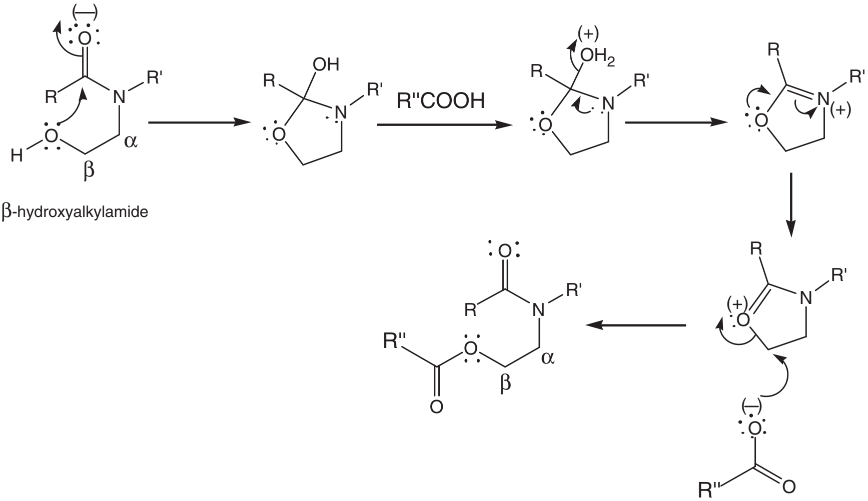
9.19 (a) Crosslinking reactions of hydroxyl-terminated polyester with epoxides; (b) bisphenol A epoxy resin.

powders are also often described as hybrid powders [117, 118], and are characterized by very good film smoothness and mechanical properties. Epoxy-polyester powder coatings possess very good flow properties and yellowing resistance at high temperatures. These powder coating products are widely used where good chemical and detergent resistance is required; they offer good stoving stability combined with excellent decorative appearance and ease of application. Figure 9.19(a) shows the crosslinking reactions of hydroxyl-terminated polyester with epoxides. In any event, by varying the ratio of polyester to epoxy, different properties can be achieved. The mixing ratio between epoxy resin and polyester resin varies between 60/40 and 10/90. The curing temperatures for polyester/epoxy coating powders are between 160°C and 220°C. The resultant powder films are less liable to 'go chalky', and also have excellent mechanical qualities. Epon 1001F from Shell Chemical Company, having an equivalent weight (EEW) of 525–550, was used as a crosslinking agent for the polyesters. Epon 2002 (Shell Chemical) is a standard 'Type 3' bisphenol A epoxy resin shown in Fig. 9.19(b) with EEW 675–760. Epon 1001F has a very low equivalent weight among commercially available epoxy resins.

Hybrid UV cured powder coatings based on methacrylated polyester with acrylated epoxy resins give an interesting blend of properties when cured. Inclusion of a polyester backbone improves light resistance of the coatings in weathering tests, while the epoxy backbone gives outstanding chemical resistance, improved adhesion and smoothness. Polyester-epoxy powder coatings are widely used for a variety of indoor applications, such as transformer covers, oil filters, air conditioning housings, and power tools.

9.9.3 Polyester-β-hydroxyalkylamide coatings

Thermoset powder coatings based on polyester resins and triglycidylisocyanurate (TGIC) hardeners are widely used for exterior decoration as

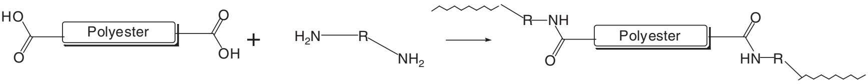


9.20 Curing reaction of β-hydroxyalkylamide coatings.

well as corrosion protection. Applications of polyester-TGIC powder coatings include outdoor furniture, air conditioning units, steel and aluminum automotive wheels and various aluminum extrusions. TGIC polyester powder finish provides a uniform high-quality surface with superior resistance to corrosion, chipping, scratching and fading. However, TGIC presents a formulation with toxicity problems and requires relatively high cure temperatures. As an environmentally preferable competitor to TGIC and PT-910 (a trimellitic acid triglycidyl ester, developed by Ciba), a new curing agent, β-hydroxyalkylamide, was developed by EMS-Chemie (commercial name 'Primid'). Powder coatings cured with β-hydroxyalkylamide are completely safe from a toxicological point of view [119, 120]. With this type of coating, the crosslinking reaction (Fig. 9.20) occurs as an esterification between the hydroxyl of the β-hydroxyalkyl amide and the carboxyl of the resin, which involves the formation of water. β-hydroxyalkylamide is a tetra-functional, white, crystalline solid with melting point around 100–120°C and reacts with acid groups at relatively low temperatures, i.e. around 150°C. The increased reactivity of β-hydroxyalkylamides with carboxyl groups has been explained by the fact that esterification of β-hydroxyalkylamides is carried out through an intermediate product with an oxazolinium structure [121, 122].

9.9.4 Polyester-amide and polyester-imide coatings

Polyester-amides are polymers with ester as well as amide linkages in their main chain, resulting from the condensation reaction of diamines with



9.21 General synthesis path for polyester-amide coatings.

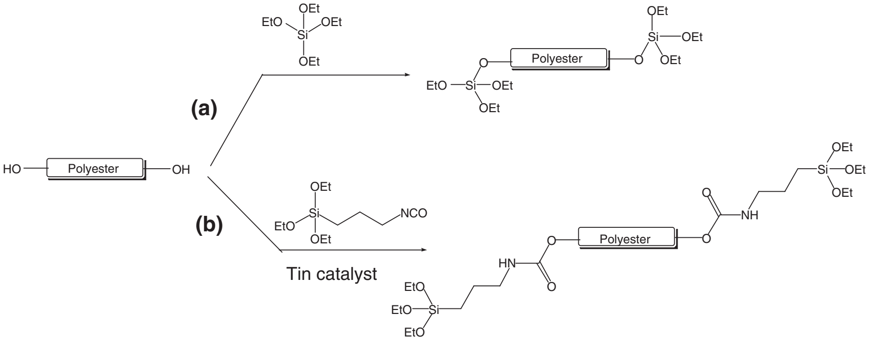
carboxyl-terminated polyester resin (Fig. 9.21). Polyester-amide coatings show the hybrid properties of both ester and amide groups. Since polyamides show very good mechanical and thermal properties because of strong internal association via hydrogen bonding, these coatings are used to improve the mechanical properties of polyester coatings [1].

The main aim of using polyester-imide coatings is to incorporate the imide group, which has sufficient stability against thermal and mechanical deformation, thus improving the properties of the polyester coating. Methods used to prepare polyester-imide coatings are as follows [123, 124]:

- Polycondensation reaction of a diol with bisimide dicarboxylic acids, derived from trimellitic acid and a diamine
- Esterification reaction of an imide group containing diacids with diols
- Reaction between ester containing dianhydride group and a diamine
- Esterification of a diol and diacids with 4-carboxy-*N*-(hydroxyphenyl)phthalimide
- Imide-forming condensation reactions between a polyamine and an anhydride connector.

9.9.5 Polyester-alkoxysilane hybrid coatings

Recently, organic–inorganic hybrid materials have received considerable attention because of tunable properties derived from the hybrid combination of soft organic and hard inorganic counterparts. Hybrid materials are formed through the hydrolysis and condensation reaction of an inorganic component, i.e., the alkoxysilane. Polyester–alkoxysilane hybrid coatings are of great interest since they impart both organic and inorganic characteristics. The organic component usually accounts for flexibility of the composites, whereas the inorganic component is responsible for hardness and mechanical impact resistance. The sol–gel process can be either acid or base catalyzed or moisture cured. Usually, both hydrolysis and condensation of silicon alkoxide in the sol–gel method can occur by acid- or base-catalyzed bimolecular nucleophilic substitution reactions [125]. For example, the reaction of hydroxyl end-groups of polyester with isocyanatopropyltriethoxysilane (ICPTES) results in covalent bond formation between the organic and inorganic components as shown in Fig. 9.22. The moisture curing reaction of this type of coating results in inorganic–organic hybrid



9.22 (a) Crosslinking reactions of hydroxyl-terminated polyester with tetra-alkoxysilane; (b) silane-modification of HO-terminated polyester with ICPTES.

networks with improved mechanical properties such as hardness and abrasion resistance.

9.10 Conclusion

The demands for high-performance industrial coatings are increasing rapidly. Today's strict environmental laws pose significant challenges for coatings end-users. In this respect it is essential to know the changes that are taking place in coatings research as well as the basic chemistry involved in this development. In this chapter, different ways to formulate polyester coatings with different crosslinkers and their chemistry have been included along with some interior and exterior applications. Attention was paid towards the chemistry of saturated polyester-melamine and polyester-urethane coatings. Part of the chapter also discusses the chemistry, structural features and use of polyester-acrylate, polyester-epoxy, polyester-amide, polyester-imide and polyester-alkoxysilane hybrid coatings. We hope that the present chapter will give ample information to the reader about the basic chemistry involved in saturated polyester coatings for the future development of high-performance and eco-friendly coatings for application in different industrial sectors.

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10

Glassflake coatings for corrosion protection

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10.1 Introduction

The vast majority of coating systems are organic in nature, the basic premise of these coatings being to provide a film of material which prevents attack from corrosive ions. Normally, for industrial applications onto steel, two- or three-coat systems are used comprising:

1. Sacrificial primer
2. Build, intermediate or tie coat
3. Top or veilcoat.

The primer will generally contain corrosion inhibiting or passivating compounds. If freely exposed to the environment these may be consumed and eventually stop working as a corrosion inhibitor. General practice is therefore to use an intermediate or tie coat to reduce the amount of corrosive species reaching the primer and substrate, the topcoat often being used to provide cosmetic appearance and durability (e.g. UV resistance).

The molecular structure of organic materials allows for the passage of water vapour. In practice it is not possible to stop entirely the passage of water vapour through the paint film, so the above three-coat system is often referred to as a sacrificial paint system. However, the moisture vapour transmission rate will vary depending on a number of factors, including the resin and fillers used and the cure of the paint film. If permeation can be reduced to very low levels, the need for a sacrificial primer layer can be removed. This allows for the production of materials known as barrier coatings. The best filler to achieve this is corrosion resistant glassflake.

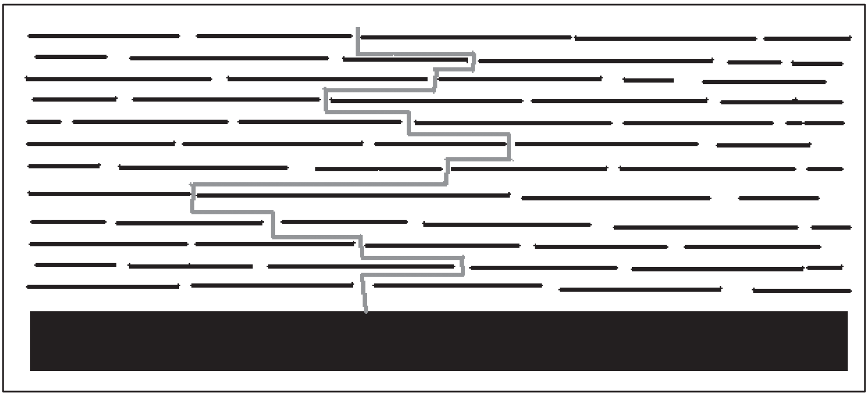
10.2 The development of glassflake coatings

Glassflake was developed in the United States in the late 1950s and was initially used for the reinforcement of polyester roof-light panels. It had been found that these panels distorted in strong sunlight and a means of improving modulus and dimensional stability was sought. Initially glass fibre was used, but this severely reduced light transmission when it was added at the required volume to obtain the required tensile properties. When glassflake was used as a substitute for the fibre, not only was the modulus substantially improved but the light transmission was barely affected. While this seems to have been the first use of the product, glassflake quickly found its way into the coatings industry and this was the bulk of its usage for many years; only later were the advantages of glassflake in other areas identified.

Particles of a high aspect ratio (low elevation to plan aspect or low thickness to surface area), for instance platelets or flakes, when incorporated into the film, overlap each other and present a barrier to the passage of moisture and gas diffusion in that film, by extending the path length through it. This effect is sometimes known as the tortuous path effect (see Fig. 10.1). Particles of a granular or spherical nature cannot overlap in this manner and offer only limited resistance to osmosis. High aspect ratio fillers are therefore referred to as barrier pigments and offer significant improvements in permeation resistance.

The benefits of using flake-like barrier pigments, such as mica and micaceous iron oxide, in anti-corrosive paints and coatings to reduce moisture vapour transmission have been known for a substantial number of years. Other barrier or flake pigments with varying attributes such as aluminium and zinc have also been used as combination chemical and barrier fillers with varying degrees of success. More recently there has been considerable interest in the use of organo-clay based nano-flake technology.

Other barrier pigments commonly used in coatings are opaque and often strongly coloured; micaceous iron oxide in particular makes coatings and paints difficult to tint in light shades, while glassflake is clear. Glassflake is



10.1 The tortuous path effect.

also highly chemical resistant and inert in most environments, has good mechanical properties and is generally considered a simple dust hazard or non-hazardous, particularly when compared with fibres and some metallic pigments. Glassflakes have a large aspect ratio and unlike mica they are not stepped, are totally impervious to moisture vapour and, if manufactured correctly, are consistent in composition.

Glassflake was introduced into coatings around 1960 and gradually gained popularity. However, in the early years, glassflake coatings were somewhat crude trowel- or brush-applied materials basically designed as a fibreglass composite layer, but with the glassflake substituting for fibre. It was the mid-seventies before good spray-applied glassflake coatings were available and these were generally thought to be exotic, difficult to apply and expensive. They were produced predominantly with the polyester resins used previously for hand layup but they were also manufactured with vinyl ester for improved chemical resistance. Epoxy formulations containing glassflake only came later and until more recent times were few and far between.

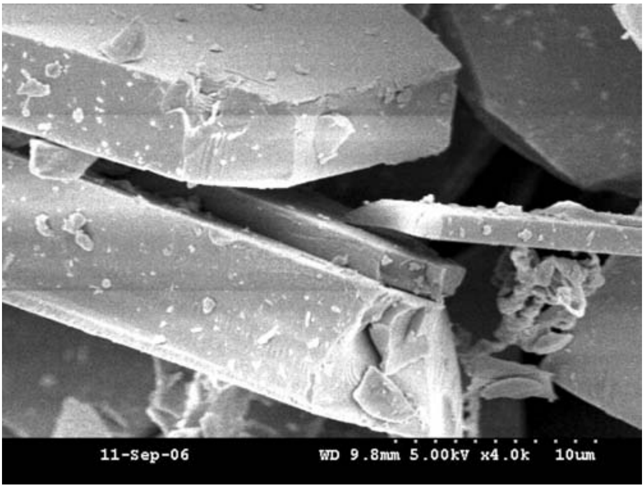
From the early eighties glassflake coatings started to become more acceptable, as the performance and benefits of long life became apparent. At the same time prices compared with other coatings dropped, leading to greater acceptability within the marketplace. It was during this period that a great deal of research was carried out into the use of glassflake as a barrier pigment and the types of paint and coating using it multiplied significantly, this work eventually spilling into other fields. Unfortunately, the effects of using different concentrations, flake aspect ratios and the unusual effects on viscosity and critical pigment volume concentration were rarely understood and little work was done in this area. There was also poor understanding of how the glass bonded within the various resin matrixes.

10.3 Factors affecting the effectiveness of glassflake coatings

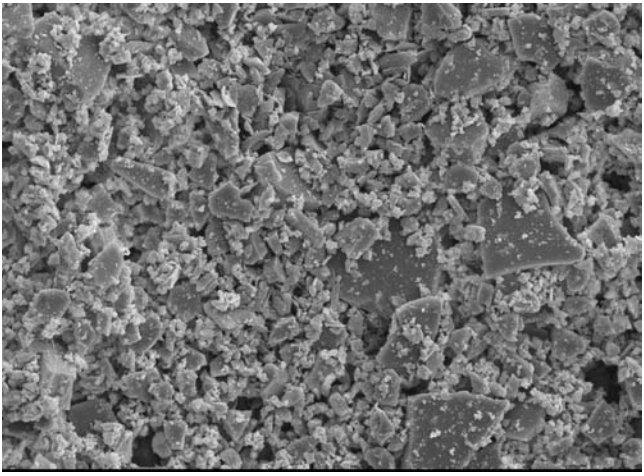
It is important to understand that although glassflakes are impervious to moisture vapour and gas diffusion, they do not present a continuous barrier in a resin matrix. The resin carrier therefore plays a very important role, i.e. glassflake cannot make a poor resin film into an excellent coating, although it may substantially improve it, but even excellent resins can benefit from addition of flake. In addition, flake offers differing aspects to mechanical reinforcement than those attained by adding fibre.

It is important to assess the quality and composition of glassflake being used. With respect to the composition modern glassflake materials are generally produced from ECR (extra chemical resistant) glass. This gives significantly better chemical resistance than the e-glass often used in glass fibre and the composition of the glassflake should be assessed.

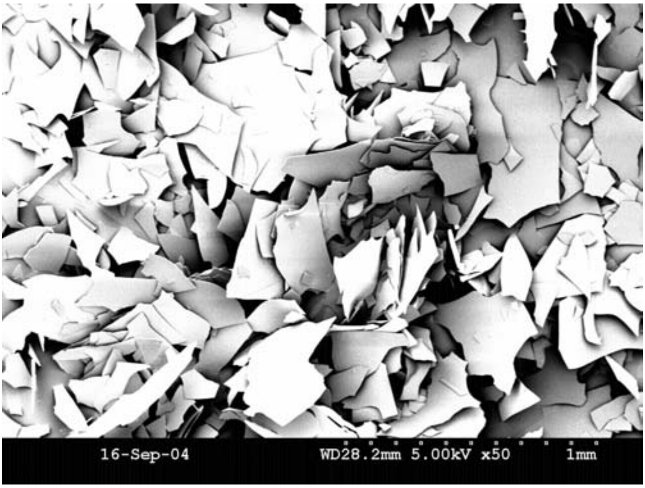
The glassflake chosen should be flat, of uniform thickness and of the diameter required for the desired performance characteristics. It is worth spending the effort to assess these factors before commencing research and development work on formulated products. Problems with processing and process control can result in non-uniform glassflake being produced. Glassflake as shown in Fig. 10.2 will clearly have a negative effect on the packing within the resultant coating. Figure 10.3 shows a grade of glassflake



10.2 SEM image of glassflake.



10.3 SEM image of micronised glassflake.



10.4 Advanced glassflake.

sold as micronised glassflake. In some cases the high thickness of the original glassflake from which this material was milled makes the resultant material more akin to ‘chunks’ than flakes. Comparison with these images shows that the material manufactured in the UK is of consistent quality (Fig. 10.4).

Today many different types of paint or coating resin carrier can be used with glassflakes, including but not limited to unsaturated esters, epoxies, chlor-rubbers, alkyds, coal-tars, polyurethanes, Vinyls and water-based acrylics. The addition of flake will generally improve the moisture vapour transmission resistance of almost any coating film or membrane and there may be other benefits with new properties being imparted or improved. However, the level at which the glassflake should be added, the particle size distribution and adhesion to the carrier are of paramount importance.

Although glassflakes with aspect ratios as low as 10:1 will give some benefit, generally the higher the aspect ratio the better the barrier presented. This premise has to be tempered to some extent, however, as out of alignment very large aspect ratio flakes can afford a more direct path through the film and where the film is less in thickness than the nominal diameter of the flake or cause stress raisers for crack propagation. In addition there are some properties that may be adversely affected when using large flakes, such as flexibility and elongation to break. Also for consideration is the practicality of using large flakes. For instance, when a coating has to be sprayed, the gun tip size is limited by several factors and the flake will have to be small enough to pass through the spray tip without causing blockages. Large flakes also tend to produce rougher surface finishes. It is therefore common that flakes of around 500 μm and below are used for spray application, while flakes above this size, i.e. as large as 1500 μm are rarely used, except for hand-applied materials. One particular area where such flake is used is in the manufacture of highly viscous trowel-applied coatings and fillers, generally used as high build repair materials.

Flake size and thickness are only two of the issues involved in obtaining performance. The quantity of glassflake added and particle distribution are also critical. It is obvious that if thin flakes of glass are used there are many more flakes than if thick ones are used for the same weight, and therefore the surface area to be wetted with the thin flakes is vastly greater. This means that it is impossible to state simply the requirement for an amount of glassflake, e.g. 20% by weight. It may be possible to add 20% by weight of flake at a thickness of 5 μm and not exceed the critical pigment volume concentration to resin ratio (CPVC). If the same quantity by weight of a flake at 2 um thickness were added, then the surface area of this flake will be at least two and a half times that of the thicker one. There may now be insufficient resin to wet out this increased area and the PVC level may be exceeded. In any case the viscosity may become so high when changing from the thick flake to the thin flake that addition at the same level becomes impossible.

It is obvious from the preceding statements that once a thickness of flake has been chosen it is important to optimise the addition level. That level will depend upon the type of resin being used and what other pigments or fillers are being used in conjunction with it.

A further consideration is whether or not coupling or bonding agents are used to provide better adhesion of the glassflake to the resin and of the coating to the substrate. Adhesion plays a substantial role in the performance of organic materials in corrosion protection. The bonding of fillers into the resin is also a very important facet in obtaining performance, both from a corrosion resistance point of view and in mechanical performance.

There are a number of alternative materials which claim to improve adhesion within coating systems and these should be evaluated for the resin system in use. Silane adhesion promoters have been used for many years in the glass fibre industry to improve bonding within GRP laminates and consequent performance. This improvement in performance is seen as both an increase in some mechanical properties and a decrease in moisture vapour transmission. In thermoset resins it is possible to get substantial improvements in performance, simply by adding the silane chosen to the resin component either just before or just after the glassflake is added. With thermoplastic materials, however, addition during processing is generally not possible and it is the glassflake which has to be pre-treated with silane during manufacture. It is noticeable that pre-treated flake will often improve the bonding performance not only in thermoplastics but also in thermosets, to a higher level than that achievable by adding the silane indirectly via the resin. Where the silane is added to the resin, it has been shown that there is a critical level and the optimisation peak is often very steep. This value applies for each particular resin, glass thickness, particle distribution and addition level (it should also be noted that other fillers or additives such as thixotroping agent will also affect the optimisation level).

There are number of manufacturers of silane around the world, all of whom produce silane of various types and functionalities. Using vinyl functional silane for unsaturated esters, epoxy functional silane for epoxy based, amine functional silane for epoxy hardeners, etc., would appear obvious. These will bond the adhesion promoter into the relevant polymer matrix. However, you will need to perform rigorous evaluation work on the fully formulated systems. It has been found, for example, that some silane types can adversely affect other properties such as thixotropy, and that such effects can be time dependent. Best results may also be obtained by using a blend of silane types, rather than just one material.

Where silane is added by pre-treating the glass, the level of silane used is not so critical, provided that saturation of the flake causing agglomeration is not achieved. It is also observed that with pre-treated glass a much higher level of glassflake can be added to the resin and particularly for thermosets, without exceeding the CPVC level. One downside of using pre-treated flake, however, is the cost and change in safety hazard classification.

It seems fairly obvious from the previous paragraphs that barrier pigments with high aspect ratios and in particular glassflake cannot simply be added at a nominal value if good results are going to be obtained. However, some specifiers of coatings containing glassflake often state the minimum loading of glassflake and a thickness for the product to be applied at, but what knowledge do they base this information on?

Even if the characteristics of a particular resin and formulation are known, product formulation rather than performance specification can be a dangerous method of assessment. For example, a specification could state 'Epoxy with a minimum glass flake loading of 20% by weight.' This level of addition could in many formulations exceed the CPVC level and the coating would therefore give better performance at lower glass flake loadings. In addition, neither the flake thickness nor the particle size distribution is specified. It is also possible that a coating with very high performance could be precluded from being used under such a specification regime. It is more sensible if performance criteria, rather than formulation criteria, are used to specify coatings.

With modern production methods glassflake can now be produced at a consistent thickness, which may be varied for different purposes from around 10 μm thickness to as low as 100 nanometres, almost limitless particle size distributions being possible. The effects of thickness, particle size, volume concentration, etc., were formerly little understood. A substantial amount of work has been carried out, initially evaluating glassflake coating formulations, using flakes of differing thickness and diameters, and with differing particle distributions. Some of the results were surprising, others expected. Because testing was carried out over a wide range of properties and resin systems and looked not just at diffusion and corrosion resistance, some interesting parameters were discovered.

The resin systems initially used as carrier resins for glassflake systems were those used within the GRP industry. However, before commencing work on these resin systems, bear in mind that these resins were generally developed for use in thick film systems, which are then generally post-cured prior to service. Performance values and physical properties are often quoted based on post-cure schedules which are wholly unrealistic, especially for field-applied coatings. Glassflake coatings are applied at relatively thinner films than GRP and are often not post-cured prior to service. It may therefore be necessary to significantly modify the resin chemistry in order to optimise the performance.

10.4 Testing the performance of glassflake coatings

It is crucial that whatever glassflake is used in the coating, its performance is fully quantified. The following tests are considered to be of particular benefit when comparing the glassflake and coating performance:

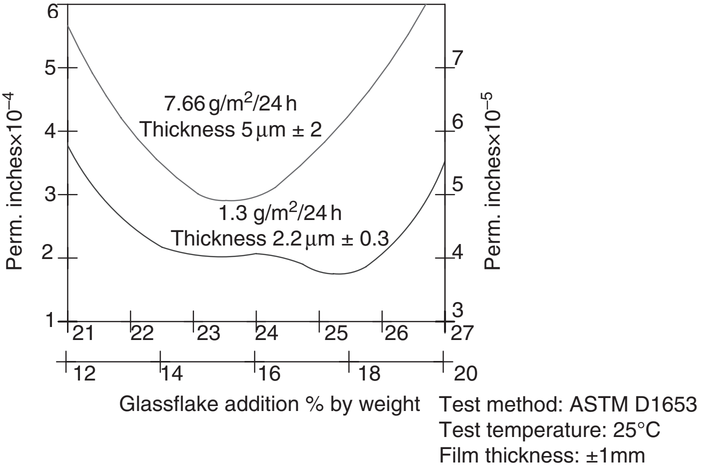
- Moisture vapour transmission (MVT)
- Water absorption
- Atlas cold wall (osmotic blister) testing
- Cathodic disbondment
- Glass transition (T_g) (DSC and DMTA)
- Abrasion resistance
- Chemical resistance
- Mechanical properties.

Tests of particular relevance to glassflake coatings are MVT testing, cold wall testing and cathodic disbondment testing. Other properties will generally fall into place, once these key factors have been optimized. When formulating glassflake coatings it should be borne in mind at all times that the high surface area to volume ratio of glassflake particles means that modest changes in addition levels may have significant effects on performance.

As can be seen from the results shown in Table 10.1 using an unsaturated ester resin, the quantity versus permeation curve is very steep, with a 1% change in the addition level changing the permeation rate from 10.61 to 3.46. A further addition of glass changes the permeation rate for the worse,

Table 10.1 Moisture vapour permeation at various glassflake addition levels, tested in accordance with ASTM D1653

Glassflake concentration	Average result of 5 samples (perm. inches $\times 10^{-5}$)
14%	10.61
15%	3.46
16%	3.64



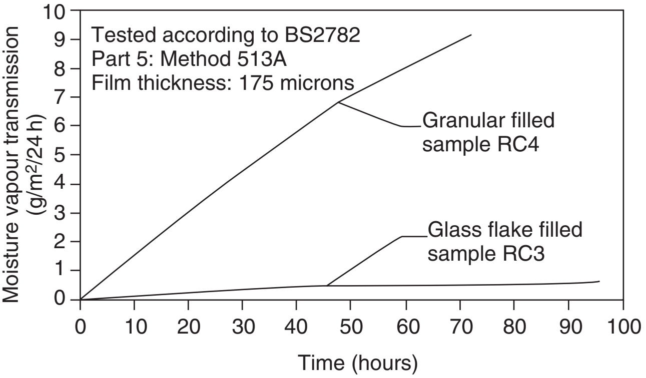
Test method: ASTM D1653
Test temperature: 25°C
Film thickness: ±1mm

10.5 Water vapour transmissions for milled glass.

but only marginally so; further additions (not shown here) showed a progressive worsening. As would be expected, subsequent additions show a rapid increase in MVT. These results are typical as the CPVC level is approached and exceeded, and this effect is also shown in Fig. 10.5.

The steepness of the MVT performance curve is not always so high. In some instances the curve is a gradual slope at both ends with a flat bottom. This type of addition/performance curve is preferred, as it not only allows some deviation for production tolerances but also allows the formulator to look at other properties, i.e. mechanical or fire retardancy, without compromising the other aspects.

Figure 10.5 shows two different curves. The top curve represents glass at a thickness of approximately 5 mm, whereas the bottom curve shows glass at a thickness of approximately 2.2 mm. There are also some differences in particle distribution, with the thicker glassflake having a wider range of nominal diameters than that of the thinner glassflake. The difference in performance with the change in glassflake type can clearly be seen. The curve on the thicker glass is much steeper and the best loading value is at



10.6 Moisture vapour transmission reduction using 2% glassflake.

approximately 23.5% by weight. A move either side of this addition level changes the MVT performance quite significantly. Conversely the thinner glassflake only requires an addition of between 14% and 18% to obtain an MVT which is almost a magnitude better. The curve is much flatter with the optimum level of addition being at approximately 18%.

It must be noted that this graph is specific to this resin system and the appropriate addition level will vary from resin to resin. In some viscous epoxy systems, addition values of only 8–12% may be required to optimise the coating. It must also be stressed that such high levels of glassflake are only suitable for 100% polymeric resin binders. Glassflake will prevent the release of solvent in a similar way to that by which it reduces vapour transmission. As can be seen from Fig. 10.6, the addition of small percentages of glassflake to solvent-borne coatings can be advantageous, in this case 2% of glassflake being substituted for a granular filler on a solvent-borne epoxy coating. Similar results have also been found in water-borne coatings.

10.5 Applications of glassflake coatings

The largest use of glassflake within the coatings industry is within heavy-duty polymeric lining, where much higher percentages of glassflake are used as discussed earlier in the text. There are many benefits to correctly formulated polyester, vinyl-ester and epoxy systems. These include:

- Very low permeation values
- High temperature resistance
- Excellent chemical resistance
- Excellent adhesion (including immersed adhesive strength)
- Resistance to undercutting at damaged sites (essential to prevent the coating peeling back and disbonding from localised damaged sites. This

is not uncommon when damage occurs on solvent-based epoxies, urethanes, rubbers and glass fibre reinforced systems)
- High abrasion resistance
- High impact resistance
- High tensile strength
- Machinability
- Dimensional stability during immersed service
- Repairability
- High resistance to cathodic disbondment
- Ability to be used over a wide range of substrates
- Good flexibility
- Durability, offering very long service lives
- Cost effectiveness.

These polymeric coatings are often used instead of expensive metallurgical solutions. They also allow for refurbishment or protection of capital equipment at a fraction of their cost. They can be used not only for corrosion protection but also to execute repairs to existing equipment. Such repairs can be carried out even on seriously corroded substrates, due to the high tensile strength and composite stability. This work is often combined with engineering modifications, to improve the design and functionality of plant. The coatings are often used as composite repair materials which can be machined back to the original dimensions of the component on the protection and refurbishment of engineering components.

The ranges under which these materials have been used around the world make all their applications too diverse to list in this text. But taking just one area of work, glassflake materials have a proven track record of use in offshore and onshore applications within the petrochemical industry. On offshore platforms areas protected by vinyl ester and polyester systems have included rig jackets, cellar decks, riser pipes, mud tanks, de-aerators, separators, filter vessels, production pipework, wellhead manifolds, ballast tanks, effluent tanks, pre-load tanks, helicopter decks, drill decks, effluent tanks, chemical storage tanks, cooling water pipework, fire water mains, superstructure steelwork, pumps, valves, heat exchangers, tube faces, water boxes and potable water makers, to list but a few.

Glassflake coatings have a proven track record in many environments, including seawater, where service lives of correctly formulated materials in excess of 25 years are not uncommon. Developments in technology are allowing these coatings to be specified now with life expectancies of 20 or 30 years or longer in aggressive service applications.

11

Fluoropolymer coatings for corrosion protection in highly aggressive environments

A S HAMDY, Central Metallurgical Research and Development Institute (CMRDI), Egypt

11.1 Introduction

Organic coatings are used widely to improve the corrosion protection performance of ferrous and non-ferrous metals against corrosive environments. Fluoropolymers are considered to be one of the most popular high performance organic coatings for their exceptional resistance to solvents, acids, and bases.

A fluoropolymer is a polymer that contains fluorine. Fluorine chemistry has played a distinctive role in many significant and highly diverse technological developments over the last decades. The singular nature of the fluorine atom, combined with the unique physical and chemical properties that the fluorine imparts to any fluoride-containing compounds, are the driving force for increasing the research interest in this area [1]. Many kinds of fluoropolymer coatings such as PVF, PVDF, PEVE, etc., have found extensive application in various fields as highly protective coatings against aggressive environments [2].

Fluoropolymers are high performance polymers with diverse applications. By virtue of their outstanding chemical resistance properties, fluoropolymers have replaced many metals and alloys for maintaining the purity of processing streams in the chemical processing, food, pharmaceutical, petroleum, polymer, semiconductor, and pulp and paper industries. Other benefits of fluoropolymer coatings include reduced friction, resistance to galling, non-stick, non-wetting, electrical resistance and abrasion resistance.

Generally, fluoropolymers are inert to strong mineral acids, inorganic bases, inorganic oxidizing agents and salt solutions. They are also inert to organic compounds such as organic acids, anhydrides, aromatics, aliphatic hydrocarbons, alcohols, aldehydes, ketones, esters, chlorocarbons, fluorocarbons, and mixtures of these organic compounds. However, in order to be effective against corrosion, such fluoropolymer coatings need to exhibit (1) good wet adhesion and (2) low aggressive solution/oxygen permeability.

By good wet adhesion is meant the adhesion of the polymer film to a substrate in the presence of aggressive solution. By low aggressive solution and oxygen permeability is meant the ability to retard aggressive solution and oxygen permeation through the polymer film to the underlying substrate [3]. Therefore, the surface pretreatment prior to fluoropolymer coating plays an important role in improving the adhesion and the corrosion protection performance of any fluoropolymer coating system [4–10].

This chapter provides an extensive study on the effect of surface treatment prior to fluoropolymer top coatings on the corrosion resistance of aluminium composites in marine environments.

11.2 Corrosion protection of aluminium metal matrix composites

The material under investigation was aluminium metal matrix composite, AA6061 T6–10% Al_2O_3 (v/v). Aluminium and its alloys are used in many industrial applications such as in the automotive and aerospace industries [11]. The demand for materials of superior mechanical, thermal and electrical properties has focused attention on aluminium metal matrix composites (AMMCs) [2]. AMMCs usually consist of an aluminium alloy metal matrix with reinforced non-metallic phases such as alumina, silicon carbide, graphite, etc. However, AMMCs have a less homogeneous structure than alloys due to the presence of reinforcing particles. Such an inhomogeneous structure can enhance the pitting corrosion susceptibility, as well as cause a preferential dissolution of the interface between the matrix and the reinforcing particles [12, 13].

In this chapter, the corrosion protection performance of AA6061 T6–10% Al_2O_3 composite, coated with a commercially available fluoropolymer coating based on epoxy primer and clear or pigmented fluoropolymer top coat, was investigated in 3.5% NaCl solutions. A comparison between commercial coating systems consisting of epoxy primer + clear fluoropolymer system and novel surface treatments based on vanadia, ceria or molybdate salts + clear fluoropolymer system will be carried out under scratched coating conditions.

The novel surface treatments, based on clear fluoropolymer coating systems, were designed to overcome the effect of intermetallic particles on the aluminium surface and to offer a thick layer of aluminium oxide enriched with vanadia, ceria or molybdenum oxide. These pretreatments are characterized by superior corrosion resistance even after 30 days of immersion in 3.5% NaCl aqueous solutions [14–19], which enables them to be used as alternatives to epoxy.

A modified version of such coatings was prepared by adding iron oxide and titanium oxide as pigment to the fluoropolymer top coat. Pigments such as aluminium, titanium oxide, iron oxide and bronze pigments are solid materials that are used to impart colour, control gloss, improve performance, such as infra-red reflectance or corrosion resistance, or simply occupy space in a paint film.In general, pigments in fluoropolymer coatings such as titanium oxide and iron oxide can impart special effects, chemical resistance and/or colour to a coating and are also used to decrease the porosity of the coatings [20, 21].

When selecting paint pigments, it is important to understand the conditions under which the coating will be used. The pigment must maintain its original colour under the conditions to which the coating will be subjected. The pigment must be heat resistant if the coating will be subjected to heat. The pigment must be capable of withstanding UV light and humidity if the coating will be used in an open atmosphere. The pigment must also have corrosion and chemical resistance to the environment to which it will be exposed. Other important properties, such as colour, opacity, tint strength, brightness, toxicity, and oil absorption are important factors that must be considered in selecting a pigment. The choice of pigment depends on the colour desired and the durability and performance needed.

11.3 Application of fluoropolymer as corrosion resistant coatings

The present study compares commercial epoxy-based fluoropolymer coatings with new coatings systems based on treating the aluminium composite substrate with novel corrosion resistant surface treatments prior to applying the fluoropolymer top coat. The composition of the coating systems components is as follows:

- The first component is a coating system consisting of solvent based epoxy primer (80 μm) + clear fluoropolymer top coat of FLBZ 1074 (40 μm); 40.5% fluorine. FLBZ 1074 was obtained as a clear solution in butyl acetate and consists of a proper combination of PFPE, HDI and IPDI trimer macromers. FLBZ 1074 is the trade name of a commercial fluoropolymer top coat produced at ausimont S.p.A, Milan, Italy.
- The second novel surface treatment component is a vanadia, ceria or molybdate-treated specimen. Vanadate-treated samples (Vanadia) were prepared by first pickling the aluminium composite samples in dilute potassium hydroxide solution, followed by oxide thickening in boiling water, and finally by immersion in a vanadia solution. Cerate-treated samples (Ceria) were prepared by immersion in boiling water followed by immersion in a cerate salt solution. Molybdate-treated samples were prepared by pickling the aluminium composite samples in dilute potassium hydroxide solution followed by oxide thickening in

boiling water followed by immersion in a molybdate salt solution for 1 h at open circuit potential (Molybdate 1) or at –500 mV (Molybdate 2). After the sample treatments, a commercially available top coat of fluoropolymer clear FLBZ 1074 was applied to all samples.

To investigate the effect of pigment addition on the corrosion resistance of the above coatings systems, a modified version of such coating systems was prepared by adding iron oxide and titanium oxide as pigment to the fluoropolymer top coat. Electrochemical impedance spectroscopy, EIS, was used to evaluate the coating performance after immersion in 3.5% NaCl solution. The salt spray chamber test was used to measure the durability of such new coatings. The adhesion performance was also measured. The mechanism of protection was investigated.

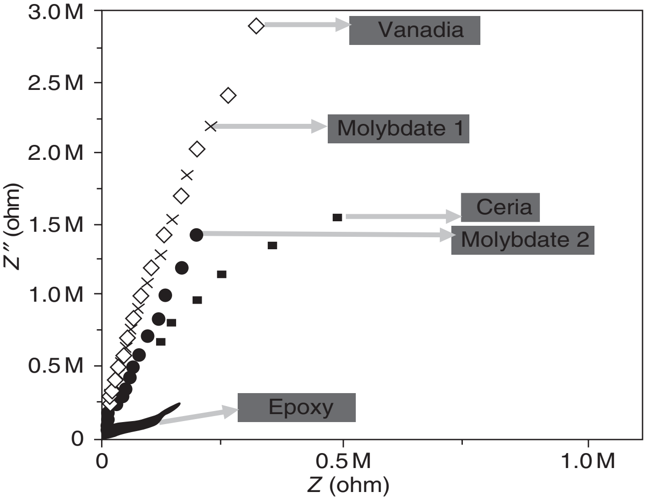
11.4 Evaluating coating performance using electrochemical impedance spectroscopy

11.4.1 Clear fluoropolymer top coat

EIS has been successfully applied to the study of corrosion systems for 30 years and has proved to be a powerful and accurate method for measuring corrosion rates, especially for coatings and thin films. An important advantage of EIS over other laboratory techniques is the possibility of using very small amplitude signals without significantly disturbing the properties being measured. To make an EIS measurement, a small amplitude signal is applied to a specimen over a range of frequencies.

The expression for impedance is composed of a real and an imaginary part. If the real part is plotted on the z-axis and the imaginary part on the y-axis of a chart, we get a 'Nyquist plot'. However, Nyquist plots have one major shortcoming: frequencies are not designated on the plots. Therefore other impedance plots such as Bode plots are important to make a correct interpretation. In Bode plots, the impedance is plotted with log frequency on the x-axis and both the absolute value of the impedance ($|z| = z_0$) and phase-shift on the y-axis. Unlike the Nyquist plot, the Bode plot explicitly shows frequency information.

In this work we used both Nyquist and Bode plots to evaluate the coating performance after immersion in 3.5% NaCl solution. According to the EIS results, the corrosion rates of the epoxy primer-based, clear fluoropolymer-coated samples increased dramatically after less than 30 days of immersion in NaCl under scratched conditions (after drilling a 1 mm hole at the coated surface). Severe filiform corrosion was observed around the scratched area. Conversely, the samples pretreated with vanadia, ceria or molybdate salts prior to applying a clear fluoropolymer top coat showed outstanding

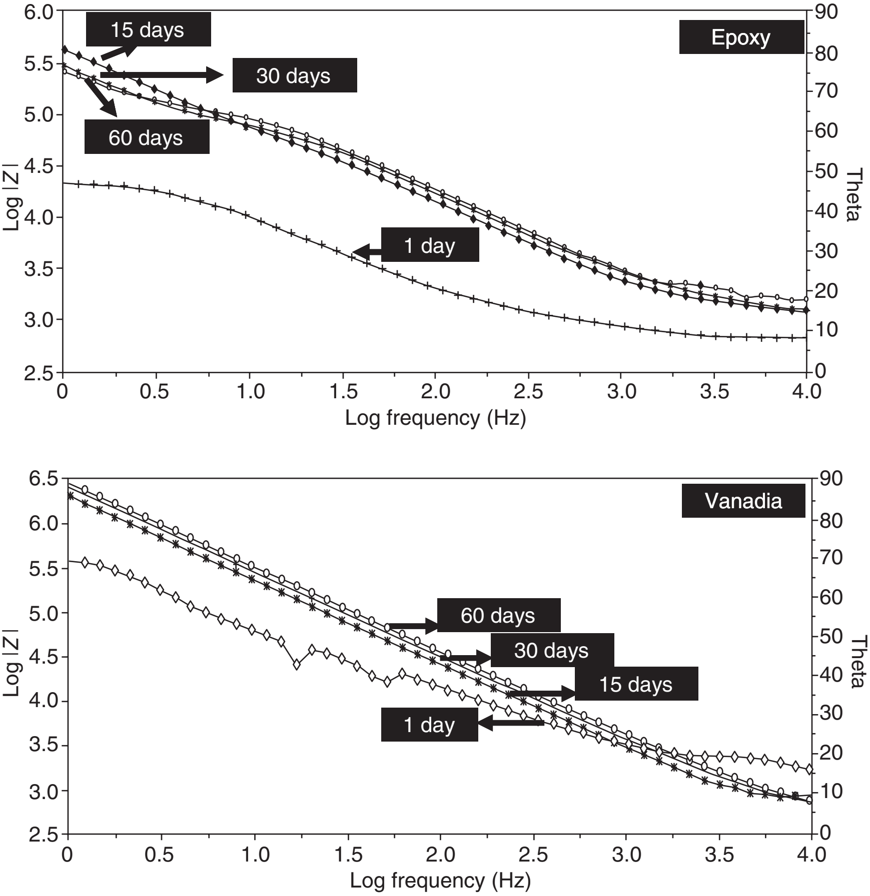


11.1 Comparison between the novel pre-treatments and epoxy-treated with the same clear fluoropolymer top coat after 60 days in 3.5% NaCl under scratched conditions.

corrosion protection even after 60 days of immersion in 3.5% NaCl (Fig. 11.1).

One of the interesting properties of the coatings based on novel surface treatments is that the degree of protection increases by increasing the immersion time up to 60 days. Conversely, the corrosion resistance of epoxy-treated specimens showed a sudden decrease when increasing the immersion time in NaCl, as shown by the resistance curves of the Bode plots (Fig. 11.2).

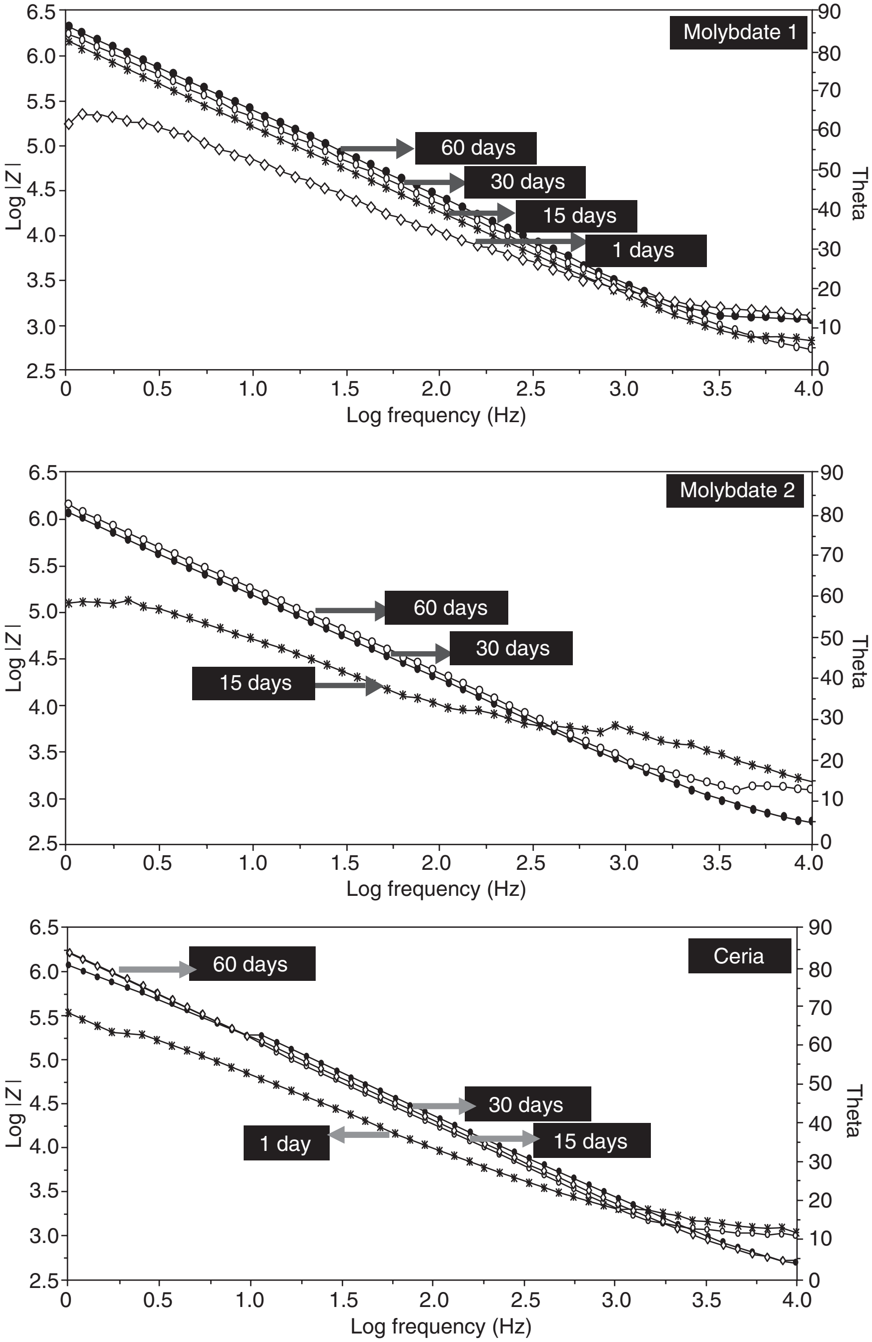
A general equivalent electrical circuit model (Randles Circuit) (Fig. 11.3) was used to analyse the ac impedance spectra obtained from the novel surface treatments after two months of immersion in NaCl. Table 11.1 summarizes the fitting results. In this circuit, R_1 is the electrolyte resistance, C the coating capacitance, R_2 the coating resistance and Q the constant phase element associated to a capacitance because the CPE power n is equal to 0.9 (see Table 11.1). The n values of the CPEs are in the interval $0 \leqslant n \geqslant 1$. The same equivalent circuit was used to analyse the unscratched specimens of epoxy primer + clear fluoropolymer top coat that showed excellent corrosion resistance in 3.5% NaCl [4, 6]. Based on the fitting results, visual inspection and microscopic examinations, the novel surface treatments + clear fluoropolymer top coat specimens showed promising protection against filiform corrosion. In this case, when a small defect or a scratch has been created in the coating, part of the substrate is directly exposed to the corrosive environment. Consequently, an aluminium oxide layer enriched



11.2 Comparison between Bode plots of epoxy-treated and novel surface treatment coated clear fluoropolymer over two months in NaCl.

with vanadium, cerium or molybdenum will be formed [5, 7–10] to seal the damage site in the coatings and, hence, improve the resistance against filiform corrosion. Such processes are usually referred to as 'self-healing' coatings.

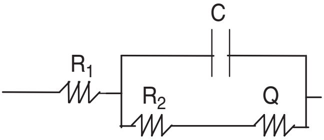
According to the fitting data (Table 11.1) and Bode plots in Fig. 11.2, the coating capacitances of the novel treatments decrease by increasing the immersion time in NaCl. The decrease in capacitance indicates a decrease in water uptake and, hence, an increase in the resistance to filiform corrosion. This can be explained by the continued formation of a vanadium, cerium or molybdenum enriched Al oxide film, which protects the metal against the attack of chloride ions.



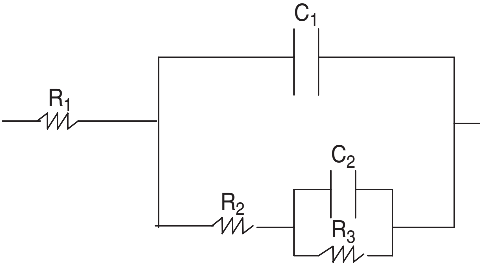
11.2 Continued

Table 11.1 Data fitting of the novel treatments + clear fluoropolymer top coat under scratched conditions

Pretreatment + clear FLBZ 1074 top coat	Immersion time (days)	R_1 (kΩ)	C (nF)	R_2 (MΩ)	Q	n
Vanadia	30	0.50	47	35	0.18e-08	0.9
	60	0.50	39	40	0.18e-08	0.9
Molybdate 1	30	0.50	62	25	0.29e-08	0.9
	60	0.99	50	34	0.28e-08	0.9
Molybdate 2	30	0.50	90	10	0.40e-08	0.9
	60	0.99	59	14	0.67e-08	0.9
Ceria	30	0.50	60	1.9	0.56e-08	0.9
	60	0.99	57	7	0.70e-08	0.9



11.3 The equivalent electrical circuit for the novel surface treatment-based fluoropolymer coatings under scratched conditions (Randles Circuit).



11.4 The equivalent electrical circuit for scratched epoxy-based fluoropolymer coatings.

On the other hand, as a result of the filiform corrosion process that took place in the scratched epoxy primer + clear fluoropolymer top coat specimens, the equivalent electrical circuit described in Fig. 11.3 that was suitable to fit the EIS spectra of the same coatings under uniform coatings [4, 6] became unsuitable to fit the impedance curves after scratching. A new equivalent electrical circuit (shown in Fig. 11.4) was proposed to model the EIS spectra after scratching, considering the new corrosion process due to filiform corrosion. In this circuit, R_1 is the electrolyte resistance, C_1 the

Table 11.2 Data fitting of scratched epoxy pretreated FLBZ 1074 top coat

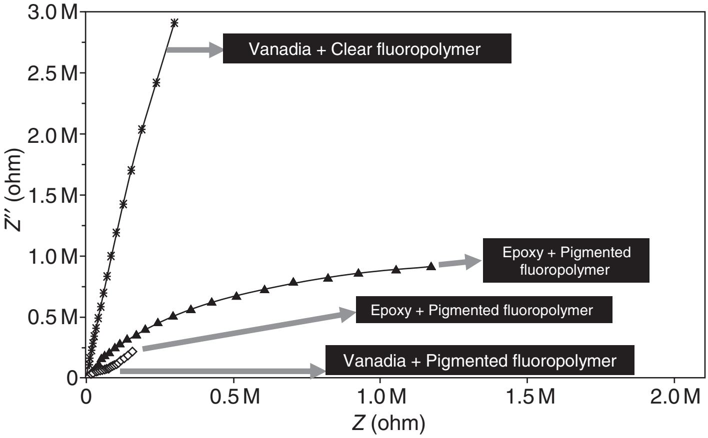
Epoxy + clear FLBZ topcoat	Immersion time (days)	R_1 (kΩ)	C_1 (nF)	R_2 (MΩ)	R_3 (MΩ)	C_2 (μF)
Epoxy	30	0.99	85	0.10	0.60	0.50
	60	0.99	80	0.12	0.65	0.60

coating capacitance, R_2 the coating resistance, C_2 the capacitance of the double layer at the base of the scratch, and R_3 the charge transfer resistance of the corrosion reaction at the base of the scratched part in the coat. The data fitting is shown in Table 11.2. It can be seen from Fig. 11.2 that the corrosion resistance decreased by increasing the immersion time in NaCl, indicating the weak performance of the epoxy primer to protect the metal from corrosion (mainly filiform corrosion). Moreover, the passive film breakdown occurred after 15 days only, whereas such breakdown did not occur till 60 days for the novel surface treatment specimens as shown from the relation between the resistance and frequency in the Bode plot (Fig. 11.2).

11.4.2 Pigmented fluoropolymer top coat

The corrosion resistance of epoxy treated samples was increased by pigment addition. Conversely, the novel treatments showed a dramatic decrease in the corrosion resistance. Pigment addition affects negatively the adhesion performance for epoxy treated specimens and the novel treatments as well. Severe filiform corrosion was observed after less than 30 days of immersion in NaCl.We suggest that the presence of pigments in the epoxy layer increases the capacitance of the resin because Fe^{3+} can capture water and be hydrated to iron hydroxide. The hydrated oxides partially block the pores of the resin, and hence the corrosion resistance of epoxy primer pigmented fluoropolymer top coat specimens showed some improvement in comparison with the epoxy primer clear fluoropolymer top coat ones. Moreover, the presence of iron oxide and titanium oxide as pigment decreases the porosity of epoxy and hence improves the corrosion resistance [20, 21].

The previous explanations were confirmed by the impedance measurements (Fig. 11.5) in which the surface resistance of the epoxy primer pigmented fluoropolymer top coat specimens ($12 \times 10^5\ \Omega\ cm^2$) was about six times higher than the resistances of epoxy primer clear fluoropolymer top coat ($2 \times 10^5\ \Omega\ cm^2$). This result indicates that porosity plays a vital role in the mechanism of protection [20].



11.5 Comparison between the corrosion resistance of clear and pigmented fluoropolymer for the epoxy-treated specimens and the novel treatments.

On the other hand, the addition of iron oxide and titanium oxide as pigment to the fluoropolymer top coat affects negatively the corrosion resistance of the novel surface treatments in NaCl. According to the Nyquist plots (Fig. 11.5), visual inspection and microscopic examinations [20], the surface resistance decreased dramatically from about $2.8 \times 10^5\ \Omega\ \text{cm}^2$ to $0.1 \times 10^6\ \Omega\ \text{cm}^2$.

The dramatic decrease in the corrosion protection and the adhesion performances of the novel surface treatments can be attributed to the competitive action due to formation of two different oxides, one from the treatment layer (vanadium, molybdenum or cerium oxide) and the other from the pigment (namely iron or titanium oxide) when the aggressive solution ions diffuse through the top coat. Formation of two different oxides makes the surface film inhomogeneous and hence water can easily diffuse through the pores among the oxide particles, causing filiform corrosion.

11.5 Salt spray chamber and adhesion performance tests

Epoxy-based + clear fluoropolymer coatings showed filiform corrosion after less than 40 h of exposure to salt spray. Conversely, the novel surface treatments + clear fluoropolymer top coat did not show any sign of filiform corrosion even after 2000 h of exposure in the salt spray chamber.

The presence of pigments improves the durability of the epoxy-treated specimens up to 170 h. However, the novel surface treatments + pigmented fluoropolymer top coat specimens were affected negatively by adding the

Table 11.3 Durability of clear and pigmented fluoropolymer coatings to salt spray chamber test using ASTM B117

Surface treatment	Clear fluoropolymer top coat (h)	Pigmented fluoropolymer top coat (h)
Epoxy	40	170
Vanadia	>2000	30
Molybdate 1	>2000	27
Molybdate 2	>2000	24
Ceria	>2000	26

Table 11.4 Adhesion performance of clear and pigmented fluoropolymer coatings using ASTM D 3359-87 cross-cut method

Surface treatment	Clear fluoropolymer top coat (h)	Pigmented fluoropolymer top coat (h)
Epoxy	100	75–85
Vanadia	75–85	50–60
Molybdate 1	75–85	55–60
Molybdate 2	75–85	50–55
Ceria	75–85	50–60

pigments and showed a dramatic increase in filiform corrosion after less than 30 h (Table 11.3).

The presence of a vanadia, ceria or molybdate component enables the fluoropolymer component to be uniformly applied to the substrate, so as to provide impermeability for the coating. Moreover, the presence of one of these components promotes the uniformity of the dry mix, to provide the opportunity for the application of a uniform composition to the substrate.

The novel treatments, when applied with clear fluoropolymer top coatings, have improved both wet adhesion and low water/oxygen permeability and have maintained these performance characteristics over protracted periods of use.

11.5.1 Adhesion performance tests

Table 11.4 compares the adhesion performance of the novel treatment and epoxy-treated specimens after applying clear and pigmented fluoropolymer top coat. It seems that the presence of pigments affects negatively the adhesion performance of both the epoxy-treated and the novel surface treatments.

11.6 Conclusions

1. Newly developed fluoropolymer coating systems based on novel surface treatments using vanadia, ceria and molybdate salt solutions were proposed as alternatives to the commercially available epoxy-based fluoropolymer coating systems.
2. The performance of the new coating systems was compared with that of clear and pigmented epoxy-based fluoropolymer coating systems from the corrosion protection, adhesion and durability points of view.
3. The novel surface treatments showed outstanding corrosion resistance even after two months under scratched coating conditions. The durability of such new coatings using a salt spray chamber test was very promising (>2000 h), while filiform corrosion was observed for the epoxy-treated specimens after only 40 h of exposure.
4. The novel surface treatments are characterized by their safety to the environment and human body, very low cost, ease of application and very fast curing (not exceeding 5 min).
5. The mechanism of protection using the novel treatments depends on the formation of a highly protective aluminium oxide layer enriched with vanadium, molybdenum or cerium, which has a dual effect of improving the corrosion resistance and of maintaining the adhesion performance within the acceptable range.
6. Pigment addition affects negatively the adhesion performance for both epoxy-treated specimens and the novel treatments.

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12

Polysiloxane coatings for corrosion protection

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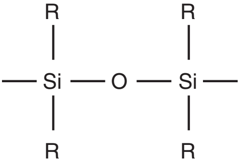
12.1 Introduction: what is a polysiloxane?

Polysiloxane and silicone are synonymously used expressions. Although silicone is the more commonly used term, we mainly use the term polysiloxane in this chapter, because it is clearer with respect to the chemistry and avoids misunderstandings with the metal silicon, which is the chemical core of any silicone or polysiloxane chemistry.

Before getting into the functions per formed by polysiloxanes, let us first answer the question, 'What is a polysiloxane?' A polysiloxane is any one of a class of synthetic materials characterized by silicon and oxygen linked together in the siloxane bond, having organic groups attached to silicon which have a distinct bearing on the properties (see Fig. 12.1). Using siloxy units with different numbers and types of organic substutients, one can synthesize a broad variety of polymer types. These polysiloxane materials may take the form of fluids or oils, elastomers, greases, resins or even a water-soluble salt. The resin types are the ones used in the protective coatings field.

Just as carbon atoms are the building blocks in conventional organic chemistry, so are silicon atoms the basic blocks to which we add organic side chains to build polysiloxane compounds having a wide variety of usages and properties. Since carbon and silicon are the first two members of the fourth group in the Periodic Table of the elements, we can expect certain similarities, but we should likewise be mindful of significant dissimilarities. To begin with, both have a valence of four, and both form analogous series of hydrides. A significant difference is the relative reactivity of analogous carbon and polysiloxane compounds. In contrast to those of carbon, the hydrides of silicon are very vulnerable to thermal degradation and oxidation. The very strong tendency of silicon compounds to combine with oxygen is illustrated by the large quantities of silica, such as beach sand, found in nature, and the equally great scarcity of unoxidized silicon. In



12.1 The siloxane bond.

contrast, elemental carbon abounds in the earth's crust in the form of coal, graphite, and diamonds.

Illustrating the differences in reactivity is the ready hydrolysis of silane and silicon tetrachloride, as opposed to the complete inertness of carbon tetrachloride towards water:

$$SiH_4 + 4H_2O \rightarrow Si\,(OH)_4 + 4H_2$$

$$SiCl_4 + 4H_2O \rightarrow Si\,(OH)_4 + 4HCl$$

$$CCl_4 + 4H_2O \rightarrow \text{no reaction}$$

These are only a few of the many chemical similarities and differences between carbon and silicon, but they are adequate for illustration.

Three different methods are now mainly used by industry to produce the basic chlorosilane intermediates from which polysiloxanes are made. The three methods are (1) the direct method, (2) the Grignard method, and (3) the olefin addition method.

12.2 Direct method for producing polysiloxanes

In the direct method the intermediate chlorosilanes are prepared directly from finely divided silicon metal by reaction with methyl chloride in the presence of a metallic copper catalyst.

This reaction can be represented by the following equation, where the letter R represents a methyl group:

$$RCl + Si \xrightarrow{\text{Cu catalyst}} \text{mixture of } SiCl_4,\ RSiCl_3,\ R_2SiCl_2,\ R_3SiCl,\ R_4Si$$

This mixture of various silanes can be separated by distillation. The specific silane can then be hydrolysed and polymerized (see Section 12.5).

By substituting chlorobenzene (phenyl chloride) for methyl chloride and using a silver catalyst in place of the copper, phenyl chlorosilanes are produced.

The direct method was discovered by E. G. Rochow in the General Electric Research Laboratory in 1940 and was patented by General Electric.

12.3 Grignard method for producing polysiloxanes

In the Grignard method, organic magnesium chloride is reacted with silicon tetrachloride to yield chlorosilanes. This reaction can be represented as follows:

$$2RMgCl + SiCl_4 \rightarrow R_2SiCl_2 + 2MgCl_2$$

This is the most versatile method but it is expensive and hazardous because the reaction is carried out in an ether solution.

12.4 Olefin addition method for producing polysiloxanes

The third method is the olefin addition method which, as the name implies, consists of the addition of an olefin to a chlorosilane. This is illustrated by the following reaction:

$$SiHCl_3 + CH_2 = CH_2 \xrightarrow[\text{platinum catalyst}]{\text{Peroxide or}} CH_3CH_2SiCl_3$$

Several modifications of this method are possible, whereby different chlorosilanes may be produced, but any further discussion of this phase of the chemistry is inappropriate here.

12.5 Polymerization

Regardless of the method used to produce the chlorosilanes, the subsequent steps are very similar. As indicated, any given reaction produces many reaction products, but certain controls can be effected to minimize the yield of the least desired materials. Whatever the mixture, it must be fractionally distilled to separate, with a high degree of purity, the individual products. From this point on, it is the ingenuity of the product development chemist that determines the type and properties of the polysiloxane end products. From the variety of available chlorosilanes, certain ones are selected in various proportions, blended, hydrolysed and polymerized to produce many different types of polysiloxane materials.

As we have already noted, organosilicon compounds are very reactive. Accordingly, so are the chlorosilanes. The next manufacturing step after blending the chlorosilanes is the hydrolysis, or reaction with water, to form the corresponding alcohols, called silanols. In certain instances alcohols may be used in place of water to form alkoxy intermediates. The silanols are then bodied by a condensation reaction, with the liberation of water, to produce a polysiloxane. Whether it be a fluid, gum or resin depends on several things, one of the most important of which was the original choice of chlorosilanes.

One final consideration in the fundamental chemistry of the polysiloxanes is the types of polymers that may be produced. We have already noted that the initial manufacturing reaction produced a mixture of mono-, di-, and trichlorosilanes. All three could be hydrolysed and polymerized individually, but none would have much value as an end product. However, each contributes to the product into which it is incorporated according to its individual chemical properties.

The monochlorosilane yields the monosilanol and polymerizes only to the dimer stage:

$$\text{Hydrolysation: } (CH_3)_3SiCl + H_2O \rightarrow (CH_3)_3SiOH + HCl$$

$$\text{Polymerization: } 2(CH_3)_3SiOH \rightarrow (CH_3)_3Si\text{–}O\text{–}Si(CH_3)_3 + H_2O$$

Since this is the extent of polymerization of the monosilanol, it forms convenient terminals for higher polymers and is appropriately named a chain stopper.

The dichlorosilanes similarly yield disilanols, but these can be, and are, polymerized to all types, from short to very long straight chains of linear polymers. These are the bases of the fluids and gums, and in turn of the various other products made from the fluids and gums:

$$\text{Hydrolysation: } (CH_3)_3SiCl_2 + 2H_2O \rightarrow (CH_3)_2Si(OH)_2 + 2HCl$$

$$\text{Polymerization: } 2(CH_3)_2Si(OH)_2 \rightarrow (CH_3)_2(OH)Si\text{–}O\text{–}Si(OH)(CH_3)_2 + H_2O$$

This equation illustrates the polymerization of just two molecules, but any number could be added onto the chain through the terminal OH groups. The chain-stopping material which we have just discussed would terminate the chain.

Finally, we have polymers derived from alkyl and aryl trichlorosilanes. These are three-dimensional and generally are so hard and brittle that they are of little value in themselves. The brittleness can be tempered by copolymerizing some of the intermediates that yield linear polymers. By judicious blending and copolymerizing we produce three-dimensional crosslinked polysiloxane resins:

$$\text{Hydrolysation: } CH_3SiCl_3 + 3H_2O \rightarrow CH_3Si(OH)_2 + 3HCl$$

$$\text{Polymerization: } 4CH_3Si(OH)_3 \rightarrow CH_3(OH)_2Si\text{–}(O\text{–}Si(CH_3)(OH))_2\text{–}O\text{–}Si(OH)_2CH_3 + 3H_2O$$

This polymer, derived from only four molecules, the siloxy units, is representative of a very large polymer extending in three dimensions. With linear polysiloxane polymer chains attached, at various points where OH groups are now shown, this would be representative of a polysiloxane resin.

As said above, if alcohols are used instead of water in the hydrolysation step we would get alkoxy functional polymerizates instead of silanol functional ones.

12.5.1 Co-condensation with organic resins

As an interesting corollary, note that the key to this polymerization is the hydroxyl or alkoxy group. Organic resins such as alkyds, epoxies, polyesters or acrylics are characterized by hydroxyl groups. It is by means of condensation through these hydroxyls that, for example, alkyd/polysiloxane copolymers are made:

$$\text{organic polymer–OH} + \text{HO–polysiloxane} \rightarrow \text{organic polymer–O–polysiloxane}$$

Of course, this is extremely simplified but it is nevertheless characteristic of the copolymerization reaction. More details about this process can be found in Section 12.6.1.

12.5.2 Interjections

Firstly, at this point it is desirable to emphasize a very sharp and very important distinction between polysiloxane resins and polysiloxane fluids, or oils. Structurally, the fluids are two-dimensional, linear polymers, while the resins, characterized by a bulk of trifunctional silanes, are three-dimensional. But a more significant difference is found in their behaviour, a difference most important to coatings formulators, manufacturers and users. Even a slight excess of certain polysiloxane fluid can cause cratering of the film in which they are incorporated and/or be responsible for 'crawling' or other surface defects in subsequently applied coatings of any type. This is not true for polysiloxane resins. Coatings based on them can be overcoated with impunity with more polysiloxane resin-based coatings or with conventional, organic resin-based coatings. Equally important is the fact that the equipment used for processing polysiloxane resin-based products is not contaminated in any way and may be used interchangeably for all types of coatings manufacture. It is also not true for organic modified polysiloxane fluids, which play a major role as, for example, flow promotors: see Section 12.8.

Secondly, as said before, all the reactions described before for silanol (OH) functional polysiloxanes and/or silanes apply also for alkoxy (OCH_3 or OC_2H_5) functional types.

Finally, instead of the mainly mentioned methyl (CH_3) group, a phenyl group plays a major role in polysiloxane resins for protective coatings.

12.6 Siloxanes for protective coatings

Polysiloxane resins are distinguished from most organic resins by their specific properties and performance, which make them highly valuable for use in (protective) coating applications. We focus basically on two main points: the strong chemical bond and the low surface energy. The following overview compares the bonding energy of siloxane structures with organic carbon structures:

- Si–O: 373 kJ mol^{-1}
- Si–C: 310 kJ mol^{-1}
- C–O: 293 kJ mol^{-1}
- C–C: 243 kJ mol^{-1}.

This strong chemical bond leads to interesting properties for coating applications, i.e. high heat resistance and long-term weather resistance (see next sections).

The surface tension of polysiloxanes is approximately 20 mN m^{-1}, water has 70 mN m^{-1} and organic resin-based coatings are in the range 30–40 mN m^{-1}. Hydrophobicity, release properties, good substrate wetting and improvement of flow and levelling are results of the low surface energy. This is more about this in Sections 12.7. and 12.8.

Concerning the properties of polysiloxane, we also need to consider the relationship between property and composition. As shown above in Section 12.2, the most important technical process, the 'Direct Method', in the first step leads to mono-, di-, tri-, and tetrafunctional silanes, which are the basic units for all polysiloxane syntheses. For resin production the di- and trifunctional silanes are almost the only units used. Monofunctionals are used to a certain extent to control the reaction – the molecular weight. We speak about the T/D ratio. Furthermore, we have heard that R might be alkyl, phenyl or another organic group. Since this chapter is about polysiloxanes for protective coatings, particularly about resins which can be used as binders or to modify organic binders, it is mainly the methyl and phenyl groups that play a role, and the other groups can be neglected at this point. We speak here of the M/P ratio.

Based on the above, we now come to the property:composition relations. An increased amount of phenyl groups increases compatibility with organic resins, heat resistance and weather resistance; while an increased amount of methyl groups gives higher hydrophobicity, dirt repellence and release properties. The more trifunctional units there are, the higher is the hardness, the faster is the drying, but also the more brittle are the respective coatings. Trifunctional units also improve compatability with organic polymers. Difunctional units control flexibility but also reduce drying properties.

12.6.1 Weather resistant coatings

Organic resin-based coatings are subject to thermal or UV-initiated oxidation, and combined with the impact of chemicals and/or high humidity when exposed to the environment they will lose gloss, change colour and become brittle. As said before, the strong chemical Si–O bond of the polysiloxanes leads to superior weather resistance, i.e. better gloss and colour retention and less degradation from attack by chemicals or high humidity. This is true not only for straight polysiloxane resins; they also improve the weather resistance of organic resins if used in combination with them. Chalking, gloss and colour retention are significantly improved if more than 20% of polysiloxane resins are used in the said combinations. These combinations could be blends where the organic resins and the polysiloxane resin are just added to the formulation during the paint manufacturing process. The reactions as shown in Section 12.5.1 will then take place during the coating drying process and a while later. Better results can be achieved when the co-condensation of the organic resin and the polysiloxane resin are done prior to the coating formulation.

Co-condensation of siloxane–organic resins

Polysiloxane resins can be chemically combined with most of the available film-forming materials so long as they contain sufficient reactive hydroxyl groups to condense with the silanol, which characterizes this resinous intermediate. Processing is in accordance with conventional methods currently in use in the resin industry.

The one-stage process for a silicone/alkyd resin, using fatty acids, may be either a fusion or solvent-reflux cook. In either case, all of the ingredients are charged to the kettle at the start, and the copolymer is formed directly. In the event that whole oil is used in place of fatty acids, an alcoholysis of the triglyceride is accomplished first. Next, the remaining resin raw materials, including the silicone intermediate, are added and the one-stage cook proceeds as above. Alternatively, in the first stage an alkyd or other polymer is preformed and cut with some solvent, and then in the second stage of the cook it is coreacted with the silicone intermediate. Moderate variations in procedure, to accommodate particular situations, may be made without altering the net result.

The progress of the cook, whether in one or two stages, can be followed by making a simple, clear-pill test. A drop of the cooking resin is removed from the kettle and placed quickly on a glass plate, and then examined for clarity. This is done periodically during the cook until a clear cold pill is observed. This indicates complete homogeneity of the kettle charge. This test is most important in the one-stage cook or in preparation of the organic portion for a two-stage cook. In the latter, when the silicone intermediate is added, there will be a clear pill at once, in many cases, because of the compatibility of the silicone portion with the organic (alkyd, in particular) portion.

Again, in the one-stage cook or in the alkyd resin preparation for a two-stage copolymerization, the progress of the esterification is determined by periodic acid number determinations. It is most important that these resins are cooked to low acid numbers if they are intended for use as vehicles for pigmentation. The low acid number is essential for good pigment compatibility and stability.

Progress of the degree of polymerization is determined by periodic stroke-cure tests on a 200°C cure plate. For short to medium oil length resins, cure rates of 10–20 seconds by the above test indicate a stage of polymerization that is safe from gelation and will have at least reasonably good shelf-life stability. Stroke-cures below 10 seconds point up the need to check the cook promptly to avoid gelation, and even if this is not imminent, to avoid poor shelf stability. With longer oil length resins, cure rate is not as critical. Even considerably longer cures than 20 seconds on the plate are still indicative of good curing resins because of the oxidation potential of the oil content.

Within the limits of safe cooking as indicated by cure-plate tests, the resin can be carried to such a degree of polymerization that will yield the desired solution viscosity. The time to reach this stage will vary depending on several factors, among which are desired solids concentration and desired solvent. Periodic withdrawals of resin (or resin solution if a solvent cook) should be made and the resin cut to desired solids with preselected solvent. A quick viscosity check can be made on small samples through the use of Gardner–Holdt viscosity tubes or any other device that one may choose. The important factor is speed, so that too much polymerization does not occur between the sampling and the decision that the cook is completed.

Silicone/alkyd copolymers made with polysiloxane resins may be cut in a variety of solvents and/or solvent blends, depending on the silicone content and oil length. Silicone/epoxy resins will always utilize substantial quantities of polar solvents because of their more demanding solubility requirements. Short oil silicone/alkyds, regardless of silicone content, should be cut in aromatic solvents, preferably fortified with 20–33% (of total solvent) *n*-butanol. The selection of solvent for medium oil length copolymers will be dependent on such things as silicone content, actual oil length within the medium range, and desired viscosity. The range of solvents then can vary from aromatic hydrocarbon fortified with up to 20% *n*-butanol through pure aromatic hydrocarbon to an aromatic/aliphatic blend. Long oil alkyd/silicone copolymers can be cut in hydrocarbon blends or, in some cases, in straight aliphatic solvents. Examples of formulations are shown in Tables 12.1 and 12.2.

Table 12.1 Silicone-alkyd: long oil, oxidizing, 25% siloxanes (OH functional)

Formulation – Part I / Alkyd	% by weight
Soja fatty acid	58.3
Glycerol (99.5%)	6.4
Pentaerythritol (mono)	13.6
Phthalic anhydride	21.7
Xylol (for azeotropic distillation)	5–10% of kettle charge

Procedure
Charge all ingredients to kettle, heat to 180°C and hold for 30 minutes. Raise temperature slowly to 230–235°C over a period of one hour and hold at that temperature for acid number of 5 or less. Cut with mineral spirits to 65–70% solids. Cooking time: approx. 5 hours.

Formulation – Part II / Silicone-Alkyd	% by weight
Part I alkyd (65% solids)	76.1
Polysiloxane resin (69% solids) (silanol functional)	23.9

Procedure
The alkyd portion is in the kettle as a high solids solution, just as prepared in Part I. Add the polysiloxane intermediate resin to the kettle. With the kettle equipped for a solvent cook, raise temperature to 165°C and adjust xylol content, if necessary, to hold reflux at that temperature. Cook for 5 to 7 hours. Towards end of cook, solution will clear and a clear cold pill will be obtained. Reduce with xylol and mineral spirits to yield a final solvent blend of 2:1 mineral spirits to xylol.

Technical data for silicone-alkydresin

Non-volatiles	65%
Acid number	2
Viscosity	400–600 mPa s

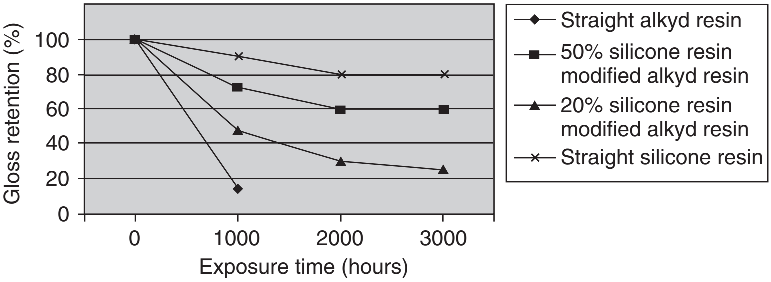
Table 12.2 Silicone epoxide: 25% silicone (C_2H_5OH functional)

Formulation	% by weight
Epikote 1001 X75	63.00
Polysiloxane, ethoxy functional, 100% active	18.01
1-Methoxy propyl acetate-2 (MPA)	17.14
Monomeric butyl titanate	0.064
Isobutanol for cooling	3.29

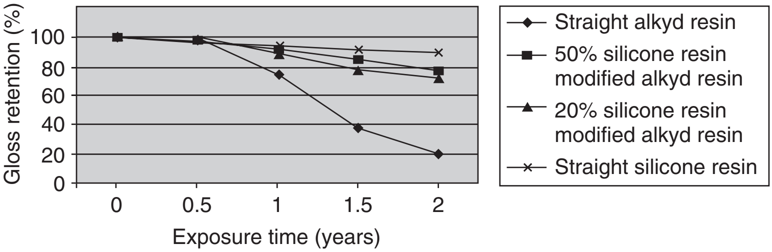
Procedure
Charge all ingredients in above-mentioned sequence to kettle. Raise temperature to 150°C by complete distillation of the overflowing solvent. Cook for 2 hours until desired viscosity is achieved. Add the isobutanol for cooling and cool to 50°C and cut with white spirit to 60% solids.

Technical data

Viscosity:	1200–2000 mPa s
Solid content:	61%
Acid value:	≤10 ppm HCl



12.2 Weather resistance with Weather-o-Meter.



12.3 Weather resistance with outdoor exposure in Pacific Region.

Test results

Figures 12.2 and 12.3 show the gloss retention of a long oil alkyd after 3000 hours of accelerated weathering (Weather-o-Meter) and after two years of exterior weathering in a tropical climate. In both cases we can clearly see that the silicones improve the gloss retention (weather resistance), and already with a moderate modification (20% polysiloxane), particularly in the exterior test, a more than significant improvement can be achieved. Straight silicone resins might be an even better option. However, straight silicone resins are somewhat weak in mechanical properties, while the modified resins are close to the organic ones in these properties and drying or curing conditions. Finally, also the cost/performance calculation speaks more for the modification.

12.6.2 Coil coatings

A specific topic is coil coating for exterior applications, such as corrugated iron roofs, aluminium window blinds or wall claddings. Beside the use of straight polyesters, PVDF or polyurethanes, siloxane-modified polyesters play a prominent role. Processes that are similar to those described before are used to formulate the polyester–polysiloxane copolymer – see Table 12.3. Figure 12.4 shows the Florida test results. Again we see the

Table 12.3 Weather-resistant silicone-polyester resin: 27.5% siloxane, C_2H_5OH functional

Formulation – Part I / Polyester	% by weight
Trimethylol propane	51.00
Glycerol	1.80
Isophthalic acid	32.70
Adipic acid	14.36
Polymeric butyltitanate, 10% in xylene	0.14
Xylene (see formulation)	

Procedure

Gradually heat all components together with a small proportion of xylene to 220°C in an agitator and control to an acid value of 9–12 (OH value: 360–400). Reaction time: 5–6 hours. Continually remove the resultant water together with the xylene proportion.

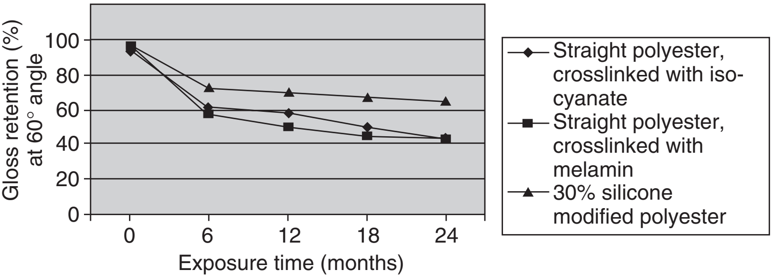
Formulation – Part II / Co-condensate = silicone-polyester	% by weight
Polyester resin, according to Part I	43.4
Polysiloxane, ethoxy functional, 100%	18.6
1-Methoxy propyl acetate-2 (MPA)	18.3
Solvesso 150	10.7
Xylene (see formulation)	
After co-condensation, added for controlling the solid content:	
Solvesso 150/butanol 8:5	9.0
	100.0

Procedure

Briefly preheat the polyester resin, possibly predissolved in the indicated quantity of 1-methoxy propyl acetate-2, together with a small proportion of xylene to 140–150°C in an agitator to remove residual amounts of water. After cooling to approx. 90–100°C, add polysiloxane intermediate and possibly 1-methoxy propyl acetate-2 as well as Solvesso 150. Subsequently stir the reaction mix under reflux at approx. 165–170°C. Time: approx. 2 hours. Continually remove the methanol resulting during the reaction. Then cool down to 90–100°C and control to a solids content of approx. 60% using a mixture of Solvesso 150 and butanol.

Technical data for silicone polyester co-condensate

Silicon content based on solid resin	approx. 27.5%
Solids content	approx. 60%
Viscosity, DIN 53015, 23°C	approx. 2.5 Pa.s
Density at 20°C	approx. 1.1 g/ml
Acid value	4–6
OH value	130–160



12.4 Weather resistance with outdoor exposure in Florida.

significantly improved gloss retention, which indicates the good weather resistance.

12.6.3 High heat resistant coatings

Polysiloxanes themselves can be heat resistant up to 300°C depending on the specific composition. With coatings based on polysiloxane resins, heat resistance up to 650°C can be achieved. How does that work? At temperatures above 160–180°C all siloxanes release their organic groups, mainly methyl or phenyl as we have seen before. Other organic groups will be released faster and already at lower temperatures. This decomposition of the Si–C bond is a very slow process at temperatures below 300°C (it may last years until completed) and is significantly accelerated when the temperature gets into the range of 400°C. At that temperature it is just a question of minutes or a few hours until all organic groups are released. Particularly in the presence of oxygen, the Si–C bond will be replaced by Si–O–Si. Contrary to the above siloxane bond (recall that we speak about siloxane when we have the Si–O–Si bond and organic groups attached to the Si), we now get a silicate, similar to the structure of quartz. During the decomposition of the organic groups, we get very reactive groups that are able not just to form the silicate but also to a certain extent to react with inorganic pigments and/or fillers.The best reactions with fillers and the best heat resistance will be achieved with aluminium pigments (flakes), micaceous iron oxide and mica. This combination of decomposed polysiloxane, i.e. reactive silicate and the inorganic fillers, forms films that are heat resistant to 650°C. Because of differences in the coefficient of temperature expansion of the metal substrate and the silicate-based coating, the film thickness is limited. Depending on the kind of resin, the kind of substrate and the substrate preparation, the film thickness should not exceed 30 μm in the case of one-layer systems and 80 μm in the case of two-layer systems.

Table 12.4 Heat resistant polysiloxane coating; top coat micaceous iron oxide; long-term thermal stability approx. 650°C

		% by weight
Polysiloxane resin solution, 50%		26.1
White spirit		–
Xylene		7.5
1-Methoxy propyl acetate-2		7.4
Bentone 38, 7.5%		6.6
Micaceous iron oxide		52.4
		100.0
Composition:	binder	13.1
	pigments	51.2
	additives	0.5
	solvents	35.2
		100.0

Application
Application method: spraying
Dry film thickness: approx. 15 μm

Drying
The coating dries at room temperature to form tack-free films resistant to the knocks of assembly/installation. The final resistance properties and hardness are only attained after exposure to high temperature, i.e. through normal operation of plant.

Application viscosity
Flow time, DIN 53211, 23°C: approx. 20 s (DIN 4 cup)

Principally, all siloxane resins, particularly those used for high heat resistant coatings, are heat-curing resins, i.e. they cure at a temperature in excess of 180°C only. Nevertheless, quite often low temperature drying or drying in environmental conditions is required. This can be achieved by the choice of a polysiloxane resin that dries at ambient temperature either physically or if a small amount (3–5% on solid resin) of organic resins, such as ketone resins or cellulose derivates, e.g. cellulose aceto butyrates (CAB), is added to the paint formulation. The standard polysiloxane resins are from the composition T/D = approx. 1:1 and phenyl/methyl = 1:1 on a molar basis – see Section 12.2 above.

Tables 12.4 and 12.5 show two guideline formulations with which heat resistance to 650°C can be achieved. These coatings are resistant not only to such high heat but also against fluctuations of temperature and thermal shock. Long-term anti-corrosion properties at high heat can be achieved if a polysiloxane-based zinc dust primer is used too – see Table 12.6.

Table 12.5 Heat resistant polysiloxane coating; aluminium bronze top coats; long-term thermal stability approx. 600°C

		% by weight
Polysiloxane resin solution, 50%		16.6
White spirit		–
Xylene		23.4
1-Methoxy propyl acetate-2		23.4
Bentone 38, 7.5%		3.2
Aluminium bronze		33.4
		100.0
Composition:	binder	8.3
	pigments	21.7
	additives	0.2
	solvents	69.8
		100.0

Application
Application method: spraying
Dry film thickness: approx. 15 μm

Drying
The primer dries at room temperature to form tack-free films resistant to the knocks of assembly/installation. The final resistance properties and hardness are only attained after exposure to high temperature, i.e. through normal operation of plant.

Application viscosity
Flow time, DIN 53211, 23°C: approx. 20 s (DIN 4 cup)

12.7 Concrete protection

Concrete is perhaps one of the most extensively used construction materials. Highways, tunnels, bridges, airport runways, hotels, office buildings and skyscrapers of every kind are made from concrete. Its importance is steadily increasing and it seems to be an almost unlimited construction material.

To get sufficient compressive and tensile strength, reinforcement such as steel bars is incorporated into concrete, making a reinforced concrete section. This is much more efficient in carrying tensile forces due to bending or direct tension than a plain concrete section with the same dimensions would be. The alkaline chemical environment provided by portland cement causes a passivating film to form on the surface of steel, making it much more resistant to corrosion than it would be in neutral or acidic conditions.

Although well known for its long durability, concrete is subject to erosion, with constant attack from humidity and chloride ion penetration. Not only

Table 12.6 Heat resistant polysiloxane primer; zinc dust primer; long-term thermal stability approx. 500°C

	% by weight
Polysiloxane solution, 50%	18.6
Xylene	1.4
Bentone 38, 7.5%	11.0
Zinc dust	69.0
	100.0
Composition: binder	9.3
additives	0.8
pigments	69.0
solvent	20.9
	100.0

Technical data
Pigmentation level, calculated on solid binder: 740%
Storage stability: >3 months

Application
Application method: usually by spraying, though also by brushing or rolling, providing the maximum film thickness is not exceeded.
Dry film thickness: max. 50 μm (single-coat system)
max. 30 μm per coat (two-coat system)

Drying
The primer dries at room temperature to form tack-free films resistant to the knocks of assembly/installation. The final resistance properties and hardness are only attained after exposure to high temperature, i.e. through normal operation of plant.

does this have a destructive impact on the concrete itself, but even more important is the effect it has on the reinforcement steel used to improve the tension of the concrete structure. When rebar corrodes, the rust expands, cracking the concrete and unbonding the rebar from the concrete.

The water in the pores of the cement is normally alkaline; this alkaline environment is one in which the steel is passive and does not corrode. Carbon dioxide from the air reacts with the alkali in the cement and makes the pore water more acidic. This acidity, in combination with humidity, will lead to corrosion of the rebar. Chloride ions will further promote the corrosion of steel rebar.

All these destructive reactions require water. Keeping the concrete dry is an important goal of concrete protection and maintenance. Water-repellent protection that leaves the concrete surface breathable (vapour permeable) and reduces (or suppresses) the chloride ion penetration is required. Broadly used for that purpose are bitumen coatings. However, bitumen coatings are reported to have limited durability and after a while the above-mentioned destructive impact will start. Modern alternatives are siloxanes and the most modern are water-based siloxane emulsions. Tests for roadwork applications (such as tunnels, bridges, etc.) carried out by independent and authorized institutes in Germany and Sweden have proven their efficiency. The most recent tests for US highway applications according to the National Cooperative Highway Research Program Report 244-II (Report 244) confirmed the European test results.

The main subjects of the tests have been:

- Water absorption
- Drying (vapour permeability)
- Chloride ion absorption.

For this test the concrete formulation used was:

• Type I Portland Cement	439 parts
• Eau Claire Sand	1500 parts
• Eau Claire Coarse Aggregates	1758 parts
• Water	225 parts

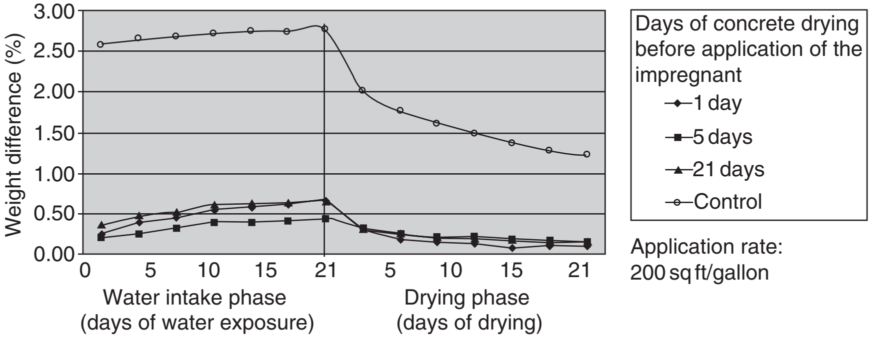
A siloxane emulsion which is supplied with 60% content of active ingredient was diluted with water in the ratio 1:3, i.e. the content of active ingredient of the applied material was 15%. The application rate was 400 square feet per gallon = approximately 5 m^2/litre.

The diluted siloxane emulsion was applied on the concrete after one day of drying of the concrete as well as after 5 days and 21 days of the concrete drying (curing). After 7 days of the curing of the impregnant, the prepared specimen was exposed to aqueous 15% NaCl solution and the water intake was measured frequently up to 21 days. Then the specimens was stored in dry conditions and the water evaporation (drying) was also measured frequently up to 21 days. Parallel to the water absorption, the intake of chloride ions after 21 days of exposure to the salt bath was analysed. Of course, the test was done in comparison with an untreated reference. Details of the test report are shown in Figs 12.5 and 12.6.

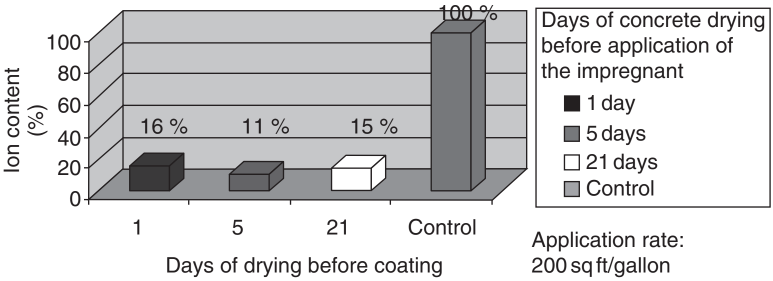
Water repellence, breathability and reduction of chloride ions could be proved impressively, thus the rebar will be protected from corrosion, and freeze–thaw resistance will also be improved significantly.

The above discussion of siloxane emulsions as a more modern solution serves to introduce some ideas about the durability of a siloxane impregnation. One can subdivide the silicones or silanes used in the hydrophobation of constructions or construction materials into three classes (Fig. 12.7), essentially:

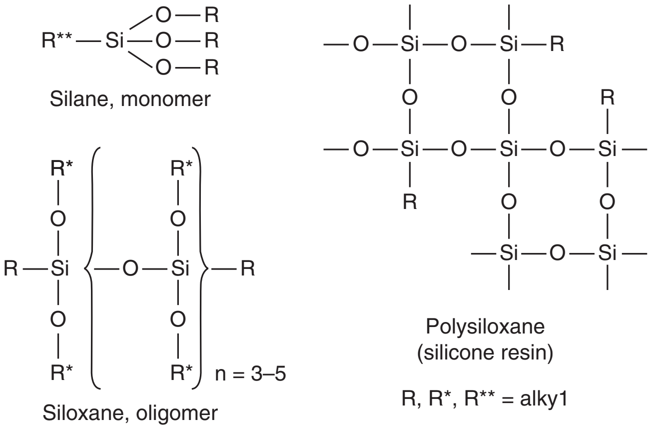
- Monomeric alkyl alkoxy silanes
- Oligomeric alkyl alkoxy siloxanes
- Polymeric siloxanes (methyl silicone resins).



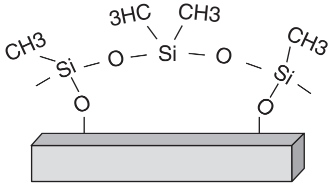
12.5 Siloxane emulsion, 15% active ingredients, water intake and evaporation (test according to US National Cooperative Highway Research Program report 244, performed by CTL, Chicago).



12.6 Siloxane emulsion, 15% active ingredients; reduction in chloride ion content (%) after 21 days' exposure to salt solution (test according to US National Cooperative Highway Research Program report 244, performed by CTL, Chicago).



12.7 Structure principles of silanes and siloxanes.



The siloxane backbone reacts with silicate from the substrate and forms a durable connection, while the alkyl groups protect the substrate like umbrellas

12.8 Principle of water repellency.

Table 12.7 Properties of silane, siloxane and polysiloxane

	Silane	Siloxane	Polysiloxane
Structure	monomeric	oligomeric	polymeric
Penetration; capillar activity	very deep	deep	poor
Application form (% active ingredient)	20–100	1–10	3–8
Efficiency	approx. 40%	approx. 80%	100%
Optical effect to the substrate	none	none to some	darkening, 'wet-look' effect
Water vapour permeability	high	high	medium
Beading	poor	poor	significant

It is common for all three types that they build in the end use after curing a stable, three-dimensional, resin-like network. The chemical similarity to the silicate components of building materials leads to stable and durable bonds with most mineral substrates. At the same time, the alkyl groups orient to the exterior (air) side and protect the surface like little umbrellas against penetration of humidity (see Fig.12.8).

Depending on their chemical structure (see Table 12.7) one must distinguish the mode of action or the site of attachment of the siloxanes. While polysiloxane creates a film particularly at the substrate surface, the low molecular weight silanes and oligomeric siloxanes penetrate into the available pores, i.e. the low molecular weight products are subject to capillary absorption. Embedded in the pores and chemically reacted to the building material, they reduce the capillary absorption of water, the well-known sucking effect of all capillaries. Therefore, low molecular weight silanes and oligomer silanes have almost no influence upon the substrate surface, and the appearance of the building material remains visually unchanged. The polymeric siloxanes, on the other hand, form a surface film which leads to a visual change, i.e. a dark, wet-looking surface.

Oligomeric siloxane emulsions quite effectively penetrate into the pores of the concrete and do not change the surface appearance. Because they do not remain on the surface of the substrates, the emulsions are recoatable and can be used as a primer, e.g. for coatings and plaster. The strong chemical bond of the product leads to a very efficient long-term durability.

12.8 Siloxanes as paint additives

As said above (Section 12.6), siloxanes have low surface energy, i.e. are surface active materials. Particularly the linear structures (D based only), which we call polysiloxane fluids, with just methyl groups as organic groups attached, are very surface active. In Section 12.5.2. we learned that just this class of products can cause cratering and recoatability problems. These issues are closely related to the molecular weight or the chain length of the siloxanes – the higher the molecular weight the more severe the problem. How can we overcome this issue? On the one hand we have a surface active material which might be able to improve substrate wetting as well as flow and levelling, while on the other hand it causes craters and adhesion problems due to extreme incompatibility. The solution is to organically modify the polydimethyl siloxane. The modifiers most often used are polyethers. Various properties can be controlled by the siloxane : polyether ratio, but also by the type of polyether – ethylene oxide and/or propylene oxide, random or block structures. The place of the modification, on the chain side or on the end, plays an important role in achieving the intended properties, too. Finally, of course, a very significant factor for the overall behaviour is the chain lengths of the siloxane and the polyether. The fact that this strategy is very successful shows that there is no automotive top coat that does not contain a small amount (approximately 0.1% of the total paint formulation) of this kind of modified siloxane.

There are two main ways to modify the siloxane with polyether, the following showing them schematically:

1. condensation of an OH-functional siloxane with a butanol-initiated polyether:

$$-\text{O}-\text{Si}-\text{OH} + \text{C}_4\text{H}_9\text{O}-(\text{EO})_X(\text{PO})_Y \xrightarrow[\text{e.g. amine}]{\text{catalyst}}$$
$$-\text{O}-\text{Si}-\text{O}-(\text{EO})_X(\text{PO})_Y + \text{C}_4\text{H}_9\text{OH}$$

2. Addition of allyl-initiated polyether to a hydrogen-functional siloxane:

$$-\text{O}-\text{Si}-\text{OH} + \text{C}_2\text{H}{=}\text{CH}-\text{CH}_2-(\text{EO})_X(\text{PO})_Y \xrightarrow{\text{Pt catalyst}}$$
$$-\text{O}-\text{Si}-(\text{CH}_2)_3-(\text{EO})_X(\text{PO})_Y$$

Both reactions can be done on the side or on the end of the siloxane chain, depending on where you functionalize the siloxane.

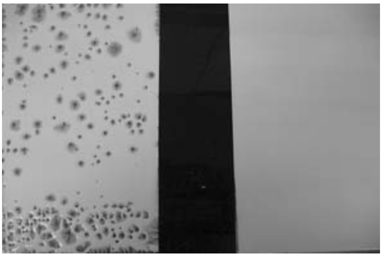
As said, these materials are surface active products and interact with the various surfaces:

- coating surface ⇔ air
- substrate ⇔ coating

These surfaces are obvious, but within the paint formulation there are also various surfaces such as pigment ⇔ binder, and filler ⇔ binder; adding solvents (or water) and various other additives, one can easily imagine that there so many surfaces that it is difficult to foresee what would happen if a surface active material is added. If the uncountable number of paint formulations are considered, it will become impossible to predict the behaviour. So the right choice of siloxane paint additive has to be related to a specific test. Independently of the above-mentioned difficulties, there are some general rules that might be considered:

- Generally, siloxane-polyethers with Si–O–C bonds are not stable against hydrolysis, and not recommended for water-based systems (reaction 1 above).
- Those with Si–C bond are stable against hydrolysis (reaction 2 above).
- Linear siloxane-polyethers mainly result in increased slip and mar resistance, as well as defoaming.
- Side-modified types improve flow and levelling.
- Low molecular weight grades have more surfactant properties; they improve substrate and pigment wetting.

Figure 12.9 shows a water-based polyester polyurethane coating applied on uncleaned steel. The left panel lacks a siloxane paint additive, while the right panel contains 0.1% of a siloxane-polyether of structure 2 with low molecular weight, where the siloxane chain is side-modified. There is no doubt that substrate wetting is improved.



12.9 Water-based polyester polyurethane coating applied on uncleaned steel.

12.9 How do siloxane paint additives work?

There are mainly three effects resulting from the use of the siloxane-polyether paint additives:

1. Reduction of surface tension
2. Surfactant structure of the organically modified siloxanes
3. Concentration of the products on top of the coating.

Before we come to discuss these effects in more detail, recall that the siloxanes are surface active materials. Siloxanes have a surface tension of approximately 20 mN m^{-1}. The polyether modification results in products with surface tensions of approximately 21–25 mN m^{-1}.

12.9.1 Reduction of surface tension

The addition of approximately 0.1% of these products to paint formulations reduces the surface tension of wet paints from approximately 30–35 mN m^{-1} to a level of 25–28 mN m^{-1}. The exact level depends on the structure and molecular weight of the siloxane-polyether and the total paint formulation. It is well known that the wetting of surfaces with liquids depends on the surface tensions – the surface tension of the liquid must be lower than that of the substrate. The lower the surface tension of the liquid (paint), the better the wetting.

12.9.2 Surfactant structure of the organically modified siloxanes

Particularly if the polyether in the modified siloxane is ethylene oxide based and if there is a linear AB structure, i.e. an end-modified siloxane-polyether where A represents the siloxane and B the EO-polyether, we get a product with a significantly hydrophilic side (polyether) and an oleophilic side (siloxane). These hydrophilic and oleophilic sides interact respectively with the corresponding hydrophilic or oleophilic parts in the paint formulation and/or between paint and substrate. Thus substrate and/or pigment wetting is improved.

12.9.3 Concentration of the products on top of the coating

Another well-known surface tension-related effect is that in liquids the parts with lower surface tension tend to migrate to the top of the liquid (liquid/air surface) and to spread there. During drying of liquid paints (water or solvent based) the diluent evaporates from the top, increasing the surface tension there. The lower parts of the wet film now have lower surface tension and go up to the top and spread there, suppressing the material that has been on the top before. Again the diluent evaporates and a circulation starts; this is repeated until the wet paint is no longer moveable, due to increased viscosity. This circulation results in hexagonal cells (under ideal conditions), called Benard cells. In coatings we can see the results of this effect as ‘orange peeling’ or horizontal pigment separation. Now, after adding siloxanes (or modified siloxanes), without doubt they are the ingredients with the lowest surface tension, i.e. they migrate to the top and spread there in a very thin layer (from a monolayer to one some molecules thick). As there is nothing in the paint formulation that has a lower surface tension, there will be no circulation in the paint during drying. Smooth films without Benard cell-related defects will be achieved.

Of course, in reality the above-mentioned effects are always overlapping, but depending on the paint formulation and/or the chemical structure of the siloxane-polyether copolymer, one or the other effect dominates. Quite often the best results are achieved by combinations of different structures that influence different parameters, and quite often the resulting effect is a truly synergistic one, not just an addition of the single effects.

13

Waterborne coatings for corrosion protection

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13.1 Introduction

A conventional coating consists of a resin, pigments and additives, dispersed in a suitable solvent. Film formation and solvent evaporation start simultaneously after coating application. Complete evaporation of solvent is a must for complete curing of a coating. However, evaporation of solvents during the curing process affects the health not only of the paint applicators but also of persons in the vicinity. The most commonly used solvents are toluene, xylene, methylethylketone, etc. Some of the health effects caused by these solvent vapours are cardiac arrhythmia, fatigue, sleepiness, headaches and nausea, and irritation of the nose, throat and eyes.

13.2 Alternatives to solventborne coatings

Due to the diverse effects on human health and the environment, stricter legislation has been imposed on the paint and coating industries to reduce and monitor the amount of hazardous volatile solvents. There are two possible ways to make coating formulations environmentally friendly:

- Use of solvents that are not hazardous to health and the environment as well as use of hazardous vapour collection equipment during application of coatings.
- Development of waterborne coatings, high solid coatings and solventless coatings.

A brief introduction to these alternative coating technologies is presented in Table 13.1. The alternative paint formulations are high build systems where the solvent level is reduced to less than 15–20%, and solventless systems where the solvent level is reduced to 1–5% by volume. An additional formulation is to use alternative solvents such as water, which is available abundantly and is much cheaper. This class of coating is called waterborne coatings.

Table 13.1 Environment-friendly alternative coating technologies

Nomenclature	% Solid content	Advantages	Disadvantages
High-build coatings	60–80%	Higher thickness per coat, low VOC	High viscosities, slight difficulty in brush application
Solventless coatings	100%	Very high thickness per coat	Costly equipment; airless spray technique used for coating
Waterborne coating	Same as solvent-borne system	Low VOC emission; low viscosity; reduced toxicity; no odour and non-flammable; conventional application processes; suitable for thin film application	Resins for waterborne formulations are costly compared with conventional coatings; tendency to form foam; requires longer drying times or increased oven temperatures

13.3 Waterborne coatings

Waterborne means something derived from water. A coating formulation that utilizes water as the main volatile medium (at least 80% water as the main volatile medium) to disperse its components is called a waterborne coating. Most regulations require waterborne coatings to have a VOC of less than 425 g per litre of paint. The increasing importance of waterborne coatings also lies in the environmental as well as the biological importance of water, which is highlighted by the water-covered Earth and the essentiality of water to all known forms of life. Water has been referred to as the naturally occurring universal solvent.

13.4 Classification of waterborne coatings

Many types of resins are available in a waterborne version, including vinyls, two-component acrylics, epoxies, polyesters, styrene-butadiene, amine-solubilized, carboxyl-terminated alkyd and urethanes. Waterborne coatings can be classified either on the basis of how the resin is fluidized or in terms of the polymer particles they contain (Table 13.2). The three main types are water-soluble/water-reducible (solutions), water-dispersible/colloidal (dispersions) and emulsions (latex) paints (the most commonly used form). Within each category, the physical properties and performance depend on the type of resin used [1]. Before discussing the specific features of water-

Table 13.2 Classification of waterborne coatings

On the basis of resin fluidization		
Water-soluble/water-reducible (solutions)	Water-dispersible/colloidal (dispersions)	Emulsion
Paints whose individual molecules of water-soluble resins dissolve completely in water. Water-soluble resins are generally produced via polycondensation or polymerization reactions in an organic medium.	Paints that have small clusters of insoluble solid resin particles that are suspended in water. Mechanical agitation is sufficient to suspend the clusters.	Emulsions are formed from dispersion of liquid in polymer in water.
On the basis of size of resin particle		
True solution	Dispersion	Emulsion
<0.01 μm	0.01–0.1 μm	0.1–1.0 μm

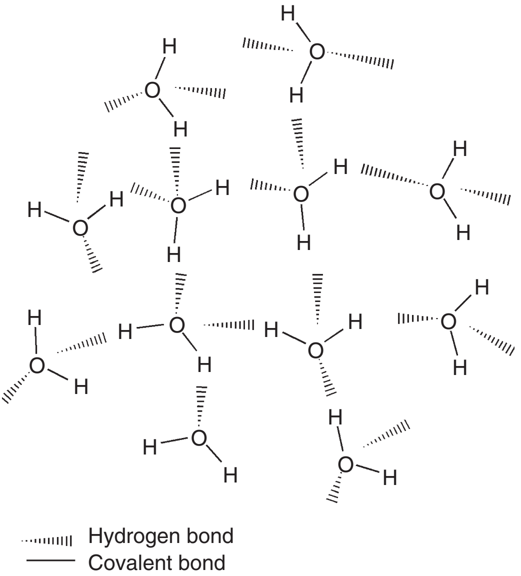
borne coatings, a basic introduction to the physical properties of water which are dramatically different from those of solvents used in coatings, is necessary. The effects of these unique properties on the performance of waterborne systems are outlined below.

13.5 Water properties influencing coating formulation

In this section, the physical and chemical nature of water that influences the recipe of the coating as well as its end user properties will be discussed. The surface tension, evaporation rate and freezing point of water are dramatically different from those of other solvents used in coating formulations. The explanation for water's unusual behaviour lies in its molecular structure.

13.5.1 Polarity

Water (H_2O) is a polar molecule consisting of two hydrogen atoms covalently bonded to a single oxygen atom. The oxygen pulls the electron of the hydrogen towards itself because of the higher electronegativity of oxygen than that of the hydrogen atom. This accumulation of electrons towards the oxygen leads to the generation of a negative charge on the oxygen and a positive charge on the hydrogen.



13.1 Association of water molecules.

13.5.2 Association of water

The three-dimensional water molecule is held together by strong hydrogen bonding between oxygen and hydrogen (Fig. 13.1). The hydrogen-bonded structure of water makes it more resistant to cleavage by normal molecular vibration. Therefore, hydrogen bonding increases the heat energy requirement for the conversion of water to vapour as compared to other solvents used in coating formulations. The high surface tension of water is also caused by strong cohesion between the water molecules. Various properties of water are compared with those of solvents widely used in coating formulations in Table 13.3.

13.5.3 Freezing

The higher freezing point of water than that of organic solvents of introduces the need for special storage systems in climates where low temperatures are possible. The storage temperature should be at least 10°C. The anomalous density/temperature characteristics of water should also be considered, to avoid thaw, separation and/or coagulation of the coating formulation during storage.

Table 13.3 Properties of water in comparison to various solvents and substrates

Properties	Solvents			
	Water	Acetone	Xylene	White spirit
Melting point (°C)	0	–94	–25	
Boiling point (°C)	100	56	138–142	152–198
Flash point (°C)	non-flammable	–17	25	36–41
Specific heat capacity	73	24	30	18
Latent heat of vaporization (cal/g at b.p.)	540	135	94	115

Surface tension (dyne/cm)

Solvent (in air at 20°C)	Water 72.8	Xylene 28.2	C_2H_5OH 22.7	$CHCl_3$ 26.8	Benzene 28.8
Substrate	Treated steel 40–50	Aluminium 45	Untreated steel 30	Teflon 18	Glass 70–80

13.5.4 Evaporation rate

Complete evaporation of the solvent from the coating is necessary and is the most important criterion for a good coating formulation. The evaporation rate of the solvent depends on the boiling point and latent heat of vaporization. As with surface tension, water has a high value for the latent heat of vaporization as compared to solvents used in coating formulations (Table 13.3). Therefore, waterborne coatings use up more heat energy for the complete evaporation of water than do solventborne coatings for the evaporation of the solvent. Also, the rate of evaporation of water, unlike that of organic solvents, is influenced by the relative humidity of the atmosphere. At higher relative humidity, the capacity of the atmosphere to accept more water vapour decreases. This leads to a slower rate of evaporation of water from waterborne coatings.

13.5.5 Surface tension

The surface tension of a coating formulation is related to the wetting and adhesion of the coating to the substrate. For good wetting, the surface tension of the coating formulation should be lower than that of the substrate on which it has to be applied. Table 13.3 shows that water has a very high surface tension when compared to widely used solvents for coating formulations as well as common substrates. Therefore, waterborne coatings require some modification to reduce the surface tension for easy wetting and good adhesion to low surface energy substrates. Modification involves the addition of surfactants and wetting agents. However, the non-flammability, non-toxicity and easy availability of water favour its use as a potential solvent for coating formulations. Also, strict regulations on the use of non-toxic materials for coating formulations have encouraged greater use of water in industrial coatings [2].

13.6 Technology behind development of waterborne coatings

13.6.1 Development of water soluble/reducible resin

In this section, the techniques of synthesis of water-soluble/reducible polymers by incorporation of specific moieties into the polymer backbone are discussed. Such moieties are water loving or can be made water loving after appropriate modification. These water-loving moieties can be incorporated using one of the following techniques:

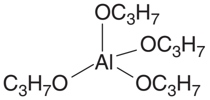
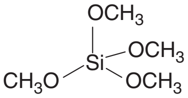
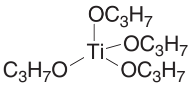
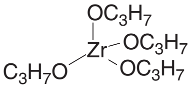
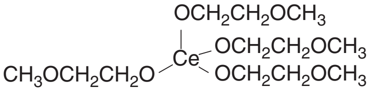
- Salt formation, or simply the incorporation of carboxylic or amino groups onto the backbone of the polymer. These can be converted into anions or cations by a number of acid–base reactions.
- Introduction of non-ionic groups such as polyols or polyethers into the backbone. These polymers are of lower molecular weight and can remain water-sensitive.
- The formation of intermediate zwitterions (groups containing both positive and negative charge).

13.6.2 Development of sol-gel derived waterborne coatings

Apart from conventional techniques of waterborne coating formulation, the sol-gel process [3] is one of the emerging technologies for the development of high-performance waterborne coatings. It has provided a new tool for the efficient incorporation of inorganic moieties into organic polymers through the *in situ* formation of an inorganic network by hydrolysis and polycondensation of metal alkoxide $R(MX_3)_n$ where X = OR, R, H, Cl and M = Ti, Si, Zr as shown in Table 13.4.

Silicon alkoxides are extensively used metal alkoxides for the incorporation of inorganic moieties into organic networks. Organically modified silicon alkoxides such as alkyl silanes, amino silanes, epoxy silanes and

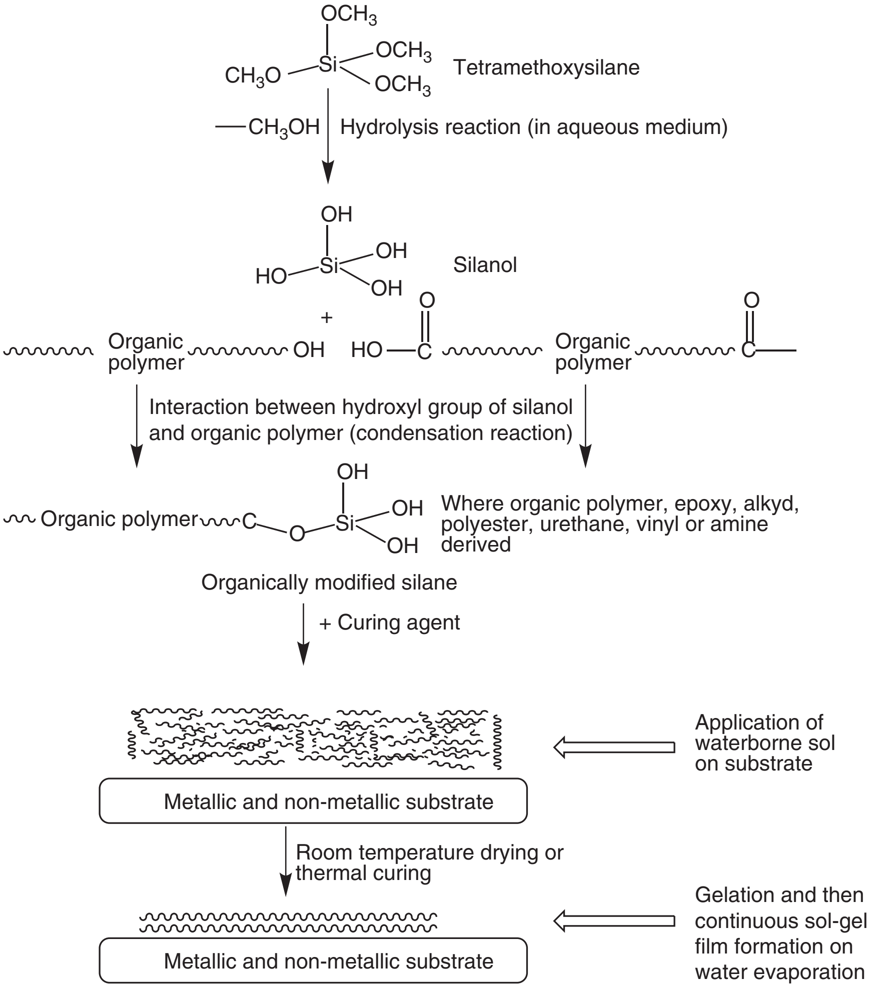
Table 13.4 Metal alkoxide for sol-gel coating

Element	Alkoxide (OR)	Structure of alkoxide
Aluminium	—OCH_3, —OC_3H_7	
Silicon	—OCH_3, —OC_2H_5	
Titanium	—OCH_3, —OC_3H_7, —OC_4H_9	
Zirconium	—OC_2H_5, —OC_3H_7	
Cerium	—OC_3H_7, —$OCH_2CH_2OCH_3$	

acrylic silanes are formed by the silane crosslinking principle or by complex formation which involves hydrolysis and condensation of liquid monomers in solution. The result of the hydrolysis reaction is a sol (colloidal solution) as an intermediate product which is converted to a transparent gel on subsequent condensation. The solution-based nature of the sol allows the incorporation of appropriately functionalized organic moieties into it that can undergo the same condensation reaction as the silicon dioxide sol.

Sol is a system that allows a chemical species (macromolecules and particles) to become weightless suspended bodies in solution. It is made of solid particles of diameter a few hundred nanometres. The hydrolysis and condensation reaction starts between the chemical species when the sol is applied to the substrate, resulting in gelation (three-dimensional network formation). After gelation, a highly solvated solid forms in which the solvent is trapped, which further gives rise to a dense film on the substrate after removal of the solvent by evaporation or thermal treatment as shown in Fig. 13.2. The sol-gel coating formulation and its application process to the substrate involves three steps, namely:

1. Generation of sol (colloidal suspension) of coating recipe
2. Application of sol onto substrate and its thermal curing
3. Continuous and dense film formation on solvent evaporation.



13.2 Sol-gel technology for organic modification of silane and application of sol to substrate.

Sol-gel coatings have found use in different applications, for example abrasion resistance, anti-soiling and anti-fogging coatings on various substrates. In particular, it is found that they can provide good corrosion resistance for metal substrates, because they blend the mechanical and chemical characteristics of the constituent organic and inorganic networks [4]. Sol-gel films are durable, scratch resistant, adherent to the metal substrates, flexible, dense, and functionally compatible with organic polymer paint systems. The structural characteristic of various precursors and coating formulations will be discussed later.

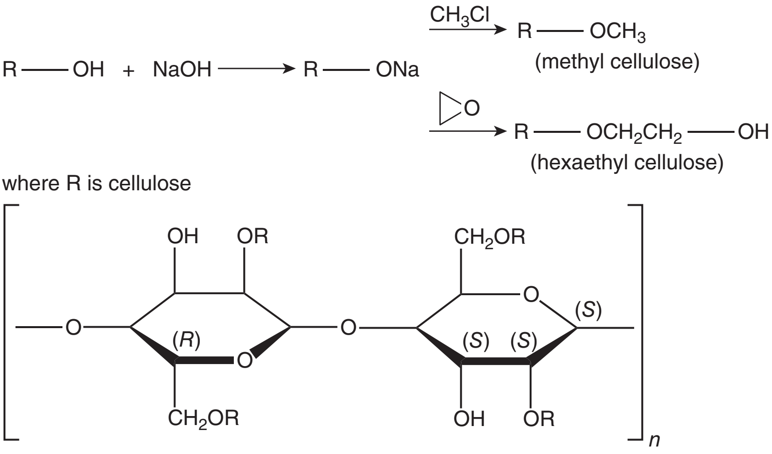
13.7 Development of resins for waterborne coating formulations

13.7.1 Cellulose ether

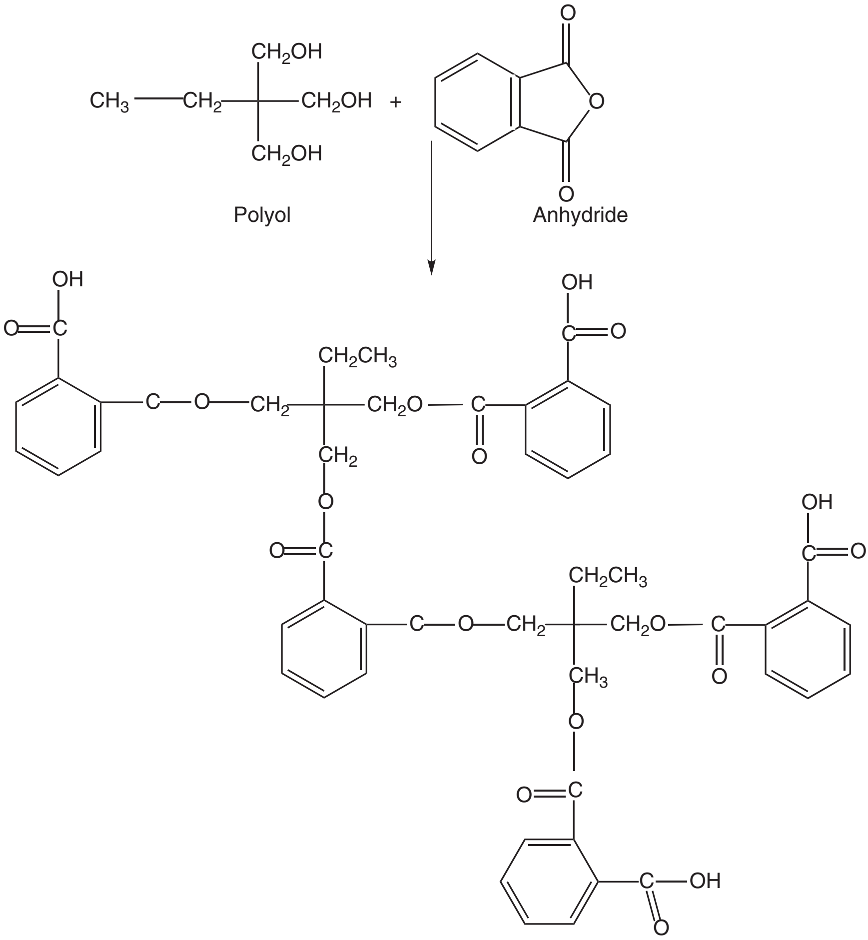
Cellulose ethers are derived from cellulose fibres which find application as a film former or thickener in textile, paper coating and adhesive applications. Cellulose fibres are insoluble in water. To make them water soluble, it is necessary to replace some of the hydroxyl group by other substituents. Water-soluble cellulose ether can be produced by replacing the hydrogen atom. For this, cellulose is first converted to alkali cellulose by reaction with sodium hydroxide and then the alkali cellulose is reacted with the appropriate moiety to introduce the required groups (Fig. 13.3).

13.7.2 Polyester

Polyester resins [5] are the reaction product of the esterification of di- or polyhydric alcohol with di- and polybasic acids or anhydride (Fig. 13.4). The method of preparation of waterborne polyester is similar to that of waterborne alkyds. It involves the use of either hydroxy acids such as dimethylpropionic acid, or acid anhydride such as trimetallic anhydride (Figs 13.5 and 13.6). In both cases, there is a considerable residual acid functionality on the polyester chain. In case of trimetallic anhydride ring, only the anhydride ring of the acid is initially involved in the synthesis reaction. At the coating formulation stage, the residual acidity is neutralized with amines to form a salt, rendering the polymer water soluble. In



13.3 Conversion of cellulose to water-soluble ether derivatives.



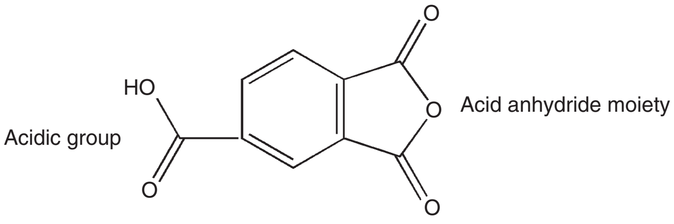
13.4 Synthesis of a conventional solventborne hydroxy functional polyester resin.

case of dimethylolpropionic acid, the hydroxy acid is condensed through the OH group, leaving the carboxyl group for neutralization.

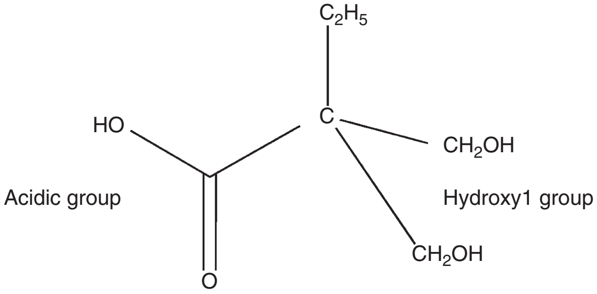
13.7.3 Alkyd

Alkyds [6] are reaction products of polyhydric alcohol, polybasic acid and fatty acid (Fig. 13.7). Some techniques to incorporate the water solubility in alkyds are as follows:

- The oldest method of making waterborne alkyd involves an interrupt reaction technique in which conventional polymerization is halted at a

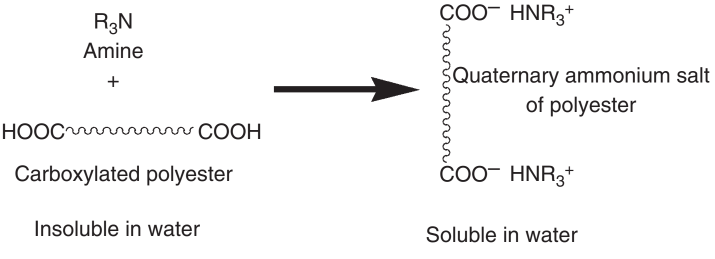


Trimetallic anhydride acts as an acid



Dimethylpropionic acid acts as a polyol

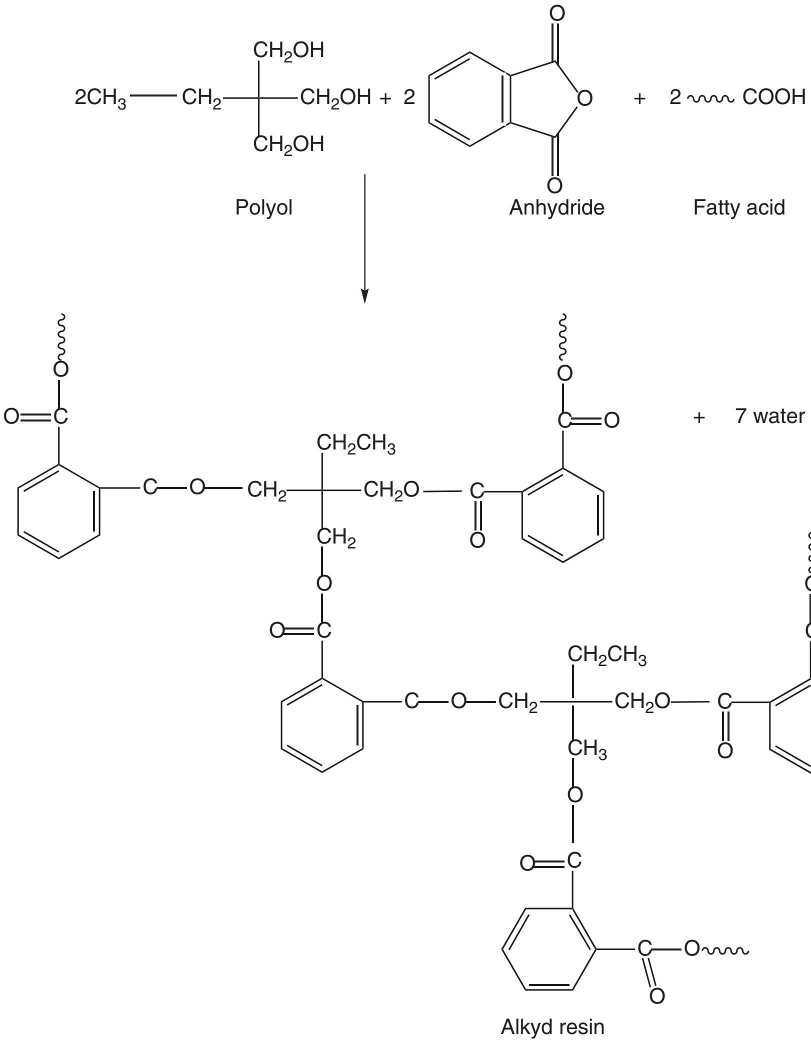
13.5 Precursor for waterborne polyester: hydroxy acid as polyol and trimetallic acid as acid.



13.6 Solubilization of carboxylic group-terminated polyester.

high acid value, allowing the resultant polymer to be neutralized and water solubilized.

- Modification of alkyds with water-loving polyether polyols such as di- or triethylene glycol also makes them water soluble. However, these water-loving groups remain in the film after drying and make the coating more sensitive to water.
- In this technique, alkyds are produced with residual acidity (pendent carboxylic acid groups) and further neutralized with volatile amines to get a temporary water-soluble amine salt. When used in coatings during curing, the amine salt dissociates as the amine evaporates.

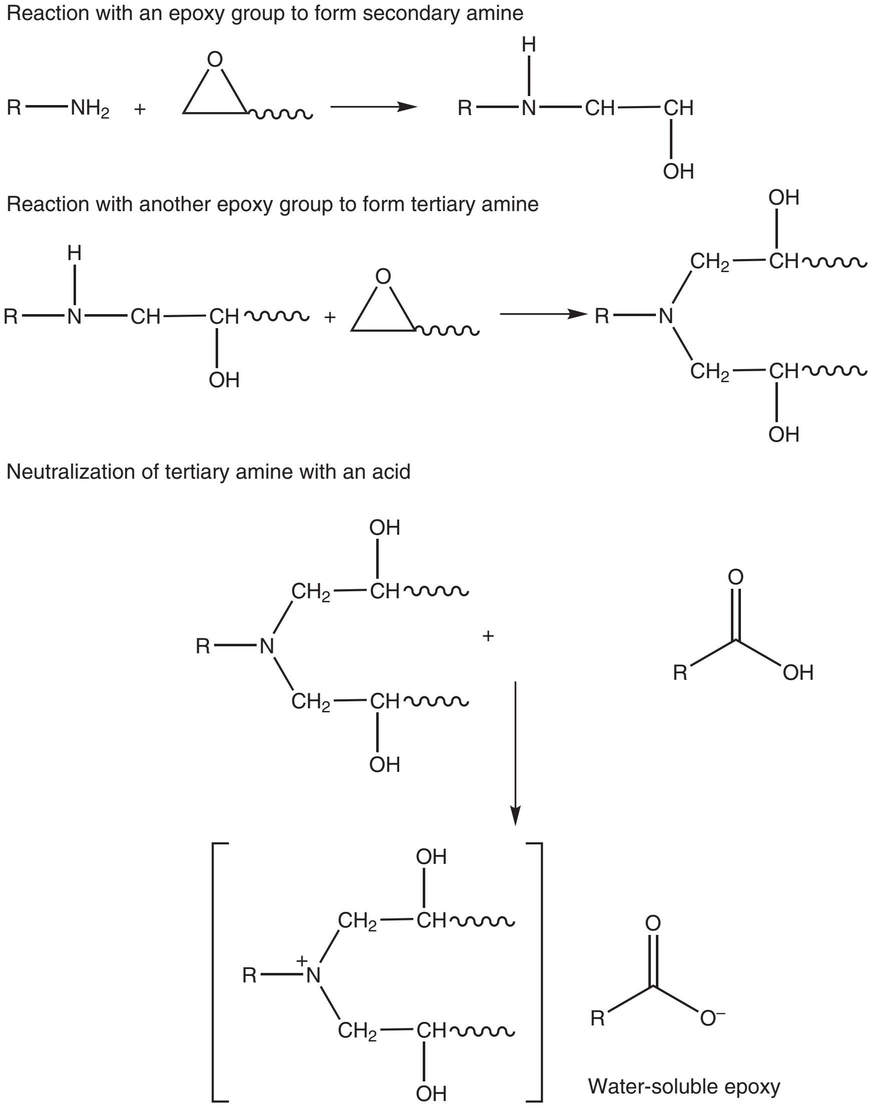


13.7 Synthesis of an alkyd.

- Higher molecular weight polymers can be produced by a two-step reaction which involves the initial polymerization of an alkyd with a hydroxyl value higher than normal hydroxyl value, and then reaction of the produced material with additional anhydride to give the carboxylated polymer.

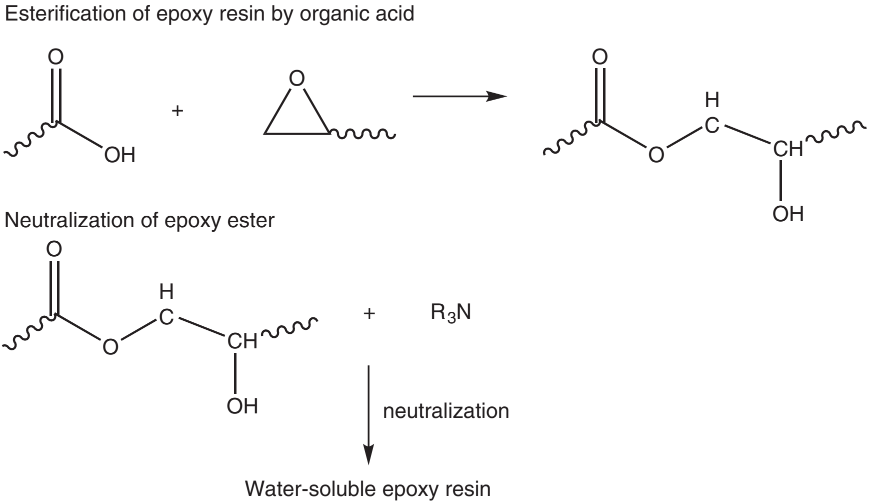
13.7.4 Epoxy

Epoxies [2] are hydrophobic in nature and can be made water soluble by reaction with a suitable amine or an acid. The final product between epoxy

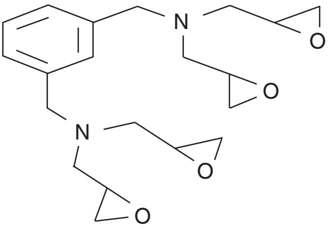


13.8 Solubilization of epoxy resin by reaction with amine and neutralization by acid.

resins and primary or secondary amines is a tertiary amine which can be neutralized with an acid to form a water-reducible quaternary ammonium salt. Whereas acids on reaction with epoxy resin give acid-functional epoxy ester which can then be neutralized with organic amine (Figs 13.8 and 13.9), the tertiary nitrogen atoms on the epoxy molecule react with an acid to generate a water-soluble ammonium salt. Figure 13.10 shows commercially



13.9 Solubilization of epoxy resin by reaction with organic acid followed by amine neutralization.

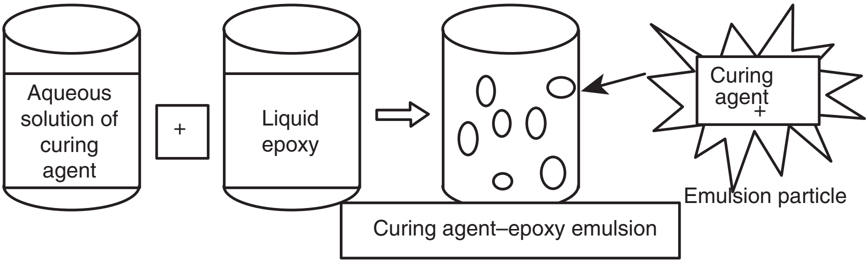


13.10 Chemical structure of *N*,*N*,*N*′,*N*′-tetraglycidyl-meta-xylylenediamine.

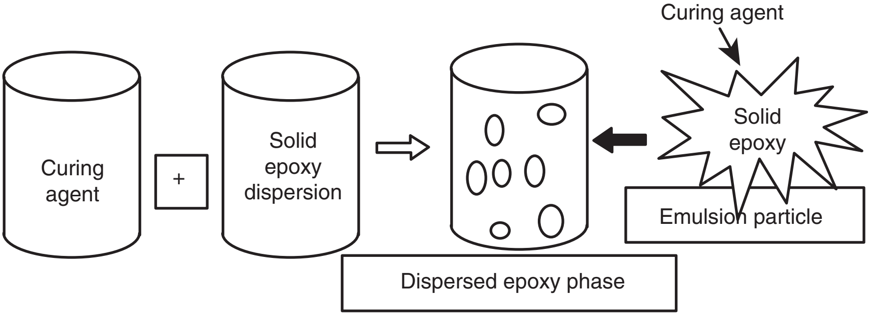
available liquid *N*,*N*,*N*′,*N*′-tetraglycidyl-meta-xylylenediamine which can be made water soluble by reaction with acetic acid.

In the liquid epoxy resin system, the curing agent component is a waterborne/water-reducible modified amine which serves the dual function of curative and emulsifying agent for the resin. The curing agents are modified polyamides or polyamine-epoxy adducts which are rendered water soluble by salting with a volatile organic acid such as acetic acid.

There are two fundamentally different methods to solubilize epoxy resin. The first method utilizes liquid epoxy resin. Typically, the amine curing agent serves as an emulsifier for the epoxy, and the emulsion is formed when the liquid epoxy and the aqueous solution of the amine components are mixed together. The dispersed resin particles contain both epoxy and curing agent (Fig. 13.11). In the second method, solid epoxy resin pre-



13.11 Solubilization of epoxy resin: method 1.



13.12 Solubilization of epoxy resin: method 2.

dispersed in water and co-solvent was used (Fig. 13.12). The dispersed resin particles contain only solid epoxy resin, so that the curing agent must migrate from the aqueous phase into the dispersed epoxy particles for reaction to occur.

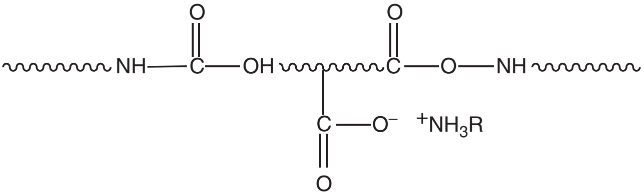
13.7.5 Polyurethane

Polyurethane [7, 8], an ester of carbamic acid, is the reaction product of an isocyanate (—NCO) and an alcohol (—OH). Polyurethane can be made water soluble using either dispersing agents or by ionic stabilization (Fig. 13.13). Ionically stabilized polyurethane is a one-component, linear structured polymer that does not contain any free isocyanate group.

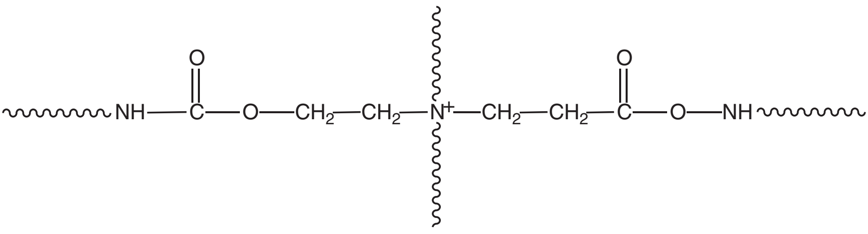
Cationic polyurethane dispersion

These polymers are prepared by incorporating tertiary amine functionality into the backbone followed by quaternization with an alkylating agent or protonation with a suitable acid. The degree of solubility of these polymers in water depends on the degree of quaternary ammonium group concentra-

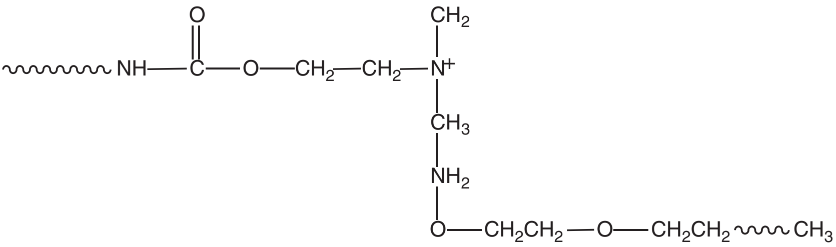
Anionic polyurethane dispersion



Cationic polyurethane dispersion



Non-ionic polyurethane dispersion



13.13 Polyurethane dispersions.

tion. However, the compatibility of these polymers with pigments, additives and other dispersions is inadequate.

Anionic polyurethane dispersion

Anionic polyurethane dispersions are generally prepared from diols and bifunctional isocyanates, with dispersible functional groups such as carboxylic acids built into the backbone. Acidification is generally achieved by using small amounts of an auxiliary diol such as dimethylpropionic acid. A tertiary amine such as trimethylamine can also be used to produce a stable dispersion of the product in water. Here again, the general method of obtaining a polyurethane dispersion involves incorporating hydrophilic centres as internal emulsifiers into the chain of the polyurethane.

Non-ionic polyurethane dispersion

In non-ionically stabilized polyurethane dispersion, the hydrophilic centres consist of polyether chain segments that are attached to or incorporated in polymer.

During drying or film formation of urethane dispersions, there probably occurs a certain physical crosslinking caused by:

- Electrostatic forces between hydrophilic groups (coulomb force)
- Hydrogen bonding between urethane groups
- Interaction between hydrophobic segments of the chain.

13.7.6 Acrylics

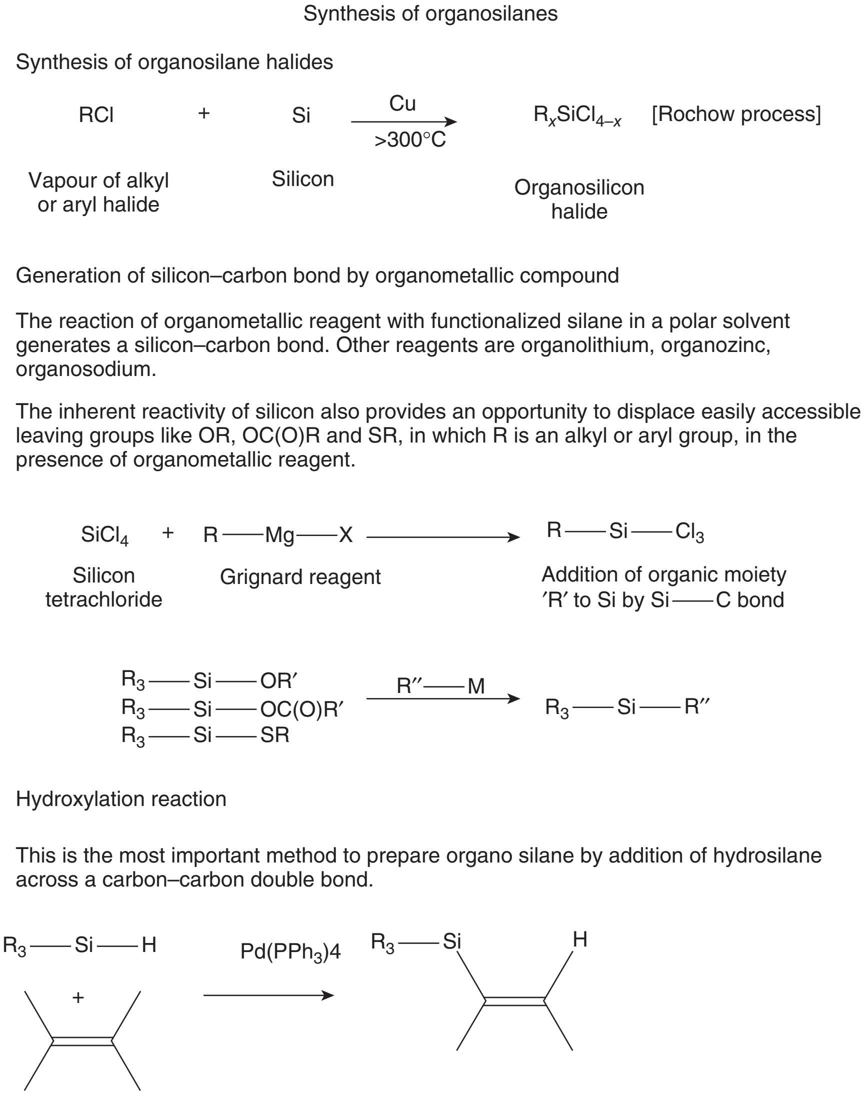
Carboxylic acid-functional acrylic polymer of molecular weight between 20 000 and 50 000 with a minimum acid value of 50 mg KOH/g can be made water soluble by neutralizing pendent carboxylic acid using amines. Acrylic monomers have been copolymerized into the polyurethane and dispersions of this true copolymer are widely available on the market. Typical systems are prepared from IPDI and polypropylene glycol copolymerized with methyl methacrylate and butyl acrylate.

13.7.7 Silicone

Silicone polymers [9] are a class of hybrid organic/inorganic polymers that have been used in aqueous as well as non-aqueous systems. Silicones show excellent performance as surface active agents in both aqueous and non-aqueous systems in reducing the surface tension to as low as 21 mN/m. However, on a nanometre scale silicone often forms a third phase instead of solubilizing in hydrophilic and a variety of hydrophobic solvents. It can either be used as an emulsifier or acts as the continuous/disperse phase of the emulsion. Silicone emulsions typically consist of water, silicone oil and a surfactant.

Silicon readily expands its valence shell under nucleophilic substitution more easily than its carbon analogues. Chlorosilanes are the most common substrate for displacement reactions, producing a number of organosilanes on substitution of chloride by varieties of organic moieties (Fig. 13.14).

Chlorosilanes, which undergo nucleophilic substitution, are the most common substance for the preparation of precursors for sol-gel coating under mild conditions. They can be prepared by the Rochow process (synthesis of organosilicon halides) and organometallic coupling reactions (Grignard reagent). Silicon alkoxide can also be incorporated into the polymer backbone via free-radical polymerization through a vinyl moiety,



Synthesis of organosilanes

Synthesis of organosilane halides

$$RCl + Si \xrightarrow[>300^\circ C]{Cu} R_xSiCl_{4-x}$$ [Rochow process]

Generation of silicon–carbon bond by organometallic compound

The reaction of organometallic reagent with functionalized silane in a polar solvent generates a silicon–carbon bond. Other reagents are organolithium, organozinc, organosodium.

The inherent reactivity of silicon also provides an opportunity to displace easily accessible leaving groups like OR, OC(O)R and SR, in which R is an alkyl or aryl group, in the presence of organometallic reagent.

$$SiCl_4 + R—Mg—X \longrightarrow R—Si—Cl_3$$

$$\begin{matrix} R_3—Si—OR' \\ R_3—Si—OC(O)R' \\ R_3—Si—SR \end{matrix} \xrightarrow{R''—M} R_3—Si—R''$$

Hydroxylation reaction

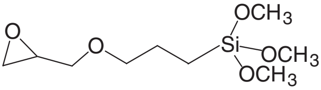
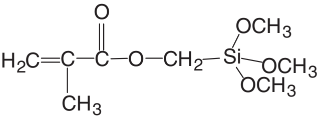
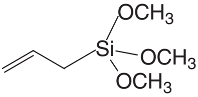
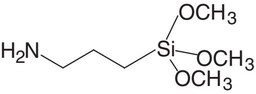
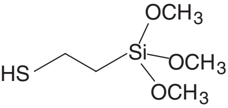
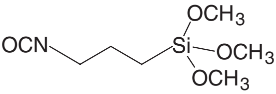
This is the most important method to prepare organo silane by addition of hydrosilane across a carbon–carbon double bond.

13.14 Synthesis of precursors for sol-gel coating.

via a condensation reaction with an organic moiety on the silicon alkoxide monomer, or via a post-reaction (such as a hydrosilylation reaction).

Silicones are water repellent, heat stable, and highly resistant to chemical attack as compared to their organic counterparts. Owing to these special properties, silicones are finding applications in paints. Commonly used silicone polymers as shown in Table 13.5 are polydimethylsiloxane, epoxy silane and amino silane and their derivative polymers that have been com-

Table 13.5 Organically modified silane

Epoxy silane 	2-(3,4-epoxycyclohexyl) ethyltriethoxysilane 2-(3,4-epoxycyclohexyl) ethyltrimethoxysilane 5,6-epoxycyclohexyltrimethoxysilane (3-glycidoxypropyl) dimethylethoxysilane (3-glycidoxypropyl) trimethoxysilane
Acrylic silane 	(methacryloxymethyl)triethoxysilane *o*-(methacryloethyl)-*N*-(triethoxysilipropyl) urethane
Vinyl-derived silane 	vinyltrimethoxysilane vinyltriacetoxysilane vinyltris(methylethylketoximino)-silane
Amine silane 	*N*-(2-aminoethyl)-3-aminoisobutyltrimethoxysilane *N*-(6-aminohexyl)aminopropyltrimethoxysilane 4-aminobutyltriethoxysilane *p*-aminophenyltrimethoxysilane 3-aminopropyltris(methoxyethoxyethoxy)silane
Thiol-based silane 	3-mercaptopropyltriethoxy 3-mercaptopropyltrimethoxy
Isocyanate-based silane 	3-isocynatopropyltrimethoxysilane 3-isocyanatopropyltrimethoxysilane
Others	ureidopropyltriethoxy, fluorotrimethoxysilane

mercialized extensively. These organic moieties should have a hydrophilic nature or can be made hydrophilic before utilizing them in waterborne coating formulations.

13.8 Additives in waterborne coatings

Additives in waterborne coatings are used to improve the rheology, wetting, thaw stabilization, corrosion resistance and stability in UV. Additives may be in the form of surfactants, thaw stabilizers, dispersants, corrosion inhibitors, light and heat stabilizers, or coalescing agents [2, 10].

Table 13.6 Function of co-solvents in waterborne coatings

Solvent properties	Function	Example
Coalescing agent for latex	Reduces glass transition temperature (T_g) of resins	Hexylene glycol, *n*-methyl-2-pyrrolidone
Freeze/thaw stabilizer	Depresses the freezing point of water	Alcohols, non-ionic surfactants
Levelling aid	Prolongs wet film mobility	Propylene glycol
Wet edge extender	Reduces viscosity of paint and evaporation rate of solvent	Propylene glycol, diethylene glycol monoethylether
Defoamer	Imparts low surface tension to foam cell wall	Octanol, pine oil, mineral spirits
Dispersant	Provides good wetting and dispersion of pigments	*n*-Methyl-2-pyrrolidone

13.8.1 Co-solvents in waterborne coatings

Although water is an environmentally friendly solvent for the coating industry, it requires some additives to make it suitable for waterborne coatings owing to its unique chemical and physical nature. In most waterborne systems, the inclusion of some co-solvent is necessary to improve coalescence, freeze–thaw stability, levelling and wetting. Solvents speed up water release, adjust the drying time, assist pigment dispersion and control foaming. Some of these co-solvents and their functions in waterborne coating formulations are listed in Table 13.6.

13.8.2 Surfactants

The constituent particles of liquid and solid, which may be ions, atoms or molecules, in bulk are attracted to their neighbours on all sides, whereas those in the surface layer are attracted on only three sides. This results in an unbalanced force, known as the surface tension. The establishment of this surface tension in water causes the adoption of the minimum possible area (a spherical shape) by the water droplets, which results in poor wetting of the substrate by waterborne coating formulations. Therefore, a waterborne coating requires some surfactants to reduce the surface tension of the coating, which improves the wetting of the substrate. Surfactants may also be added to aid substrate wetting, to assist stabilization of the latex or to maintain dispersion of pigments. There are three major functions of surfactants:

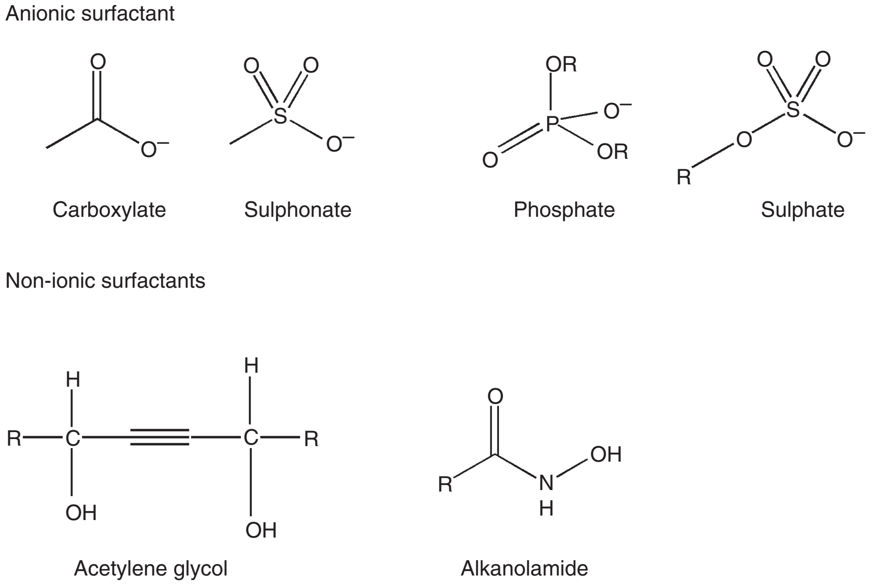
- To improve substrate wetting
- Stabilization of latex
- Proper dispersion of pigment.

Surfactants consist of polar (hydrophilic) and non-polar (hydrophobic) moieties. The non-polar moiety experiences a repulsive force by water molecules, which leads to the relative depletion of surfactants from the bulk of the liquid water and accumulation at the surface where they have to reduce surface tension. Thus, in the presence of surfactants, the surface energy of the interface will have a lower energy state than in the bulk.

Surfactants are divided into three groups: anionic, cationic and non-ionic (Fig. 13.15). Anionic surfactants possess a negative charge in solution and are typically used as soaps, detergents, emulsifiers, dispersants and wetting agents, whereas cationic surfactants possess a positive charge in solution and are typically used as antibacterial agents, fabric softeners, corrosion inhibitors, ore flotation additives, emulsifiers and dispersants. One example is quaternary ammonium compounds, R_4N^+, though in coatings their use is limited.

However, these surfactants are present in the paint formulation but are not reactive (no covalent bonding with polymeric particles) in the polymerization process. They result in the destabilization of the paint formulation under high ionic strength, freezing and high shearing. Poor adhesion, water sensitivity and low-dimensional stability have also been observed when the film was exposed to water or high conditions of humidity. The bad performance of film is due to desorption of surfactant from the particle surface or migration towards the film surface, and formulation of hydrophilic domains within the film upon phase separation. There are two possible ways to avoid these difficulties: by using either reactive surfactants or polymeric surfactants. Reactive surfactants are able to participate in one of the chemical reactions involved in the polymerization process. The other way to avoid the desorption of the surfactants from the particle surface is to use polymeric surfactants that are very difficult to desorb.

Guyot [11] reviewed the performance of reactive surfactants and their applications in the synthesis of latexes for waterborne coatings. A large number of reactive surfactants, non-ionic, anionic, cationic or even zwitterionic (Fig. 13.16), have been prepared and tested in emulsion, mini-emulsion, micro-emulsion or dispersion polymerizations, of styrene and acrylic monomer(s), in batch or semi-batch processes, to prepare both homopolymers and core-shell copolymers. A novel wetting agent, sodium



Hydrophobic surfactants

Linear and branched aliphatic hydrocarbons

Alkylbenzene
Alkylnaphthalenes
Alkylphenols

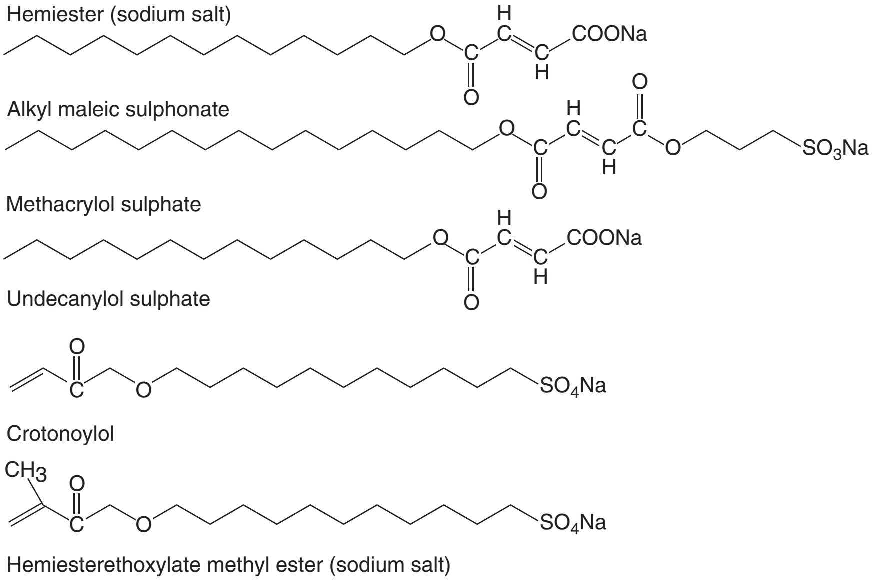
Polyoxypropylenes
Silicones
Fluorocarbons

13.15 Common surfactants used in waterborne coatings.

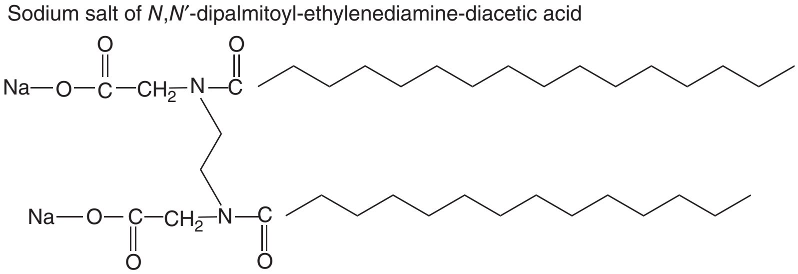
salt of *N*,*N*-dipalmitoyl-ethylenediamine-diacetic acid (Fig. 13.17), was synthesized by Bi *et al*. [12].

13.8.3 Rheology modifier

Rheology (flow properties) is the study of the deformation and flow of matter under the influence of an applied stress. The control of paint rheology is essential for the stability of the paint, the manufacturing process (pigment dispersion) and transport through pipelines as well as for its application characteristics. Thixotropes or rheological control agents for waterborne coatings are as important as those for solventborne coatings. The viscosity of latex systems is generally very low and in consequence such systems require viscosity builders. Viscosity builders include water-



13.16 Reactive surfactants.



13.17 A novel wetting agent.

soluble high molecular weight polymers such as cellulosic, alkali-activated polymers, such as those based on acrylic acid, ethoxylated urethane-based associative thickeners, and clays such as attapulgites. A list of some commonly used thixotropes and their functions is given in Table 13.7.

13.9 Film formation

13.9.1 Film formation by water-soluble polymer

Film formation involves the deposition of a polymeric solution onto a substrate and its transformation into an adherent solid coating as the water dries out. During the application process, polymer molecules tend to become stretched, owing to the following:

Table 13.7 Rheology modifiers in waterborne coatings

Thixotrope	Example	Properties
Cellulosic polymer	Methyl cellulose, hydroxyethyl cellulose, hydroxy propyl cellulose	Increases viscosity of latex
Polyacrylate	Polyacrylic acid, polymethacrylic acid and their salts	Not prone to microbial attack
Anionic thickener	Anionic polycarboxylic acid	No microbial attack
Non-ionic thickeners	Ethoxylated polyether-based urethane block co-polymer	Thicken by means of secondary valency association
Clay-type thickeners	Appapulgite clays (anti-microbial attack)	Impart viscosity by creating a network of flocculated needles
Fibrous thixotropes	Cellulosic and polyaremid fibres	

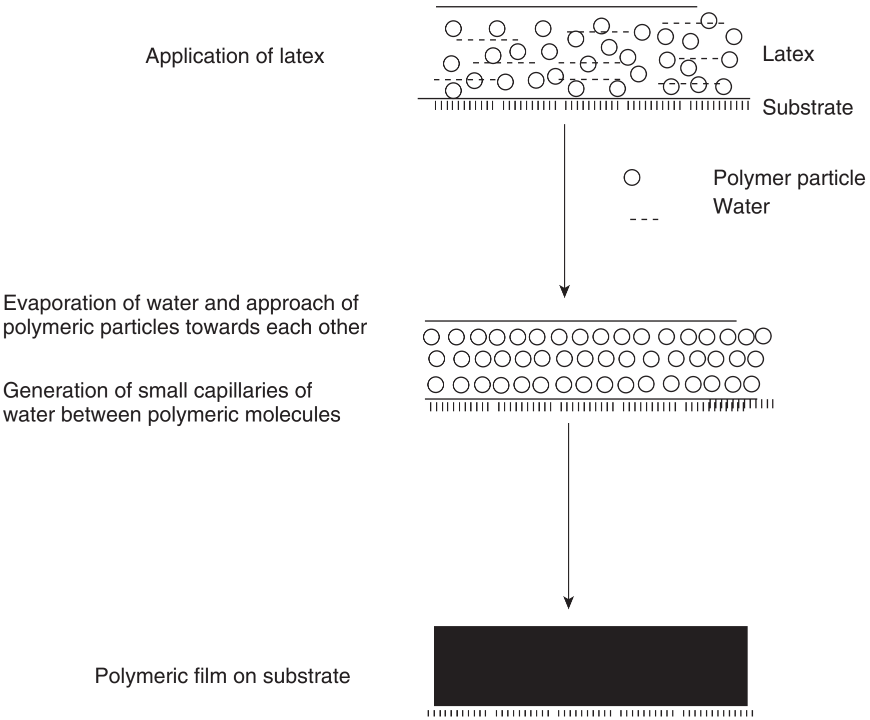
- The energetically favourable interaction between the polymer segments and the water molecule, which may be maximized by uncoiling of the polymer.
- The presence of mutual forces of repulsion in polymer.

Once the coating process is complete, the polymer molecules become free to return from a stressed state to their original configuration, as long as they have not reached their elastic limit, and form an even film, since a state of high shear exists within the coating solution during the coating application.

13.9.2 Film formation by latex paint

The mechanism of film formation in latex paint is more complex than for paints derived from true polymeric solutions. Once the film has been spread on the substrate, drying of the film starts. It involves two steps as shown in Fig. 13.18.

1. Evaporation of water by leaving behind the polymer, pigment and other constituents of paint on the substrate.
2. Once the water evaporates, flattening and coalescing of the polymer particles take place for film formation. In this step, full incorporation of the pigment particles into the film is crucial for assuring excellent performance of the resulting coating.



13.18 Film formation in latex paint.

The rate of flattening and coalescing of polymer particles is influenced by a number of factors such as the natural hardness of the polymer, the presence of coalescing solvent in the latex, and electrostatic repulsive interaction at the surface of the polymeric molecules which themselves depend on the temperature of film formation. The temperature at which latexes cast continuous and clear film is called the minimum film formation temperature. When drying, some latex paints produce continuous and strong film while others form powdery layers. Commonly, loss of water by evaporation results in a powdery finish to the coating, which has no cohesion. The glass transition temperature and the particle size of the polymer components of the latex decide the minimum film formation temperature [1].

13.10 Application methods

The application technology for waterborne coatings is comparable to that of conventional solventborne coatings. If a facility is using a water wash booth, overspray is easily recovered and reused if colours are appropriately segregated. Uncured waterborne coatings can be cleaned from equipment with water. Electrostatic spray can be used if the electrically conductive waterborne paint is isolated from the electrostatic system. However, some formulations or substrates might require special pumps and piping to prevent corrosion from water in the formulation. In addition, for product finishing, coatings need to dry or cure at elevated temperatures to ensure complete cure in a reasonable period of time.

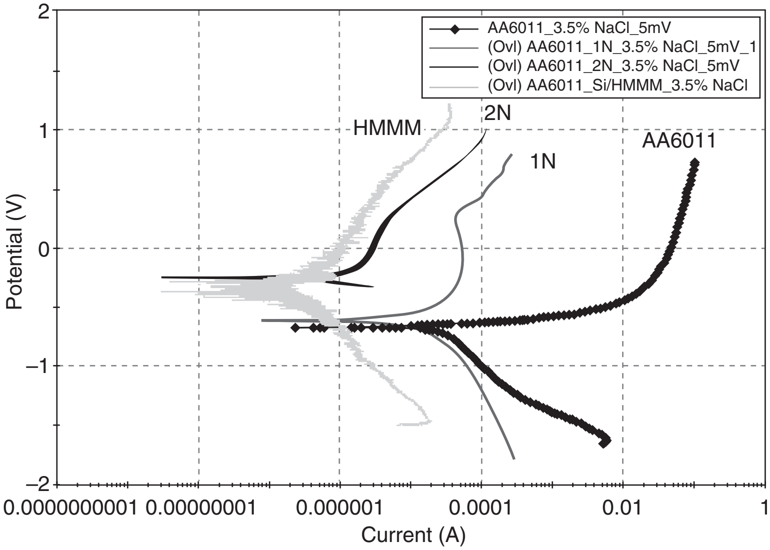
13.11 Performance evaluation of waterborne coatings

Selection of coating recipes depends on several factors such as the desired life of the coating, the nature of the substrate, and climatic conditions. There are several laboratory tests in use to demonstrate the protective behaviour of coatings and to give reliable predictions of their lifetime. It is generally expected that the test environment should be the same as or similar to that of the actual application. However, such a natural exposure test requires too long a time. For reducing the test time, accelerated natural exposures and laboratory tests have been developed. Commonly used accelerated tests such as salt spray, accelerated weathering, humidity, temperature and different contamination conditions, are traditionally used to assess the anticorrosive behaviour of the paint coatings.

Like solventborne coatings, waterborne coatings are also available for high-performance applications such as corrosion protection, abrasion resistance, UV stability, thermal stability etc. Various waterborne coatings derived from conventional polymers have been well discussed in various texts [1, 2]. A number of review articles are available on sol-gel based coatings [1, 14] but only a few address waterborne sol-gel products [15, 16]. Today sol-gel coating is one of the most promising high-performance waterborne coatings. In this section, we will discuss the performance of waterborne sol-gel coatings specially developed by our group.

13.11.1 Corrosion resistance

Excellent corrosion resistance is one of the most desirable properties of high-performance coatings. Potentiodynamic polarization, electrochemical impedance spectroscopy and salt spray tests are traditionally used to assess the anticorrosive behaviour of paint coatings. Waterborne sol-gel coatings based on methyltrimethoxysilane (MTMS) and 3-glycidoxypropyltrimethoxysilane (GPTMS) were developed [13]. Two amino-silanes, namely γ-aminopropyltriethoxysilane (1N), *N*-(β-amino ethyl)-γ-aminopropyltrimethoxysilane (2N) and hexakis(methoxymethyl)melamine (HMMM), were used as crosslinking agents. Aluminium alloy AA6011 was dip coated, dried at room temperature and placed in a furnace at 120°C for 30 min for final curing. The anticorrosive behaviour of the coatings in 3.5% NaCl solu-



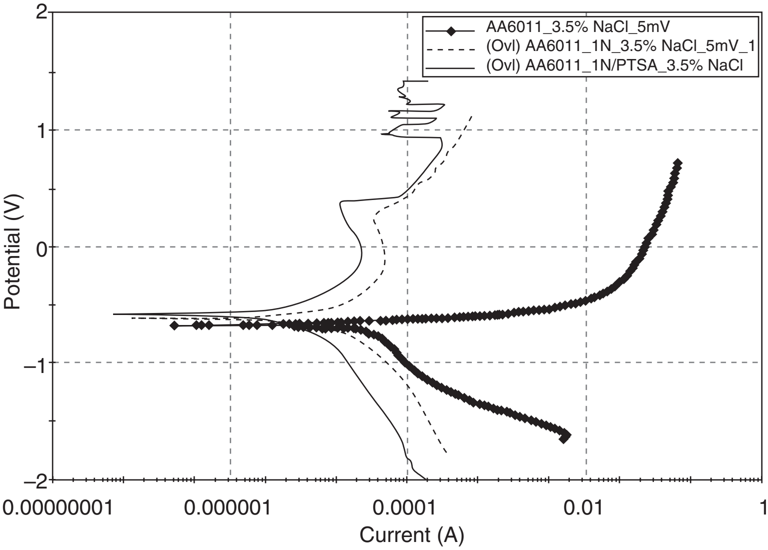
13.19 Potentiodynamic polarization curves (*E* vs log *I*) of bare and coated AA6011 in 3.5% NaCl at scan rate of 5 mV/s.

tion was found to be excellent. The corrosion currents of the coated aluminium alloy decreased by two orders of magnitude compared to bare aluminium alloy, which implied that the coating forms a dense barrier against penetration of water and chloride ions (Fig. 13.19).

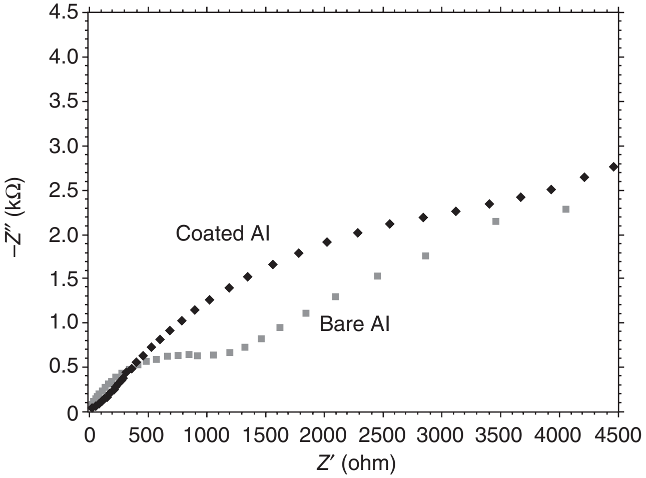
It was found that the anticorrosion ability of various crosslinkers is in the order HMMM > 2N > 1N. Addition of *p*-TSA as catalyst in the 1N coating further improved the rate of film formation as well as the corrosion resistance. The shifting of open circuit potential towards the noble direction, as compared with the uncatalysed 1N coating, and the reduction in the corrosion current from 0.67×10^{-6} A to 1.26×10^{-7} A, confirm the positive role of the addition of the *p*-TSA as catalyst (Fig. 13.20).

Although organosilanes exhibit excellent corrosion resistance, their use is limited since they are costly and difficult to apply. In recent years, cost reduction and easy handling of sol-gel materials have become important issues for manufacturers of paint raw materials, paint users and researchers. One solution to this problem is the incorporation of conventional organic polymers in silanol sol.

In order to reduce the cost, conventional waterborne alkyd and polyester resins were incorporated in the MTMS–GPTMS sol. These conventional organic polymer-incorporated sol-gel coatings have shown excellent corrosion resistance on aluminium and magnesium alloys. The impedance spectra of bare and polyester-incorporated MTMS–GPTMS coated



13.20 Potentiodynamic polarization curves (*E* vs log *I*) of bare, Si/1N and Si/1N-PTSA coated AA6011 in 3.5% NaCl at scan rate of 5 mV/s.



13.21 Nyquist plot of bare and coated (conventional polyester–MTMS–GPTMS) aluminium in 3.5% NaCl at scan rate of 5 mV/s.

aluminium confirm the superiority of waterborne coatings (Fig. 13.21). Along with their corrosion resistance, waterborne coatings also impart improved hardness and hydrophobicity and enhanced UV resistance, as discussed below.

13.11.2 Mechanical properties

Coatings, generally, are subjected to stresses when fabricated into products by rolling, bending, or other deformation processes. These stresses can exceed the flexibility or adhesive strength of the coating, resulting in fracture of the coating, exposing the substrate, scratch, or loss of adhesion to the substrate. Therefore, to withstand the stress of fabrication, coatings must adhere to the substrates on which they are applied, and be hard enough to resist scratching during fabrication and during service life. A variety of recognized methods can be used to determine how well a coating is bonded to the substrate. Commonly used measuring techniques are the cross-hatch test, the bend test, the pencil hardness test and the impact test.

Bend and impact tests suggested that all MTMS–GPTMS coatings were well adhered to the surface and were able to withstand the stresses during service. The pencil hardness of MTMS–GPTMS coatings was found to be above 6H. The hardness of 2N crosslinked coating was found to be better than that of 1N crosslinked coating. Incorporation of organic polymers to sol provides a coating of intermediate hardness between pure MTMS–GPTMS coating and pure organic polymer-derived coating. However, the hardness can be controlled by the MTMS–GPTMS and organic polymer ratios. We observed that the hardness of the polyester and alkyd modified MTMS–GPTMS coating decreases with increasing polyester/alkyd content. Figure 13.22 shows that the addition of conventional polyester in MTMS–GPTMS sol reduces the hardness of the coating from 6H to 3H, depending upon the polyester–sol weight ratios.

13.11.3 Hydrophobicity

The water contact angle is a quantitative measure of the wetting of the coated substrate by water. The total surface free energy of a sol-gel coating and its components can also be determined using Young's equation, which relates the surface tension of water in equilibrium with its vapour, with the contact angle of the water drop on the surface of a sol-gel coating:

$$\gamma_{SL} = \gamma_{SV} - \gamma_{LV}\cos\theta$$

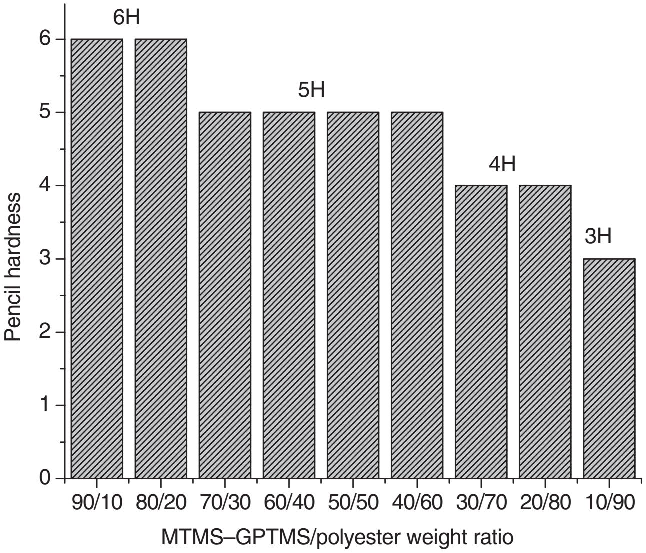
where

γ_{SL} = interfacial free energy between the bare/sol-gel coated substrate and the water

γ_{SV} = surface free energy of the bare/sol-gel coated Al in equilibrium with water vapour

γ_{LV} = surface tension of the water in equilibrium with its own vapour

θ = contact angle.

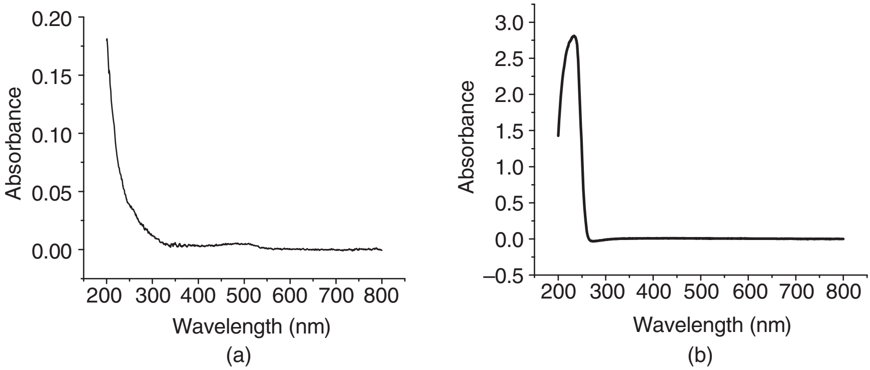


13.22 Pencil hardness of MTMS–GPTMS/polyester coating on aluminium.

A higher value of the contact angle indicates the good hydrophobic nature of the coating, while low values indicate that the water wets the surface. The contact angle measurement shows that the hydrophobicity of the coating is influenced by the nature of the crosslinking agent, the organic polymer and the MTMS/GPTMS ratios. 1N and 2N crosslinked coatings have sufficient hydrophobicity, with contact angles ranging from 85° to 103°. On the other hand, HMMM crosslinked coatings were found to have a lower contact angle (72–89°) than 1N and 2N crosslinked coatings. A further decrease of contact angle by 4–10° was observed for conventional polyester-incorporated HMMM crosslinked MTMS–GPTMS coatings. The hydrophobicity of these coatings can be increased by a suitable additive or selection of resin.

13.11.4 UV resistance

Along with oxygen and water, ultraviolet light is one of the three primary factors that induce slow degradation of the organic components of a coating. The stability of a coating in artificial and outdoor weathering depends upon the nature of the binder, pigments and additives used. However, most common organic polymeric binders do not have sufficient resistance to ultraviolet light and heat, which results in decrease in mechanical properties, loss of gloss, chalking, fading, yellowing and surface cracking and



13.23 UV-visible spectrum of (a) MTMS + GPTMS sol, and (b) MTMS + GPTMS + HMMM coating solution.

peeling. The energy associated with UV wavelengths (below 290 nm) is sufficient to break the bonds (C–C, C–H, C–O and C–N) in common polymeric materials, which leads to degradation of the coating. The use of light and heat stabilizer generally improves the UV resistance of coatings. Another solution to this problem is the use of UV-stable polymeric binder. Silanes and organically modified silanes are one of the choices. Silanes contain highly UV-stable Si–O–Si bonds. A number of studies have shown that silane-based coatings have excellent stability to weathering. UV-visible spectroscopy of MTMS–GPTMS sol and MTMS–GPTMS–HMMM coating formulations showed no significant absorbance in the range 265–800 nm (Fig. 13.23 (a) and (b)), which confirms the stability of the coatings in sunlight. However, incorporation of organic polymer in the sol-gel coatings decreases the UV resistance and also the heat stability, owing to the degradation of organic moieties present in the coating.

13.11.5 Solvent resistance

Waterborne coatings are generally known for their poor resistance to attack from water, and other solvents and chemicals, compared to solventborne coatings. This may be due to the unreacted hydrophilic emulsifier and crosslinking agent remaining within the coating after curing. The water trapped inside the coating due to insufficient coalescence during the curing process may also lead to the poor performance of the coating. Generally, for an optimum binder/hardener ratio, increasing the film thickness and curing at elevated temperature improve the chemical resistance of the coating. The curing at elevated temperature forces water out of the coating, which drives the binder–hardener reaction to completion and also thus improves the coalescence.

Table 13.8 Chemical sensitivity of various polymers

Polymer	Sensitive group	Chemical/solvent	Mode of attack
Phenolic resin	Acidic phenolic hydroxyl group	Alkali	Hydrolysis
Cellulosic Polyformaldehyde Polyvinylacetals	Acetal group	Aqueous acid	Hydrolysis
Polyester Polyamide Polyurethane	Ketone, amide, urethane linkage	Acid or alkali	Hydrolysis
Epoxy	Ether, imine	Aqueous alkaline and acidic	Hydrolysis

Only specific functional groups in the polymer cause sensitization to water, solvents and other chemicals (Table 13.8). The sensitivity of such groups is independent of the coating formulation, whether solventborne or waterborne. It is generally observed that a high crosslink density of the polymer network decreases its exposure to the environment. Polyester resins are the product of the esterification reaction of di- or polyhydric alcohols with di- and polybasic acids or anhydrides. In presence of water, polyesters have a tendency to reverse the esterification reaction, which is why polyesters have limited application to waterborne coating systems. Various studies have been done to modify the rate of hydrolysis by the proper choice of monomers.

Jones *et al.* [17] demonstrated the changes in hydrolytic stability in waterborne polyesters as a function of the change in glycol and diacid composition. It was observed that the hydrophobic nature of the glycol components of polyester improves the hydrolytic stability of the polyester. The acid component of polyester with low dissociation constants, low water solubility and steric hindrance also improves the water resistance of polyester.

13.12 Application of waterborne coatings

13.12.1 Coatings on wood

One of nature's greatest gifts to mankind is wood. Wood or wood-based products such as paper and board materials, cabinets, decorative woodwork, beautiful furniture, sports equipment, flooring, home building and thousands of other products touch our lives daily. However, the surface of wood undergoes a degradation process due to environmental attack due to moisture, radiation and biological deteriorant. Environmental attack starts with the absorption of energy from light in the UV and visible region, which leads to radical formation and radical-induced cleavage at phenolic or excited α-carbonyl units in the lignin fraction of wood and cellulose and hemicellulose fractions respectively. These degradation products are water soluble and are leached out, resulting in erosion of the wood surface. Photochemical degradation also results in cracking and splitting of wood.

Along with desired aesthetic properties like colour and gloss, coatings can protect wooden materials against uptake of moisture and the related dimensional changes, photochemical degradation of the wood surface and microbiological degradation by blue-stain and mould fungi. Waterborne alkyds and acrylics have been substituted for many solvent-thinned coatings in the last few years. Physical properties such as mar resistance and pencil hardness are equal to or better than many of the solvent-based paints. Waterborne acrylic binders are generally produced by emulsion co-polymerization of various monomers. Core-shell polymerization techniques are introduced into wood coatings to get excellent coating properties more easily. Water-soluble alkyds are mainly used in combination with acrylic dispersions (hybrids).

Adhesion of the paint film can be increased either by deeper penetration into the wood surface or by chemical bond formation between wood surfaces.

- *Deeper penetration.* It is generally observed that there is limited penetration of resins into porous wood substrates due to the much larger size of emulsion particles. Waterborne alkyds with their finer particle size and slow oxidative drying have been developed and frequently incorporated into emulsion paints to improve the penetration of wood finishes. Another approach to defeat the particle size problem is a substituted styrene-acrylate. Coatings based on styrene-acrylate penetrate better into porous wood, which results in improved adhesion.
- *Chemical bond formation.* Isocyanates are capable of developing a covalent bond with hydroxyl groups on the surface of wood and this process can improve the adhesion of wood primers. However, when isocyanates are added to waterborne systems, they immediately begin to react and so applying this concept to waterborne primers presents some difficulties.

Urethane-based water dispersion with a low level of suitable crosslinker (preferably an aziridine rather than an isocyanate) provides more effective stain sealing than a corresponding solventborne coating. A component polyurethane coating based on hydroxyl-bearing polyacrylate emulsion and hydroxyl-bearing polyurethane emulsion (or combinations) crosslinked with hydrophilically modified aliphatic isocyanate is available for kitchen units, office furniture, and parquet sealers.

Waterborne cationic epoxy primer provides good resistance against tannin staining over wood and also over nicotine stains when applied over existing interior paintwork. This is applied as a clear primer to maximize its barrier properties and protects the subsequently applied acrylic emulsion or styrene-acrylate emulsions paint against staining.

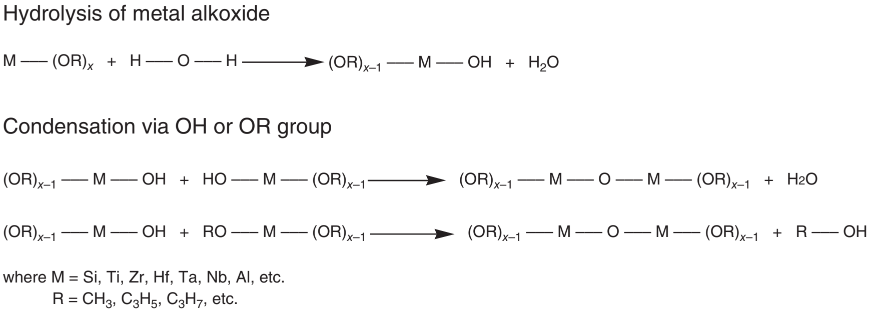
13.12.2 Coatings on glass

Coating on glass helps to achieve specific properties that make the products more useful for many applications, and perhaps without coating it would not be possible to make several products with useful properties, such as protection against shattering, abrasion resistance, colour filters, anti-static, anti-fog and anti-reflective. Coating also improves resistance to mechanical and chemical influences. The abrasive nature of glass requires some protective and lubricating coatings on glass fibres products to reduce its abrasiveness. Conventional methods to produce coloured glass involve addition of toxic metal oxides such as cadmium and cobalt oxide or very expensive metals such as gold to the glass melt. The colour resulting from conventional methods are not ecologically and economically acceptable. Compared with conventional methods for colouring glass, coating with pigmented material has a number of advantages in terms of recycling. Recycling to yield clear glass can be done, without sorting, by melting and flaming off the organic coating at temperatures between 400 and 600°C.

Various waterborne coating systems are available for coating on glass. These include water-reducible polyisocyanate with hydroxyl-bearing polyurethane dispersions, and sol-gel derived, organically modified silane coatings. Coatings can be applied by conventional application processes such as dipping or spraying followed by baking, for example, for around 30 minutes at 150°C.

Coating materials for glass fibres are called sizes and consist mainly of binder, adhesion promoter, slip agent, antistatic agents and other additives in water as a dispersion medium. Binders such as polyvinyl acetate, polyester resin, epoxy resins and polyurethane dispersion can be used to coat the glass fibres. Polyurethane-based glass fibres have good stability to shear during application, outstanding film-forming properties and excellent colour fastness.

Sol-gel technology also provides an elegant waterborne coating system that can be applied to glass. By proper selection of an organic modifier to silane, it is possible to obtain organic–inorganic hybrids, which can find application in optical waveguides for planar integrated circuits and hydrophobic coatings, and in the manufacture of transparent or translucent



Hydrolysis of metal alkoxide

$$M - (OR)_x + H - O - H \longrightarrow (OR)_{x-1} - M - OH + H_2O$$

Condensation via OH or OR group

$$(OR)_{x-1} - M - OH + HO - M - (OR)_{x-1} \longrightarrow (OR)_{x-1} - M - O - M - (OR)_{x-1} + H_2O$$

$$(OR)_{x-1} - M - OH + RO - M - (OR)_{x-1} \longrightarrow (OR)_{x-1} - M - O - M - (OR)_{x-1} + R - OH$$

where M = Si, Ti, Zr, Hf, Ta, Nb, Al, etc.
R = CH_3, C_3H_5, C_3H_7, etc.

13.24 Hydrolysis and condensation reaction of metal alkoxide.

windows, thermal and acoustic insulations. These coatings can have excellent abrasion and scratch resistance close to that of glass, very good adhesion to glass surfaces, stable basic properties, and high stability of colours (no fading). Low viscosity of the coloured hybrid sols allows the use of a great variety of coating techniques such as dipping, spinning, spraying, brush painting roller coating, felt-pen painting or screen printing. In addition, these hybrid are compatible matrices for intensive organic dyes, laser dyes and other organic compounds.

Silica nanoparticle-modified polymer coatings have also been developed for anti-fogging abilities, which can be applied to eyeglasses, camera lenses, ski goggles and even bathroom mirrors. These coating are super-hydrophilic or water-loving in nature, strongly attracting water droplets and forcing them to merge into a uniform, transparent sheet rather than forming countless individual light-scattering spheres which create fogging.

The sol-gel process generally involves the use of inorganic salts or metal alkoxides as precursors. Hydrolysis and polycondensation reactions occur when the precursors are mixed with water and catalyst. In general, different metal alkoxides are used for preparing anti-reflecting coatings. The general reactions can be expressed as shown in Fig. 13.24.

Transition metal alkoxides are generally more reactive than silicone due to the presence of highly electronegative 'OR' groups that stabilize 'M' in its highest oxidation state and render 'M' very susceptible to nucleophilic attack. Various anti-reflecting coating systems based on colloidal solutions of titanium oxide, zirconium oxide and tin oxide have been developed. Nowadays, organically modified silanes such as methyltrimethoxysilane and tetraethoxysilane along with these metal alkoxides are being used to improve crack resistance. Waterborne acrylic polymers for the formulation of pre-aluminizing lacquers are used in the manufacture of cathode ray tubes.

13.12.3 Coatings on plastics

Light weight and low cost coupled with increased flexibility and aesthetic appeal have led to the increased use of plastic. To match service requirements, like metal, glass and wood, plastics also require coating systems to improve their appearance and to protect them from physical and mechanical stresses.

Uncoated plastics are transparent to electromagnetic interference (EMI), hence they require some opacity. To allow plastics to be used as enclosures for computers, mobile phones, medical equipment and other electronic products, they should be conductive and should be able to absorb or reflect electromagnetic waves. The most common means of shielding a plastic enclosure is to apply a conductive paint to its surface. The coating application requires surface preparation. The choice of surface preparation method depends upon the size, shape and chemistry of the plastic object. Most of the coating processes require bonding between the coating material and the plastic substrate to be coated. Some plastics are highly resistant to bonding (poor wetting) and need separate treatment to activate the surface. Commonly used treatment processes are flame treatment, electronic treatment such as discharge and plasma discharge, and chemical treatment.

On the activated plastic surface, the coating can be applied. Emulsion is the best choice because of its air-dry or low-bake capabilities. Commonly used waterborne coatings are derived by combining polyester polyacrylate or polyether polyols with hydrophilically modified polyisocyanate. Polyester polyurethane dispersions are used as soft-feel coatings for plastic parts of car passenger compartments. Waterborne polyester polyacrylate dispersions are generally suitable for primer and topcoats.

Sol-gel derived methyltrimethoxysilane (MTMOS) and colloidal silica coatings are applied on PMMA and bis-A polycarbonate substrates and exhibit appreciable abrasion resistance, as well as noticeable resistance to organic solvents, oils, dilute acids and bases. Anti-scratch coatings using metal or semi-metal oxide colloids such as alumina, zirconia, titania or silica, together with epoxy and methacrylate functionalized alkoxysilanes as major components, have also been developed. Growth in the use of waterborne coatings for automotive plastics and business machines is also expected.

13.12.4 Coatings on metals

Corrosion leads to the degradation of metal and its alloys. A generic approach of corrosion control is to use coatings. Waterborne coatings of comparable performance to solventborne coatings are available today. Waterborne coatings are suitable for both fresh application and maintenance painting of machinery, storage tanks and steel structures. However, two-component waterborne paints are generally superior to one-component paints in their resistance to mechanical wear and chemical attacks. Their resistance to corrosion and exterior weathering is comparable to that of similar solventborne coatings.

Sol-gel coatings may also provide good protection [4, 13] for various metal substrates, due to their ability to form a dense barrier against penetration of water and corrosion initiators. Organically modified silanes have been extensively studied for their application on aluminium alloys. Recently some studies have also been carried out to develop coating for magnesium alloy. Khramov *et al.* [18] developed a sol-gel coating for magnesium and its alloys using diethylphosphonatoethyltriethoxysilane and tetramethoxysilane. Due to the chemical interaction between the phosphonate groups and the surface of magnesium substrate, these specially designed organosilicate barrier coatings are expected to generate protective coatings with improved adhesion and corrosion resistance for magnesium materials. Various silane-modified organic coatings are in the development process. These sol-gel based coatings can be used as future materials to provide excellent corrosion resistance to magnesium and its alloys. Among the products from this industrial segment that are being coated with waterborne paints are containers, strapping, pipes, doors, structural steels and wires.

13.12.5 Coatings on floors and walls

Waterborne epoxy resin, polyurethane and polymethylmethacrylate based coatings are available today for floor coatings. Epoxy coatings contribute the largest share at 63%, followed by polyurethane coatings with 25%. Polyester polyols ensure good solvent resistance. Polyether polyols are used for excellent resistance to acids and alkali derivatives and to derivatives of acrylic and methacrylic acids for high weatherability. Polyurethane polyol floor coatings have widespread use due to their high flexibility, hardness and high chemical resistance.

Wall and masonry paints are used for decorative purposes and also to protect surfaces. Generally, masonry is exposed to wide fluctuations in temperature, sunlight and rain. It is, therefore, necessary that masonry paints must display certain elasticity, colour fastness and resistance to chalking and microcracking. Waterborne resins such as epoxy, polyurethane, polyacrylate or polyether yield very high-quality paints.

13.12.6 Coatings on automobiles

The car industry uses a multi-layered coating system, which is one of the most technologically complex coating processes. The most important

Table 13.9 Coating system for automotive refinish

Coating layer	Function
Cathodic dip primer	Protect against corrosion
Surfacer	Smooth out the substrate and protect against stone chips
Basecoat	Provide colour and any desired effects
Clearcoat	Protect against environmental influences

requirements of automotive coatings are colour, gloss, corrosion resistance and scratch resistance. Since the first commercial-scale application of waterborne basecoats in the automotive industry began in the mid-1980s, waterborne paint technology has been replacing the traditional solventborne coating technology. The typical coating structure for automotive refinishing comprises of the following functional layers: cathodic dip primer (EDP), a primer surfacer, a metallic basecoat and a clearcoat. The basecoat (metallic, solid colour) and the direct gloss topcoat are mostly polyester/polyurethane based, whereas the clearcoat is mostly acrylic based. Modern primer surfacers are predominantly based on polyester/melamine with blocked isocyanate. In some cases the basecoat and clearcoat are combined in a one-layer topcoat.

The functions of different coating layers in an automotive coating are given in Table 13.9. The surfacer functions as a sandable corrective layer to smooth out any surface irregularities in the underlying cathodic dip primer (EDP) as well as a protective barrier against UV radiation and damage from stone chipping. Waterborne polyurethane-polyester resins have excellent flexibility (stone-chip resistance) and hardness (sandability). Surfacers comprise blocked polyisocyanates and polyester polyols as co-reactants, self-crosslinking baking urethane resins for one-component polyurethane systems and polyesters for melamine-crosslinking systems. Waterborne one-component polyurethane surfacers include hydrophilized polyisocyanates and polyol dispersions, as well as self-crosslinking dispersions.

The basecoat provides the actual colour to the automobile. The essential requirements for this coat are good pigment wetting by the binder, weather stability and good long-term colour fastness. Polyester polyurethane dispersions are the most common resins used because of their good pigment wetting, flexibility and light fastness.

Clearcoats and topcoats interface with environmental stresses such as those from ultraviolet radiation, moisture and temperature extremes, surrounding chemicals and gasoline, scratching through car-washing equipment, etc. Today, two-component waterborne polyurethane polyol based coatings are increasingly replacing conventional thermosetting acrylic coatings.

13.12.7 Coatings on appliances

Most of the coatings used in these segments are applied by electrodeposition. For more than two decades, copiers, fax machines, typewriters, printers and computers have been painted with various combinations of waterborne emulsion and other coatings. However, waterborne coatings have been less accepted in market sectors where requirements are exceptionally high for appearance and engineering. In recent years, however, the automotive OEM sector has increased its use of water-based paints and coatings in all except the heaviest coat applications. An estimated 20% of this sector now uses water-based paints, and that percentage is growing year by year.

13.13 Conclusions

Today, various types of waterborne coatings equivalent to their solventborne counterparts are available and in many cases appear to be the preferred choice for modern paint coatings for several applications. The performance of waterborne coatings is comparable to, and in some cases even better than, that of the comparable solventborne coatings. Recent developments in this field are still in progress. Thus, it is a challenge before all scientists and chemists to develop binders and additives for waterborne coatings of excellent quality and performance at lower cost.

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Part III

Applications for high-performance organic coatings

14

Organic coatings for concrete and rebars in reinforced concrete structures

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14.1 Introduction

The word 'concrete' is derived from a Latin verb which literally means to grow together [1]. Correctly engineered and constructed, concrete is one of the strongest construction materials available, which will last longer. Basically a composite material, concrete is produced by mixing together Portland type cement, aggregates (coarser and finer) and water. Concrete by itself has high compressive strength, but has low strength when loaded in tension. Reinforced concrete uses steel to provide the much-needed tensile properties in structural concrete. Rebars are thus steel rods, embedded in concrete in such a manner that the composite material resists the load on the concrete. Reinforced concrete can thus be defined as concrete in which reinforcement bars or rebars have been incorporated to strengthen the concrete material that would otherwise be brittle. Initially employed for projects of modest scale, reinforced concrete is now one of the major structural materials available and its usage by mankind is second only to that of water.

Two conditions are essential for durability of reinforced concrete:

1. The concrete should be of high quality and should not undergo environmental degradation.
2. The reinforcing steel must not be allowed to corrode.

However, due to the varied environmental exposure conditions, concrete may undergo degradation and reinforcing steel may also corrode. If left unchecked, together they lead to loss of serviceability and integrity of the structure.

14.2 Deterioration of reinforced concrete

It is important to understand the mechanism of the deterioration of concrete and the corrosion of reinforcing steel within the concrete. Direct deterioration of concrete may be physical, structural or chemical. Physical deterioration may be due to the effects of freeze/thaw, fire damage, wave impact occurring in tidal zones, occurrence of extreme temperatures, moisture, etc. Chemicals attack by destroying the cement paste, thus weakening the concrete. Sulphate attacks, acid attack, the alkali–silica reaction within the concrete, and chemical attack by natural and industrial liquids are some examples. In many cases the resistance of concrete to these forms of attack is determined primarily by its penetrability. Structural degradation may be due to poor mix design, type of cement and aggregates used, impact and overload effects, etc.

Concrete in general provides protection to steel reinforcement for the following two reasons:

1. Concrete provides a highly alkaline environment to steel reinforcement which passivates the steel surface and hence prevents it from corrosion.
2. Concrete prevents the ingress of corrosion species like oxygen, chloride ions, carbon dioxide and water.

However, the deterioration of concrete as mentioned earlier may lead to loss of such protection as a result of loss of effective concrete cover. In addition, changes to the concrete environment itself may render it corrosive. Subsequent corrosion of steel produces corrosion products which have 2–4 times the volume of the original steel [2, 3]. This in turn generates stresses, causing cracking and spalling of the concrete.

14.3 Corrosion of steel reinforcement in concrete

The hydraulic binder in concrete, usually Portland cement, reacts with water to form a porous matrix of hydration products between the aggregate particles and around the reinforcement. Thus the reinforcing steel is usually in contact with moisture containing dissolved oxygen and the necessary reactants are present to permit corrosion. However, a significant feature of cement hydration is that the aqueous phase rapidly acquires a high pH. Furthermore, the material contains a substantial portion of reserve basicity in the form of sparingly soluble $Ca(OH)_2$ and the system is therefore buffered to resist downward pH changes at a value of 12.6 [2, 3].

When steel is in contact with an alkaline solution of pH values in this range, it is normally passive. A thin oxide film covers the surface, presenting a barrier to further metal dissolution. The protective oxide layers that develop are either Fe_2O_3 or Fe_3O_4, both of which are stable in concrete. The most stable layer in concrete is Fe_2O_3 written as γ-FeOOH, formed by the interaction of O_2 with $Fe(OH)_2$ [2]. When the local environment at the rebar/concrete interface cannot maintain the passive state of reinforcing steel, active corrosion in either uniform or localized form (pitting) will occur. Corrosion of the reinforcement, forming rust, leads to a loss of bond between the steel and the concrete and subsequent delamination and spalling [2].

14.4 The corrosion process

Corrosion of steel embedded in concrete is an electrochemical process [2, 3]. The surface of the corroding steel functions as a mixed electrode that is a composite of anodes and cathodes electrically connected through the body of the steel itself, upon which coupled anodic and cathodic reactions take place. Concrete pore water functions as an aqueous medium, i.e., a complex electrolyte. Therefore, a reinforcement corrosion cell is formed, as shown in Fig. 14.1.

Reactions at the anodes and cathodes are broadly referred to as 'half-cell reactions'. The 'anodic reaction' is the oxidation process, which results in dissolution or loss of metal, while the 'cathodic reaction' is the reduction process which results in reduction of dissolved oxygen forming hydroxyl ions.

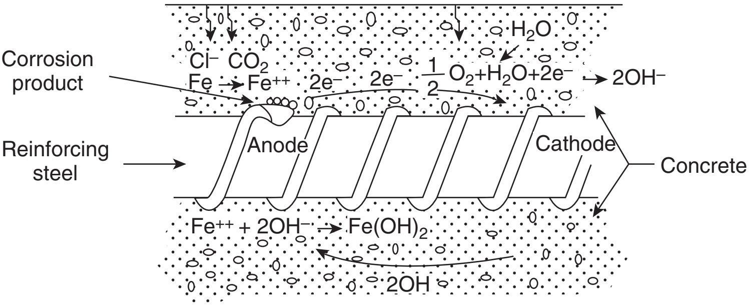
For steel embedded in concrete, the following are the possible anodic reactions depending on the pH of interstitial electrolyte, the presence of aggressive anions, and the existence of an appropriate electrochemical potential at the steel surface:

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 8H^+ + 8e^-$$

$$2Fe + 3H_2O \rightarrow Fe_2O_3 + 6H^+ + 6e^-$$

$$Fe + 2H_2O \rightarrow HFeO_2^- + 3H^+ + 2e^-$$

$$Fe \rightarrow Fe^{2+} + 2e^-$$



14.1 Schematic illustration of the corrosion of reinforcement steel in concrete as an electrochemical process.

The possible cathodic reactions depend on the availability of O_2 and on the pH in the vicinity of the steel surface. The most likely reactions are as follows:

$$2H_2O + O_2 + 4e^- \rightarrow 4OH^-$$

or

$$2H^+ + 2e^- \rightarrow H_2^-$$

14.5 Corrosion initiation and propagation mechanism

Corrosion initiation and propagation occur mainly due to the diffusion of Cl^-, CO_2, SO_2, O_2 and moisture through the reinforced concrete. The two major factors destroying the passivation of steels in concrete are:

1. Reduction in pH level by ingress of atmospheric carbon dioxide
2. Penetration of chloride from the environment [2, 3].

14.5.1 Carbonation/ingress of carbon dioxide

The pore solution has a very high concentration of hydroxide (high pH). [$Ca(OH)_2$] has a limited solubility which is markedly dependent on the OH^- concentration in the solution. Na and K, on the other hand, are more soluble and are almost completely dissolved in the concrete pore solution. As a result, very little [$Ca(OH)_2$] is dissolved in the concrete pore solution [2–4].

Carbonation of concrete results when atmospheric carbon dioxide (CO_2) dissolves in the cement pore solution to form carbonic acid (H_2CO_3):

$$CO_2 + H_2O \rightarrow H_2CO_3$$

This reacts with some of the products of cement hydration as well as neutralizing the calcium hydroxide [$Ca(OH)_2$] present:

$$H_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3 \cdot 2H_2O$$

As the reserve levels of $Ca(OH)_2$ are depleted, a zone of low pH (the carbonated zone) extends from the surface of the concrete. This fall in pH from 14.0 to about 8.0 renders the passive film unstable, since at this low pH, corrosion is initiated by destruction of the protective oxide layer (Fe_2O_3 or Fe_3O_4).

The secondary factors which influence the carbonation process are depth of reinforcement cover, moisture conditions, humidity, temperature, and the type and quantity of cement used. The carbonation process follows an equation $X = k \cdot t^{1/2}$, where X = penetration depth, t = exposure time and k is a constant which is dependent on the diffusivity of CO_2 through the concrete, the concentration difference and the quantity of bound CO_2 [4].

14.5.2 Chloride ion effect/ingress of chloride ions

Chloride may be present in concrete from different sources. The following are some of the sources:

- Aggregates containing chloride salines
- Mixing water
- Sea-coastal environment
- Road de-icing salts, etc.

The chloride ions attack the passive layer and catalyze the corrosion process. Chloride ions break down the passive layer and cause pitting of the steel reinforcement [2–4]. There are two processes which proceed simultaneously: a repair process of the disrupted protective oxide film by OH^- ions, and a breakdown process by chloride ions. The chloride ions achieve a critical concentration, dependent on the pH and pH concentration before it breaks down the passive Fe_2O_3 or Fe_3O_4 layer. In general, the chloride threshold is taken to be 0.15% of the soluble chloride by weight of cement [2–4].

The following are the major effects of chloride on the corrosion of reinforcing steel:

1. Chloride is absorbed in the protective oxide layer.
2. The oxidized iron reacts to form soluble intermediate iron complex at the anode:

$$Fe \rightarrow Fe^{2+} + 2e^-$$

$$Fe^{2+} + 4Cl^- \rightarrow (FeCl_4)^{-2}$$

3. The complex reacts with moisture to form $Fe(OH)_2$:

$$(FeCl_4)^{-2} + 2H_2O \rightarrow Fe(OH)_2 + 2H^+ + 4Cl^-$$

The pH is lowered and the concentration of chloride is increased. Once the chlorides are released on the metal surface, the process becomes self-generating and no further chloride ions are required. The repeated cycle of effects 2 and 3 continues until the protective layer of Fe_2O_3 or Fe_3O_4 is completely destroyed. One of the major forms of corrosion brought by the chloride ion is pitting of reinforcing steel. Pitting is an autocatalytic process which continues until a hole is created in the reinforcing concrete.

Besides carbonation and chloride ingress attack, the presence of oxygen, the different types of cement used, potential differences between two sites on the rebar surface, permeability of concrete, and the construction practices, all play a significant, vital role in initiation of corrosion in reinforced concrete [2–4].

14.6 Methods of corrosion control and protection

Despite the impressive progress made in controlling the corrosion of steel in concrete in the last 30 years, reinforcement corrosion in concrete structures is still a challenging problem. Important methods to mitigate reinforcement corrosion can be broadly categorized as:

- Modification of steel composition or use of a better alloy as reinforcement
- Use of admixtures
- Use of corrosion inhibitors
- Cathodic protection method
- Protective coatings: concrete coatings, rebar coatings.

14.7 Modification of steel composition

Mild steel bars conforming to IS:432 and cold-worked steel high-strength deformed bars conforming to IS:1786 (grade Fe 415 and grade Fe 500, where 415 and 500 indicate yield stresses of 415 N/mm^2 and 500 N/mm^2 respectively) are the commonly used reinforcements in concrete. However, the corrosion aspect of these steels drives the search for alternatives that will guarantee performance in every sense.

To keep pace with the rapidly changing needs and technological requirements of steels for the construction industries, continuous efforts have been made towards development of reinforcement bars (rebars) with higher strength levels and superior product attributes. Cost-effective steel, having its composition controlled to impart intrinsically improved corrosion resistance properties, reducing the rate of corrosion from the time of construction, and thus lengthening the life of the structure, is one such practical solution addressing the corrosion issue.

Thermomechanically treated steel known as TMT steel can be described as new-generation high-strength steel having superior properties such as weldability, strength, ductility and bendability and meeting the highest quality standards at international level. A tempered layer of martensite that is formed at the outer surface of the rebar protects it from mechanical damage, thus enhancing its corrosion properties indirectly.

Another development is the production of corrosion resistant steel, called CRS. Carbon content in this steel is restricted to 0.18%, manganese is absent, silicon is 0.45% and the percentage of corrosion resistant elements such as chromium is as high as 1.5%. Cu, Ni, Mo, Nb, B, Zr, W, Ti and P are the other alloying elements imparting the corrosion-resistant property to these steels [4].

Innovations and discoveries on this front are on a rise with a variety of modified steels available, which are far better in performance than the customary old black mild steel rebars.

14.8 Admixtures in concrete

Concrete admixtures are used to improve the behavior of concrete under a variety of conditions and are of two main types: chemical and mineral [5]. Chemical admixtures reduce the cost of construction, modify properties of hardened concrete, ensure quality of concrete during mixing/transporting/placing/curing, and overcome certain emergencies during concrete operations [5]. They fall into the categories of air entrainers, water reducers, set retarders, set accelerators, superplasticizers, and specialty admixtures which include corrosion inhibitors, shrinkage control, alkali–silica reactivity inhibitors, and coloring.

Mineral admixtures make mixtures more economical, reduce permeability, increase strength, and influence other concrete properties. Mineral admixtures affect the nature of the hardened concrete through hydraulic or pozzolanic activity [5]. Pozzolans are cementitious materials and include natural pozzolans (such as the volcanic ash used in Roman concrete), fly ash and silica fume. They can be used with Portland cement, or blended cement, either individually or in combination.

14.9 Corrosion inhibitors in concrete

The most practical and economical approach to minimize or eliminate the costly maintenance problem may well be to use better materials in new construction. This can be accomplished by adding corrosion inhibitors to a quality concrete mix.

Corrosion inhibitors can be divided into three types: anodic, cathodic and mixed, depending on whether they interfere with the corrosion preferentially at the anodic or cathodic sites or whether both are involved [3, 6]. In the class of anodic inhibitors, calcium nitrite, sodium nitrite, sodium benzoate and sodium chromate are commonly used. Cathodic inhibitors mainly consist of amines, phosphates, zincates, aniline and its chloroalkyl nitro-substituted form, and aminoethanol groups. Some work to create a protective barrier that stabilizes the layer of rust surrounding the steel; others

Table 14.1 Development of concrete reinforcement corrosion inhibitor technology and application methods [6]

Year	Type of inhibitor	Chemical composition	Application
1979	Anodic	Calcium nitrite	Admixture
1986	Mixed	Alkanolamines	Admixture
1990	Mixed	Water-based amine carboxylate	Surface applied
1990	Mixed	Water-based, organic (amines and esters)	Admixture
1993	Anodic	Calcium nitrite	Surface applied
1994	Anodic	Organic and inorganic	Admixture
1996	Mixed	Water based, organic	Surface applied
1997	Mixed	Amino alcohol admixture	Surface applied
1997	Anodic	Sodium monofluorophosphate	Surface applied
1998	Mixed	Ethanol amine	Pellets into predrilled holes

provide a thin protective coating that prevents chlorides from reacting with the steel. Yet others provide inhibitors that react with the iron to form a protective film or coating that either prevents chloride from reaching the steel, or reduces the corrosion of steel by acting as an oxygen barrier. Table 14.1 shows the development of concrete reinforcement corrosion inhibitor technology and application methods.

Calcium nitrite is the first corrosion inhibitor admixture commercialized on a large scale for reinforced concrete [6]. Calcium nitrite inhibits corrosion by reacting with ferrous ions to form a protective ferric oxide film. The inhibitive action of calcium nitrite depends on its reaction with Fe^{2+} ions according to the following reaction:

$$2Fe^{2+} + 2OH^- + 2NO_2^- \rightarrow 2NO\uparrow + Fe_2O_3 + H_2O$$

Calcium nitrite competes with the chloride ions for ferrous ions produced in concrete and incorporates them into a passive layer on the iron surface, thus preventing further corrosion. Long-term corrosion studies showed that in spite of the decrease in concrete resistivity, corrosion rates were significantly reduced.

Corrosion inhibitors can also be categorized on the basis of their addition at the time of construction as integral/cast-in type and those which are added to rehabilate or repair a corroding structure, i.e. the migrating type. Integral inhibitors are liquids or solids that are batched and mixed with the other concrete ingredients as a preventative measure for new construction or repair work. Migrating inhibitors are used in mature reinforced concrete structures that are showing signs of reinforcement corrosion or need additional protection to inhibit future corrosion [6]. They are applied to the surface as liquids or solid 'plugs', inserted in drilled holes, which migrate through the concrete to the reinforcement.

14.10 Cathodic protection

Cathodic protection is defined as the reduction or elimination by making the potential of the steel more negative, i.e. the potential of the metal is lowered from active corrosion potentials to immunity or passivity potentials [3]. In this way, all anodic or corroding areas of the metal are made cathodic, thereby stopping the corrosion process. When the cathodic protection system is energized, the O_2 reaching the steel surface is reduced to OH^- ions and the alkalinity generated restores the passive film on the metal. As a consequent of the current flow, Cl^- ions are removed from the steel surface, thus eliminating one of the main mechanisms of corrosion. Cathodic protection is achieved by generating a direct current flow from an anode through an electrolyte to the metal (which acts as a cathode), using an external d.c. current source (impressed current source) or connecting the steel to a Zn, Mg or Al anode (sacrificial anode system). The potential at which the corrosion rate becomes negligible is the 'protection potential' [3, 4]. The quality of concrete and the corrosive species dictate the protective potential required to stop corrosion of steel bars in concrete.

Cathodic protection of steel is considered effective when the steel potential is shifted into the range of $-85\ mV_{SCE}$ to $-105\ mV_{SCE}$ [3]. However, in the case of steel in concrete, the situation is more complex. A $-300\ mV_{SCE}$ shift in the negative direction from its original potential is a widely accepted criterion for cathodic protection. Another criterion is a 100 mV shift of the instant potential on switching off the current, which in many cases indicates complete cathodic protection [3]. The potential instantly measured in the 'off' position is called the 'depolarization potential', though the measurements may be adversely affected by high chloride contents [3].

Summing up, experience is the best guide in selecting the criteria for cathodic protection as it is strongly affected by quality of concrete, water saturation level, degree of contamination and waker to cement ratio.

14.11 Protective coatings

As the name indicates, protective coatings aim at protecting the substrate/material when applied in a thin continuous layer to that substrate/material. Protective coatings are a viable method for extending service life while providing improved appearance and additional value to concrete structures. Coatings protect concrete façades by providing a barrier between the concrete and the aggressive elements of its environment. These protective coatings protect a concrete structure by acting as either water barriers, carbon dioxide screens or chloride screens.

Concrete coatings may be either coatings directly applied to the concrete surface or coatings applied before casting on the rebar surface itself. The property of the coating material is decided according to the type of environment present. The criteria for coating selection are resistance from water ingress, resistance from chloride ions, CO_2 diffusion resistance, UV light resistance, elastic/crack bridging abilities, chemical resistance, abrasive resistance, ease of application and aesthetic appearance [4].

14.12 Concrete coatings

A major difference exists between a steel bar and the concrete surface and hence the requirements of coating specifications for both are also different [4]. Some of the important essentials for a concrete coating are:

- Elastic enough to withstand the dynamic loading in the case of bridges, etc.
- Impermeable to moisture and pollutants
- Aesthetics (important in the case of monuments and buildings)
- Suitable for use in the food chain (not toxic to animals or humans in any way).

Concrete coatings can be classified as follows, based upon their end use:

- Preservation – maintain original state and appearance
- Protection – crack bridging; mold, fungi and algae resistance; chloride and carbon dioxide permeability resistance; alkali resistance
- Decoration.

Coatings for concrete must have adequate innate adhesion characteristics and not depend on the so-called ‘porosity’ of concrete to ‘gain adhesion by penetration’ [7].

For concrete coatings a minimum of two coats, each coat having a dry film thickness (dft) of 100 μm, i.e. a total dry film thickness of 200 μm, is considered essential for an adequate period of longevity before the coating starts to disintegrate [7].

Some organic resin-bound coatings ‘dry’ or are hardened by means of a co-reactant, i.e. at least two ‘resins’ or components are mixed together prior to application. This co-reaction, like the reaction of inorganic cement with water, forms a 'glue' or coating with exothermic heat being produced in the chemical crosslinking action. Two-pack epoxy, polyurethane ('urethane' for short), polyester, 100% solids two-pack acrylic resin coatings and high-performance cementitious coatings all fall into this category [7].

Another very durable film-forming coating type suitable for hardened absorbent lime-bound cement renders is the silicate type. This type is available in colors and sometimes as a transparent clear coating. Silicate paints chemically bond to lime-bound rendered/applied mortar finished surfaces to result in excellent adhesion [7]. Although invented in 1895 in Germany, it is doubtful whether this type has yet been tested for pull-off tests on concrete substrates. Some types may even be quite suitable for concrete, particularly for uncured porous existing concrete.

Rubber has very high adhesive qualities and typically demonstrates high adhesion relative to other polymeric materials [7]. Suitable synthetic rubbers can be co-polymerized with acrylic monomers to manufacture acrylic–rubber co-polymer binding resins for concrete coatings.

Acrylic rubber co-polymer resins available to coatings manufacturers may be used to make excellent clear and colored single-pack coatings for concrete. These feature higher adhesion with similar or often superior durability and wear resistance compared with single-pack coatings bound with 'straight' (100%) acrylic or styrene–acrylic co-polymer resins.

All concrete coatings perform better when appropriately selected according to the specific requirements.

14.13 Galvanic coatings

Hot-dip galvanized rebar is simply bare steel that is coated with zinc. Hot-dip galvanizing produces a tough and adherent coating on steel which resists abrasion and fairly heavy handling, and which can be stored, handled and transported in much the same way as black steel [8].

Although zinc can be applied to steel by a number of commercial processes, each producing a characteristic range of thickness and coating structure, hot dipping should always be specified. Hot dipping involves the immersion of the steel bars in molten zinc at about 450°C and holding for a sufficient period to allow the development of a metallurgically bonded coating of zinc and zinc–iron alloys on the base steel [9]. According to AS/NZS 4680, the minimum specified coating thickness on steel products greater than 5 mm thick is 84 μm, equivalent to a coating mass of 600 g/m^2 per surface [9]. In routine processing, however, hot dipping results in coatings that are generally at least 100–120 μm thick [9].

Zinc is an amphoteric metal that reacts with both strong acidic and strong basic solutions, the attack being most severe below pH 6 and above pH 13. At intermediate pH ranges, the rate of attack on zinc is very slow due to the formation of protective surface layers. When embedded in concrete, zinc is passivated for pH values between about 8 and 12.5, again due to the formation of a protective surface film of corrosion product that is relatively insoluble below pH 12.5 [9]. While zinc reacts with wet cement, this reaction effectively ceases once the concrete has hardened and the barrier layer of calcium hydroxyzincate has formed.

The corrosion protection afforded by galvanized rebar in concrete is due to a combination of beneficial effects. Of primary importance is the substantially higher chloride threshold (2–4 times) for zinc coatings to start corroding compared to uncoated steel. In addition, zinc has a much greater pH passivation range than steel, making galvanized rebar resistant to the pH-lowering effects of carbonation as the concrete ages. Even when the zinc coating does start to corrode, its corrosion rate is considerably less than that of uncoated steel.

A number of minerals have been identified in the corrosion products, including zinc oxide and zinc hydroxide. A unique feature of these corrosion products is that they are friable (loose, rather than blocky) minerals and they migrate well away from the bar and into the adjacent concrete matrix where they fill voids and micro-cracks. As a result, these products cause very little disruption to the surrounding matrix and this helps to maintain the integrity of the concrete itself.

The rationale for the use of galvanized steel in concrete centers on the concept that the coating provides a safeguard against early or unexpected corrosion of the reinforcement. The coating itself should not be used as the primary or sole means of corrosion protection; rather it should be used in conjunction with an adequate cover of a dense impermeable concrete suited to the type of structure and the exposure conditions [9].

However, there is always a concern regarding the performance of galvanized coatings when they come into contact with a highly basic concrete environment, i.e. an environment with $pH > 13$ [10]. At about $pH = 13.3$, the zinc coating dissolves quickly in an active state with the evolution of hydrogen until the coating disappears totally [10]. In such cases, a minimal lower chloride content is sufficient to initiate corrosion. Above this pH value, the rate of corrosion of zinc seemed to increase approximately with increasing pH value and protection is ineffective in concrete containing higher chloride contents.

Thus, in cements with low alkali contents, protection against corrosion of galvanized coatings has been successful, but in cements with high alkali contents the performance results are unsatisfactory [10]. Thus, performance of galvanized rebars in concrete has mostly led to contradictory results in the literature.

14.14 Epoxy coatings

The organic material that has developed into that used most commonly as a protective coating for steel reinforcement is epoxy resin coatings. Epoxy resin is a thermosetting plastic that is resistant to solvents, chemicals and water. Research has shown that defect-free epoxy coatings resist the diffusion of chloride and oxygen, but are not impermeable to moisture [11]. They impart mechanical properties such as high ductility, low shrinkage during curing, and heat resistance, which make them desirable for use as a reinforcing steel coating. Most epoxies have a specific gravity of approximately 1.2 and withstand temperatures of 125°C [11].

Epoxy coatings for reinforcing steel (ECR) are generally prepared and applied by one of two methods: two-part liquid or powder.

14.14.1 Liquid epoxy coatings

Liquid epoxy is commonly prepared by mixing stoichiometrically balanced proportions of a two-part system, epoxy resin and polyamine [11]. The liquid epoxy is applied by brushing or spraying, or by immersing the bars to be coated. The former method is most appropriate for field dressing of observed damage on reinforcing bars prior to concrete placement. The liquid coatings commonly contain solvents that, upon evaporation, may result in pore formation within the cured coating. However, shrinkage due to solvent loss and curing is also a concern with the use of liquid epoxy coatings [11].

IPNet RB is a two-pack epoxy/phenolic-based interpenetrating polymer coating system (source: Krishna Conchem Products Pvt. Ltd, Mumbai, India). It is a novel type of polymer formulation consisting of more than two polymers crosslinked in a network form [12]. This interpenetrating coating system has high crosslinking density and low MTVR (moisture vapor transmission rates). Studies have shown that the performance of IPNet was poor in terms of bending, corrosion resistance and bond strength [13]. However, these properties were shown to improve on addition of polyvinyl butyral (PVB) [13]. PVB is an important member of the polyvinyl acetol family and its important coating properties are excellent adhesion to metals, film formation property, abrasion resistance, flexibility, resistance to water and other chemicals. The modified IPNet coating has shown good corrosion resistance under various surface pretreatments [13]. The modification has shown tremendous improvement in properties and has proved IPNet to be compatible with FBE coatings [13].

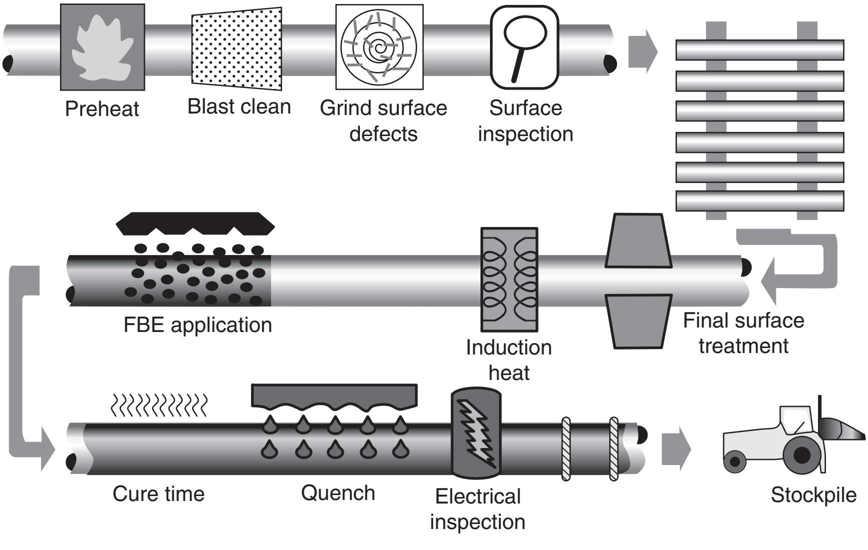
14.14.2 Fusion bonded epoxy coatings

The most commonly used fabrication method for ECR involves fusion bonding of epoxy. This is a process in which epoxy powder is applied by electrostatic spray on hot steel at a preset temperature level. The electrically charged powder particles are attracted to the preheated steel, and melt to form a continuous film, and then the system is quenched to form a solid coating (Fig. 14.2).

FBE coatings are ideally suited for protective coating on the complex surface configuration of a reinforcing steel bar. Electrostatic deposition combined with controlled melt and flow can attain uniform coating to any specifications. Rapid gel sets the coating quickly and, since they are plant-applied, the coating quality could be well maintained.

The epoxy coating cures through a combination of physical and chemical curing processes. The physical process involves the melting and sintering of powdered constituents at elevated temperature, to form a continuous film from the separate powder particles. As the powder particles melt and fuse, a reactive cure is also initiated, where a polymer network is formed from the poly-addition reaction between components in the thermosetting powder. Curing time, shrinkage and pore development within the coating are significantly reduced, since powder epoxy coatings do not require solvents.

As per ASTM A 775-81, the thickness of epoxy powder coating in order to fulfill flexibility, bonding and corrosion protection requirements should



14.2 Electrostatic coating process.

be between 130 μm and 300 μm [10]. Integrity of the coating is essential for effective corrosion protection. The film must therefore be free of pores, cracks and damaged areas.

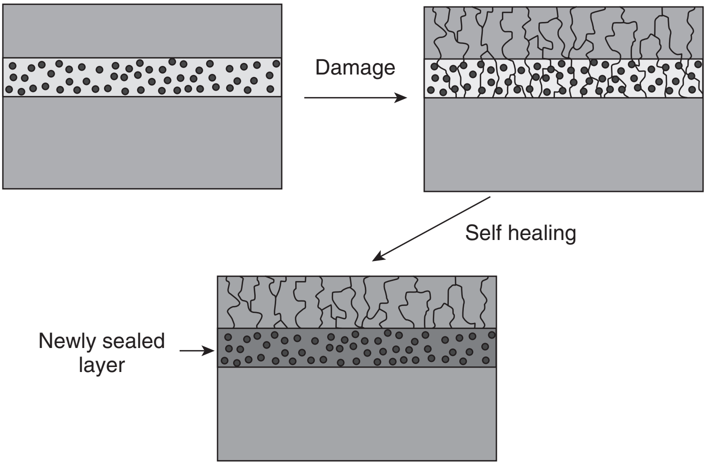
The use of epoxy coatings free of essential defects guarantees complete protection in carbonated concrete and significant reduction in rate of deterioration of reinforced concrete. However, studies have reported that epoxy coatings may have a finite tolerance limit for chlorides. Also, epoxy coatings lose their stability at temperatures of about 200°C [10]. The bond between epoxy and substrate may be affected by softening and melting of the coating. It has also been reported that epoxy coatings result in reduction in bond strength and increasing slip between reinforcing bars and concrete in comparison to uncoated rebars, with these effects increasing with increasing thickness [10].

14.15 Modified FBE coatings

One of the biggest limitations of FBE coatings is their susceptibility to mechanical damage during handling, transportation and storage and to the damage occurring when coated bars are intentionally bent (after being coated) to form a structure. Modified FBE coatings provide the solution. These are designed through the addition of microencapsulated materials, resulting in a self-healing FBE coating. The mechanical damage which weakens conventional coatings instead ruptures the microcapsules which in turn 'heal' the FBE coating, preserving its barrier properties [14]. Microencapsulation is a technique that encapsulates materials, such as oils, within a seamless, solid shell. A wide variety of shell wall materials are available – the appropriate choice is determined by a combination of the application, the material to be encapsulated, and the desired stimulus to rupture the capsule (e.g., impact, pH, or solution chemistry). In general, microcapsules are between 5 μm and 200 μm in size with wall thicknesses of the order of 1 to 2 μm [14]. Fill materials may be either aqueous or non-aqueous in nature. Once encapsulated, liquid-based fill materials behave as a solid, and as a result larger quantities of the fill material may be added to a coating system without adversely affecting its properties.

Thus, upon damage, unlike in a conventional FBE, the microcapsules are ruptured, releasing their protective chemistry (Fig. 14.3). As a result, the damaged FBE coating is healed, thereby significantly improving the performance of the coating in the damaged state as compared to conventional FBE materials [14].

Another modification of FBE, which has been carried out by DuPont and tested in our laboratory, is the use of Dual Fusion Bond Epoxy (DFBE). The DFBE consists of a two-coat system applied by a powder coating method. The primer layer consists of a FBE (~100 μm). This is followed by



14.3 Schematic illustrating the function of a single primer layer containing corrosion-preventative microencapsulated additions.

another layer of FBE with a different composition (mixed with silica). The primer layer has strong cathodic disbondment resistance while the outer layer is hard and rough. The latter helps to protect the coating from damage during handling and transportation and also in enhancing its bonding with the concrete, which when tested in our laboratory was found to be 125% compared to that of bare bar and 84% in the case of single-layer FBE. Unfortunately, there is still no practical experience to date [15].

14.16 Cement polymer composite coatings (CPCC)

The CPCC technology has been developed by CECRI, Karaikudi, India. It evolved and has been custom designed from consorted inputs originating from polymer science and electrochemistry (corrosion is an electrochemical reaction) to meet the structural engineering requirements of steel reinforcement rods. CPCC is a specially formulated indigenous technology only for reinforcement steel and pre-stressing steel and cables. CPCC is a two-coat polymer-based cement incorporating a coating system. The coating thickness required is around 150–175 μm and this coating can be applied by brushing, dipping or any other suitable method [16].

The flexibility of acrylate copolymer, its film-forming capability along with the water repellency characteristics of quinine-based polymers, are carefully tailored through the formation of a single phase in the polyblend which offers the necessary mechanical and physical properties in the coating. Besides, this precursor has the possibility of accepting rust as filler in the polyblend film, which facilitates the application of a surface coating derived from this polymer precursor or rusted steel surface, thus making surface preparation non-critical. Further, the cement polymer composite based on these polymers is expected to serve as a precursor for the formulation of a topcoat which will take care of the alkaline environment that is anticipated in the concrete structure. An additional feature of this system is that the curing time of the coating can be manipulated to suit the specific process requirement.

The highlight of this particular system is its tendency to keep the reinforcement steel in its natural passive environment and to maintain its natural pH. This is equivalent to the nature and environment of uncoated steel in concrete. The reason is the presence of cement blended with the polymer resin. Cement as an active filler serves dual purpose: it keeps the steel in its natural passive environment, which is necessary to prevent corrosion, and also it hydrates along with the curing of concrete and keeps the bond strength intact [16].

Even in the case of localized corrosion initiation due to damage or pinhole, the corrosion is not allowed to progress due to the presence of primer, which acts as a buffer and stabilizes the pH and arrests corrosion [16].

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Organic coatings for underground pipelines

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15.1 Introduction

Pipelines are the most economical, cheapest and safest mode of transportation for oil and gas. The world over, the use of pipelines is increasing day by day. Almost all developing and developed countries are increasing pipeline infrastructure at a rapid rate. This results in reducing transportation costs and ultimately benefiting the consumer.

Since pipelines are made of steel and buried underground, corrosion is bound to happen. It leads to leakages in pipelines and ultimately results in risk to nearby inhabitants, loss of product, discontinuity in production and environmental hazards. It costs a lot to engage pipeline operators in repairing leaks as well as presenting a bad image to society. Pipelines are buried in the ground for safety reasons. Corrosion on buried pipelines can only be eliminated or reduced to a greater extent by applying external and internal coatings. Since coating material can neither be ideal nor be applied perfectly over pipelines, there are always chances of external and internal corrosion. Internal corrosion can be reduced to a greater extent by reducing corroding elements from the product being transported. External corrosion on pipelines can be stopped by designing an effective and efficient cathodic protection system after proper application of coating.

15.2 History and importance of pipelines

During earlier periods of civilization, earthenware pipes, bamboo trunks and other hollow wooden trunks were used for transportation of liquids from one place to another. With the passage of time, people started using cast iron pipes for this purpose. Problems in welding cast iron pipes and large pressure drops during transportation of liquid for long distances ultimately resulted in the development of carbon steel pipelines, even though this material is more prone to corrosion compared to cast iron once buried into earth. Today the industry uses sophisticated controls and computer systems, advanced pipe materials and corrosion prevention techniques for building high quality pipelines.

Pipelines continue to play a major role in the petroleum industry, providing safe, reliable and economical transportation. As the need for energy increases and population growth continues away from supply centers, pipelines are needed to continue to bring energy to energy-deficit areas. The majority of the cross-country pipelines all over the world are used for transportation of hydrocarbon products which may be either liquid or gas. In some cases, pipelines are also used for transportation of solid material slurry like coal or iron. Throughout the world there is increasing use of cross-country pipelines. Transportation of crude oil and natural gas has broken the boundaries of the majority of countries. Energy-hungry countries have to import petroleum products for their energy security. Pipelines are able to transfer various products in the most difficult terrain in the easiest manner. Nowadays, petroleum product pipelines are known as the energy arteries of any country. The development of any country is directly proportional to the length of pipelines in that country.

In India, the first underground cross-country pipeline was laid in 1956 in the north-east, and even now the total cross-country pipelines amount to no more than 25 000 km in length. However, India is going to add another 25 000 km of pipelines within the next five years and 50 000 km in the next 10 years to transport gas, crude oil and other petroleum products to energy-starved locations. Having had a huge gas find on the east coast border and especially in the Krishna Godavari Basin, the majority of the pipelines being added will be natural gas pipelines.

Moreover, city gas distribution is gaining momentum the world over to avoid pollution in major cities. Internationally, all union, federal and state governments are giving due importance to providing a pollution-free environment to future generations. Although the majority of the city gas pipeline network consists of HDPE or MDPE pipelines, the underground cross-country pipelines are required as feeding lines.

15.3 Pipelines and corrosion

The most suitable construction material for pipe is carbon steel, which is not only strong but has well-defined performance specifications. However, the shortcoming of steel is that it corrodes when exposed to certain environments. Very little was known about corrosion control when the first cross-country pipeline was built with the best available technology. It is interesting to note that all structural materials have a strong tendency to revert to their original native state. This is because of the tremendous amount of energy used to convert them from their original form to the one enabled by manufacture. This input energy remains latent in the material and is released at every opportunity as the material reverts to a state of equilibrium with nature. In this modern society everyone is affected by corrosion, which is nothing but release of energy. Control of this process is the greatest challenge to corrosion engineers.

Corrosion is an undesired attack on metals. For example, when iron is dipped into water, it usually dissolves, but the rate at which it dissolves varies, depending on a number of external factors. Almost all corrosion takes place in aqueous solutions that can conduct electrical currents, so-called electrolytes. Corrosion cells are formed on pipelines due to the different environments available along pipelines. For corrosion cell formation, the following four conditions are necessary:

- There must be an anode and a cathode.
- There must be potential between anode and cathode.
- There must be a metallic path between anode and cathode.
- An electrolyte must be present.

The anode and cathode on pipelines are formed due to differences in aeration, soil resistivity or dissimilar material all along the pipeline. The pipeline itself works as a conductor between anode and cathode. The pipeline is surrounded by moist soil or water, which itself works as an electrolyte. This shows that all four components are there to function on the pipeline, which ultimately results in corrosion on pipelines.

15.4 The need for pipeline coatings

Pipelines which are generally made of high silicon steel start deteriorating with time in their environment due to corrosion cell formation, so it is essential to provide a barrier between the pipe and its environment to reduce this deterioration. The barrier should be such that it effectively reduces the deterioration rate in order to achieve the designed life of the operating system. This barrier is nothing but a coating on pipelines. In today's economy, it is not only essential to protect pipelines against corrosion but it is good business to do so. As a whole, the cost of repairing a leak can run to a huge amount, which includes the cost of repairing, product cost and damage to others. The tremendous economic loss arising from corrosion of buried pipe illustrates the importance of the problem which confronts manufacturers of protective coatings for pipelines. A coating is completely effective as a means of stopping corrosion if:

- the coating material is an effective electrical insulator;
- it can be applied with no break whatsoever and will remain so during the backfilling process;
- it constitutes an initially perfect film which will remain so with time.

For internal pipeline coating, controlling the surface preparation and application is more difficult compared to coating on the external surfaces. Corrosion allowance for internal corrosion is frequently used to provide additional metal for corrosion loss. Corrosion and scale inhibitors as well as biocides cannot be relied upon to be more than 90% effective; therefore, to allow for small amounts of corrosion, additional metal is added to the pipe wall thickness. The corrosion allowance should anticipate the maximum metal loss over the life of the pipeline. The cost of laying pipelines in India is more than a half million US dollars per kilometer of pipeline. Looking at the cost involved, it is essential to get the processes right, as the pipeline is the backbone for ensuring smooth transportation which ultimately leads to production. Along with the need to sustain current infrastructure, operators face a greater challenge than ever because of high corrosion failures and costly maintenance challenges. Moreover, governments are pushing forward sanctions on exploding pipes, which damage the local environment, making regulations more stringent than before.

15.5 Types of coatings for pipelines

Applying coatings on pipelines to prevent external corrosion has been practiced since the nineteenth century when coal-tar, bitumen and wax were used. These systems turned out to be unsatisfactory and the development of coatings has since changed dramatically to include liquid epoxies, liquid polyurethanes, fusion bonded epoxy and polyolefins. The continual development in pipeline coatings and the selection of these coatings has changed. An ideal coating will stop pipeline corrosion. The minimum requirement is that a coating should stop corrosion for the design life of the pipeline, but a more realistic objective is that the coating should stop corrosion as long as the pipeline remains in service. Most pipelines are operated well beyond their original design life. The cost of a pipeline should be looked at as a cost per year for the lifetime of the pipeline. This can be divided into two types of costs:

- Initial cost
- Maintenance cost.

The longer the effective life of the pipe, the less important is the initial cost and the more important is the maintenance cost. If corrosion control will lengthen the life of a pipeline besides keeping the maintenance costs down, it can be considered as the long-term insurance to the initial investment. For operating pipelines, the key coating issues can be resolved by considering the following aspects:

- Coating performance
- Impact on monitoring and maintenance costs
- Coating degradation to the point at which it is no longer sustainable.

Initially, pipelines were coated by coal-tar or asphalt coatings which were field applied. Slowly, as the technology improved, polyethylene and coal-tar tapes were field applied. For some time, extruded polyethylene was used as an external coating in Europe. Presently for major cross-country pipelines, coatings are applied in the plant after proper surface cleaning. There are large numbers of coatings which are being used for underground cross-country pipelines for corrosion protection. These coatings can be categorized as follows:

1. Coal-tar based coatings:
    - Conventional coal-tar enamel coating
    - Bitumen based epoxy paints
    - Plasticized coal-tar coating
    - Coal-tar coating with concrete as outer layer for offshore application
2. Polyethylene/PVC based coatings:
    - Extruded polyethylene coating
    - Sintered polyethylene coating
    - Heat-shrinkable PE tapes
    - Cold applied PE/PVC tapes
3. Fusion bonded epoxy powder coatings:
    - Single-layer FBE coating
    - Dual-layer FBE coating
4. Polyolefin coatings:
    - Three-layer PE/PP coating with FBE as inner layer
    - Three-layer PE/PP coating with concrete coating as outer layer
5. Asphalt enamel coatings:
    - Asphalt enamel with fiberglass reinforcement.

For cross-country pipelines, generally the following types of coatings are used, which are discussed in this chapter:

- Coal-tar enamel (CTE) coating
- Single-layer fusion bond epoxy (FBE) coating
- Dual-layer FBE coating
- Three-layer polyethylene or polypropylene coating.

15.6 Characteristics of good coatings

The importance of coating did not reach its full significance until the mid-1990s when carbon steel, because of economics, was being demanded by industry for longer life and to serve under more severe loading and pressure conditions. The coatings that could be used had to achieve the desired goals and to be compatible with the operating conditions imposed upon the pipeline itself. Coatings are effective in preventing pipeline deterioration from corrosion if they possess the following qualities:

- Water resistance
- High dielectric strength
- Chemical resistance
- Proper adhesion
- Abrasion resistance
- Ability to expand and contract
- Weather resistance
- Resistance to dirt pick-up
- Resistance to bacteria and fungi
- Pleasing appearance
- Age resistance
- Easy application
- Compatible with cathodic protection
- Environmentally friendly.

15.7 Selection of coatings

An ideal coating should stop pipeline corrosion. The minimum requirement is that a coating should stop corrosion for the design life of the pipeline. Inevitably, coatings get damaged by external forces or by a number of long-term degradation processes that affect the constituents of the coating. Typically this results in coating defects that expose the pipe steel to the environment around the pipeline and this corrosion risk can be controlled by cathodic protection. Many coatings also show a loss of adhesion as water or soil penetrates between the pipe and the coating. Ideally this failure mode should not create new corrosion threats to the pipeline but in many cases it does. Pipeline operators should learn from the experience of others. One can select the coating system and application conditions that will guarantee a long and low-maintenance life for the pipeline. The proper use of protective coatings is the extremely effective means of preventing pipeline deterioration and corrosion leaks. The function of a coating is to act as a barrier that prevents either chemical compounds or corrosion current from contacting a pipe substrate. The effectiveness of a coating for fulfilling this function depends on its degree of integrity, its ability to bond to the pipe substrate, and its ability to insulate against the passage of corrosion current.

The importance of specifying and using a proper coating system for hydrocarbon pipeline projects cannot be overemphasized. While initial expenditures for properly engineered, high performance coating systems may seem high, this investment pays off in considerably reduced long-term maintenance and operating costs and also provides peace of mind in protecting the environment as well as the health and safety of workers. In order to meet various requirements, a corrosion protective coating system should be able to meet the following three challenges:

- Environmental and safety regulations
- The economics of each project
- High performance.

Engineers must strike a balance among these three areas in refurbishing or designing a new pipeline. The ideal corrosion protective coating system should be environmentally friendly, work safe, durable and able to stop exposure of the metal surface to the environment, while also being resistant to environmental, mechanical and chemical damage from the initial stage of handling and installation to its entire service life. It should also come at a reasonable cost. Many times coatings are selected for reasons that do not take into account all the possible failure modes and the resulting consequences when they do fail. All coatings will and do fail. All coatings have openings, pinholes, micro-fissures and other methods of allowing water, oxygen and other corrosion-causing compounds to migrate through at different rates. FBE, for example, allows some water to penetrate; it maintains its insulating properties in the presence of moisture and cathodic protection current. Operating temperature is always a critical factor in choosing a proper coating system. Many coatings are affected by the operating temperature of the pipeline. Higher or lower than specified temperatures can cause coatings to deteriorate, crack, lose adhesion or gravity flow of the coating on the pipe. Higher and lower temperature coatings have been developed. The higher the operating temperature the more rapidly water will penetrate.

There are many other parameters that affect the performance of a pipeline coating, but these are some of the more critical ones. One must consider all the factors for each particular exposure and service when choosing a coating type. The selected coating system must have good impact resistance at ambient temperatures to withstand handling damage during transportation from the site and physical abuse during construction. For buried pipelines, the coating must also have good creep resistance and mechanical strength at the maximum operating temperatures. These properties are required to withstand the considerable soil stress arising initially from ground settlement and subsequently from expansion and contraction of the pipe in service. The coating must also remain well adhered to the steel over the full range of operating temperatures and applied cathodic protection potentials.

Correct selection of the coating material for a particular pipeline is equally important. The following factors should be taken into consideration when selecting a coating for a pipeline:

- Operating temperature of pipeline
- Type of environment in which pipeline will be buried
- Soil resistivity
- Geographical and physical location
- Nature of product to be transported
- Extent of pipe line handling
- Surface preparation requirements
- Physical performance requirements
- Ease of repairing coating defects
- Cost economics
- Backfill material requirements
- Experience with similar material in equal environments
- Interference on pipeline
- Size of pipeline.

15.8 Coal-tar coatings

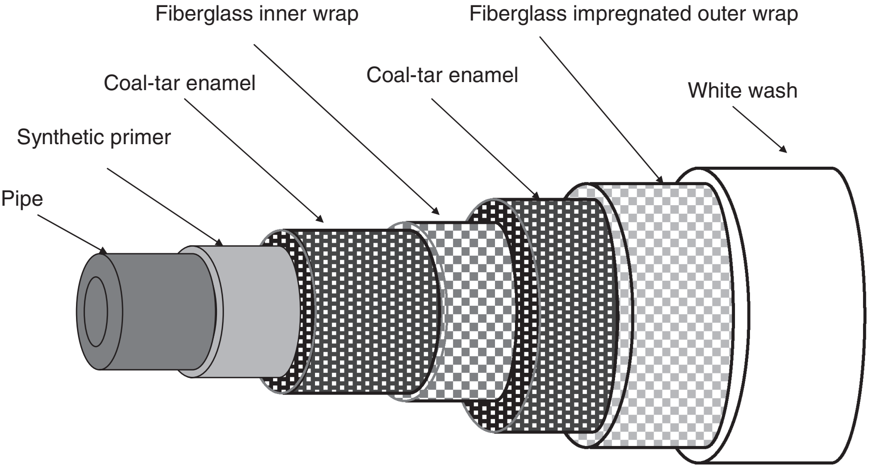
It is understood that coal-tar coating was first used around 100 years ago as an outer surface coating for underground pipelines. Later on, many improvements were carried out to reduce the brittleness of coal-tar at low temperature. The original material used for protection of pipelines was known as straight run pitch enamel where inert mineral filler was added to coal-tar pitch. These pipeline coatings have performed satisfactorily and were used in large quantities. Plasticized enamels were also developed to avoid coating damage during transportation for laying cross-country pipelines. This was achieved by blending coal-tar oils and pulverized coal with coal-tar pitch and inert mineral filler and cooking in a digester. All this resulted in coal-tar molecules with a plastic-like structure. Incorporation of reinforced glass inner wraps and asbestos felt, later replaced by glass fiber outer wraps, resulted in much increased coating strength and correspondingly an enhanced protection against impact and soil stresses. Coal-tar enamel coatings have been used during last 100 years on millions of miles of steel pipelines all over the world. Nowadays, additional glass fiber inner wrap reinforcement is used, making the total number of reinforcements to three including the outer wrap. This has resulted in an increase in coating thickness to around 6 mm against 3 to 4 mm thickness earlier. This has improved the mechanical strength of the coating. Coal-tar mastics have found a particular niche for offshore use under concrete weight coating.

All buried pipelines that were laid in the early 1950s in India were either bare or coal-tar coated. Coal-tar coating was applied over the ditch. This was a crude method of applying the coating, as the surface of the coating could not be prepared to the required level in aggressive site conditions. It was also difficult to maintain a clean environment, which is required during application of the coating. Moreover, the life of field-applied coal-tar coatings is much shorter due to poor quality application, necessitating frequent rehabilitation. Although the coating is quite thick, large numbers of holidays are left on the pipeline which ultimately leads to high cathodic protection current requirement and hence a large number of CP stations. This all results in a high cost of corrosion protection for coal-tar coated pipelines.

Considering the difficulties faced in over-the-ditch applied coating, pipeline companies later moved to factory-applied coal-tar enamel coating, with many improvements in coating materials and application techniques. This ultimately led to improvement in coating life. But fast deterioration in coating material certainly leads to early rehabilitation and a high level of cathodic protection current requirement. All pipelines up to the mid-1980s were coated with coal-tar with improved specifications and varying coating thicknesses. Major oil companies in India were using coal-tar coating for their buried pipelines as a measure of external corrosion control. The oldest cross-country crude oil pipeline in north-east India is still operating in excellent condition even after completion of more than 40 years' service in use.

Coal-tar enamels, because of their relatively low strength compared with synthetic polymers, are applied at greater thickness, from 2 mm to 6 mm typically on large diameter pipes. They are thermoplastic and tend to flow under stress. Even the harder grades may creep slightly in a matter of years under high soil stresses, and the softest grade of coal-tar pipeline coatings provide stability and added resistance to externally applied stresses. These reinforcements have added advantages, assisting in the application of uniform coatings and providing increased impact resistance to the external protection. Almost all coal-tar systems include an outer reinforcement and it is usual to incorporate inner reinforcement except in the thinnest coatings. Two inner reinforcements approximately 2 mm apart are sometimes incorporated in the thickest coatings. Inner reinforcements most commonly consist of a continuous sheet of randomly arranged glass fiber threads for application under tension. A diagram of coal-tar enamel coating is shown as Fig. 15.1.

Coal-tar enamels remain the first choice for external coatings on steel pipes for their good adhesion to less than perfect surfaces, their resistance to the ill effects of moisture and all types of biological agencies, and their resistance to cathodic disbonding. On the other hand, their mechanical properties compare unfavorably with those of various modern polymeric products. Thermoplastic materials, including polymers and coal-tar, are ductile and resilient within a limited temperature range, but below this range, which varies from material to material, they are brittle, and above it they are soft and tend to flow. Coal-tar products achieved an early popularity for anti-corrosion in water and wet conditions. Their latest success



15.1 Coal-tar coating.

on steel pipelines depended on two major developments. A large reduction of the temperature coefficient of viscosity was achieved by making a colloidal dispersion of selected coals in the coal-tar components. The use of outer as well as inner fabric reinforcement was introduced, not only to prevent this flow, but also to increase the resistance to impact during transportation and to protect against the ingress of stones from the backfill soil. In some other technological fields, modern long-chain polymers and selected rubbers, natural and synthetic, have been incorporated into coal-tar products in order to achieve superior mechanical properties. The chief gains are an improvement in balance of strength and ductility and the imparting of elasticity. This means that when deformation occurs under stress, energy is stored in the polymer-modified coal-tar, and when that stress is removed, even a long time after application, there is a recovery from the deformation. In such an application, the selected polymer must meet the requirements of compatibility and of thermal stability at the application temperature, as well as having no adverse effect on the desirable characteristics of the unmodified coal-tar.

15.8.1 Advantages of coal-tar coatings

Coal-tar enamel coatings have a number of advantages compared to other coatings. Some of these are as follows:

- Comparatively simple to apply
- Cheaper than other coatings
- Non-hygroscopic

- Easy to repair
- Resistant to soil chemicals, bacteria, root growths and marine organisms
- No cathodic shielding
- Insoluble in hydrocarbons
- Low cathodic disbondment
- Long experience (track record).

15.8.2 Limitations of coal-tar coatings

Since no coating is perfect, coal-tar enamel coatings also have limitations. Some of these are as follows:

- Comparatively poor mechanical strength
- Higher cathodic protection current requirement
- Increased cost of cathodic protection
- Require early rehabilitation of coating
- Health hazard for persons on the job
- Air-polluting fumes during coating application or rehabilitation.

15.8.3 Coal-tar coating application

Hot coal-tar enamel is poured over a rotating pipe that has been previously grit blasted and primer coated with coal-tar enamel primer. A fiberglass inner wrap, which becomes saturated with liquefied enamel, is immediately pulled over the coating. A second layer of coal-tar enamel is then applied. A second fiberglass or mineral felt outer wrap, already impregnated with coal-tar, is applied over the first wrap. Liquid coal-tar enamel spreads through the wrap seams. The glass fiber gives the coal-tar enamel system additional shear strength, providing resistance to soil stress, protection against rock damage during backfilling and improved resistance to sag at elevated temperatures. The coating is then finished with either one coat of whitewash or a single wrap of paper to prevent ultraviolet degradation of the enamel during storage in direct sunlight. Coal-tar base coatings require less surface preparation compared to other coatings. The following sequence is generally followed during coating application in the plant:

1. The pipe is heated to eliminate humidity.
2. The surface is shot-blasted to remove scale and rust.
3. Primer is applied to improve adhesion.
4. The pipe external surface is wrapped in fiberglass embedded in bitumen or coal-tar by a dipping or pouring process.
5. Whitewash is applied for protection from ultraviolet radiation.

15.8.4 Health and environmental issues

The volatile components of coal-tar are known to be toxic when ingested, absorbed through the skin or inhaled. However, when appropriate coating operation procedures and safe handling practices are followed, ingestion of coal-tar enamel can be reduced. Coal tar pitch is said to be carcinogenic. It irritates the eyes on contact and causes brown staining in the eye on prolonged exposure, and it also irritates the nose and throat. Coal-tar pitch is on the hazardous substances list because it is regulated by OSHA. It has been shown to cause skin, lung and bladder cancers. In application, coal-tar has to be applied hot at high temperature at which it produces noxious and air-polluting fumes as well as leading to the possibility of severe burns to personnel involved in the operation. Due to the health hazards of coal-tar, its use in coating is slowly reducing in developed and developing counties. The fundamental environmental issues for coatings are:

- Environmental acceptance in general
- Environmental friendliness of manufacturing process
- Environmental acceptance of application process
- Long-term effects on environment
- Whether it can be recycled or not.

15.9 Single-layer fusion bonded epoxy coatings

Fusion bonded epoxy (FBE) coatings were introduced around 50 years ago. Among external coatings for steel pipelines, thermoplastic varieties had been satisfactorily used with success for many years in a wide range of conditions. However, the conditions reached a stage where coatings with better performance as well as meeting increased environmental conditions were required. In addition to its versatility in all aspects of corrosion resistance, the high temperature usability of FBE without failure is its main advantage.

Fusion bonded epoxy coating, also known as fusion bonded epoxy powder coating, is an epoxy based powder coating that is widely used to protect various sizes of steel pipes used in pipeline construction. FBE coatings are thermoset polymer coatings. The name ‘fusion bonded epoxy’ is derived from the means of resin crosslinking and method of application which is different from that of a conventional liquid paint. FBE coatings are in the form of dry powder at normal atmospheric temperatures. The resin and hardener parts in the dry powder remain unreacted in normal storage conditions. At typical coating application temperatures, usually in the range of 180–250°C, the contents of the powder melt and transform into a liquid form. The liquid FBE film wets and flows on to the steel surface, on which it is applied, and soon becomes a solid coating by chemical crosslinking, assisted by heat. This process is known as fusion bonding. The chemical crosslinking reaction taking place in this case is 'irreversible', which means that once the curing takes place the coating cannot be converted back into its original form by any means. Application of further heating does not melt the coating and thus it is known as a thermoset coating.

Fusion bonded epoxies are available as standalone coatings as well as part of multi-layers. FBE coatings with different chemical and physical properties are available to suit application on the main body of the pipes, on internal surfaces, on girth welds and on fittings. Similarly, variations are also available to match different ranges of pipeline service conditions. All the important and essential properties expected from a versatile and high performance pipeline coating system are possessed by FBE systems. Some are as follows:

- Ease of application
- Good adhesion to pipe
- Good resistance to impact
- Flexibility
- Resistance to soil stress
- Resistance to flow
- Water resistance
- Electrical resistance
- Chemical and physical stability
- Resistance to soil bacteria
- Resistance to marine organisms
- Resistance to cathodic disbondment.

Fusion bonded epoxy powder coatings have high flexibility and outstanding impact resistance, excellent adhesion and resistance to abrasion. They are resistant to heat and cold and possess extremely low oxygen permeation and hence provide extreme resistance to corrosion. The high temperature performance, chemical resistance, resistance to soil stress and excellent resistance to cathodic disbondment in comparison to traditional coatings has resulted in the increased use of fusion bonded epoxy. FBE coatings have become more attractive due to several advances both in the application process and in the raw material. FBE coatings provide a more controllable application process and a product whose quality can be assured prior to laying of the pipeline.

FBE coatings have very effective electrical insulation when originally installed and continue to provide effective insulation even as the coating begins to absorb water. FBE continues to have low cathodic protection current requirements even after many years of installation if it remains well bonded, but definitely more than three-layer polyethylene. Even if blistering and small areas of disbondment occur, the current requirement increases marginally. However, the electrical resistance is low enough to allow cathodic protection to prevent corrosion on the pipe with disbonded or blistering coating. FBE is non-shielding. The amount of oxygen available at the cathodic area will control the rate of the corrosion process under disbonded coatings. FBE has an advantage over many other coatings because it is a good barrier to oxygen. FBE is a fail-safe coating and experience has shown that if adequate cathodic protection is available and no shielding is present, corrosion is minimal. Another interesting advantage of FBE is that when FBE fails these areas can be found more easily with direct current voltage gradient (DCVG) surveys.

15.9.1 Advantages of fusion bonded epoxy coatings

A single-layer FBE coating has been very common in North American countries for many decades, due to their well-developed infrastructure and the low cost of this type of coating compared to other coatings. Some of the main advantages of this coating are:

- Resistance to biological attack
- Better overall corrosion resistance at low and high ambient temperatures
- Excellent oxygen barrier
- Superior adhesion and hence excellent corrosion resistance
- Excellent chemical properties
- Non-shielding of cathodic protection current
- Impact damage limited to point of contact
- Easy repair in coating plant and at site
- Can be used up to high service temperature
- Excellent flexibility
- Excellent resistance to soil stresses
- Easy repair in coating plant and at site
- FBE is considered to be a ‘fail safe’ coating
- Compatible field weld coating system
- No stress corrosion cracking (SCC) problem
- Cheaper than three-layer polyethylene/polypropylene coating.

15.9.2 Limitations of fusion bonded epoxy coatings

As with other coatings, a single-layer FBE coating also has limitations:

- Susceptible to damage during handling, transportation and pipeline construction
- Sensitive to steel surface preparation and condition

- High moisture absorption and permeation, especially at higher temperatures
- Affected by UV during storage
- Hydroscopic material leading to increased cathodic protection demand as pipeline ages
- Limited impact resistance.

15.9.3 Method of application

Application of coating to the pipe is as important as the material itself. The application process for fusion bonded epoxy coatings can be summarized as follows:

- Cleaning
- Heating
- Coating
- Curing
- Inspecting.

Cleaning is by far the most important step in the application of any coating, since the performance of the coating is directly related to the surface preparation. Blast cleaning is carried out to a near white surface finish, to Swedish Standard SA 2½, with a nominal 40–70 micron anchor pattern. This is usually accomplished using one or more blasting machines with steel grit as the cleaning medium. After cleaning, the interior of the pipe is blown free of all residual grit and other contaminants. The next step in the process is to uniformly heat the pipe to a temperature in the range of 200–250°C or as per the recommendations of the coating powder supplier using a non-contaminating heat source. Three heating methods are used, i.e. electrical induction, gas-fired forced air and a combination of high velocity direct flame impingement. After the pipe has been heated to the required temperature, it passes through a powder coating machine where the fusion bonded epoxy coating is uniformly applied at a thickness of 350–500 microns or as per client requirement using electrostatic deposition. After application, the coating is allowed to cure using the residual heat in the pipe. During the curing process, the coated pipe should be carefully handled to avoid damage to the coating. After the coating has been cured, the pipe can be force-cooled with air or water to facilitate inspection and handling. Coated pipe is electrically inspected using conventional search electrodes operating at 5 volts per micron of coating thickness. Small imperfections in the coating are repaired using hot melt patch sticks or two-part ambient temperature curing liquid epoxy resins. FBE coatings are suitable for underground offshore and onshore pipelines. For offshore applications, in deep water laying, it is necessary to apply a weight coating of concrete to ensure that the pipe remains on the sea bed. The epoxy coating process includes:

- Pre-abrasive cleaning
- Abrasive cleaning of pipe
- Acid wash and chromating
- Pipe heating to required temperature
- FBE coating application
- Cooling of pipe
- Testing of coating.

15.10 Dual-layer FBE coatings

The single-layer FBE system has been found to be excellent except for the fear about damaging the coating during handling of the pipeline in difficult terrain. Many coating material suppliers have attempted to improve the coating to give better performance, and eventually they came up with the idea of a dual-layer FBE coating consisting of:

- An FBE primary corrosion coating
- An FBE abrasive-resistant outer coating.

The inner primary corrosion layer is generally of coating thickness around 250 microns and the outer layer has a coating thickness of 250 to 400 microns. The properties of the inner layer are the same as those of single-layer FBE, while the properties of the outer layer FBE are changed to accommodate high impact resistance. The higher coating thickness also improves the cathodic disbondment properties.

This unique dual-layer fusion bonded epoxy system is applied as a powder base coat and powder top coat simultaneously with the typical application system for the conventional FBE. This coating is recommended for pipelines operating in the toughest environments, including river and road crossings and rocky, mountainous terrain. It has excellent impact resistance and abrasion properties which, combined with its good flexibility, provide good protection against possible damage to the coating during pipe transportation and pipeline construction.

Modified fusion bonded epoxy coatings used offshore include dual powder coatings or multiple layer FBE coatings. Dual powder coatings are used to improve the gouge resistance and toughness of FBE during direction boring. A rough coat is frequently used to improve friction between the FBE and a cement weight coating. Rough coats also improve traction for barge laying operations and improve safety. Thicker dual powder coatings can also enhance high temperature performance. The dual powder coating system can be used at operating temperatures of 110°C or higher.

15.2 Dual-layer FBE coating.

The system was principally developed for road/river crossings and HDD applications where resistance to abrasion and gouging are considered important. It consists of:

- A primary layer of thermosetting epoxy resin powder as the corrosion barrier applied by electrostatic charge to a preheated pipe
- A secondary layer of abrasion and impact resistant epoxy resin powder to provide mechanical protection.

A diagram of a dual-layer FBE coating is shown as Fig. 15.2.

15.10.1 Advantages of dual FBE coatings

Dual FBE has all the benefits of FBE, with the following additional advantages:

- High operating temperature capabilities
- Excellent abrasion and impact resistance
- Improved handling characteristics
- Fully bendable to 1.5°/pipe O.D.
- Improved service temperature up to 110°C
- Excellent corrosion resistance
- Does not shield cathodic protection
- Excellent adhesion to steel and extremely resistant to soil stresses
- High UV resistance
- No SCC problems observed so far
- Improved cathodic disbondment.

15.10.2 Limitations of dual FBE coatings

In addition to a number of advantages, dual-layer FBE has the following limitations:

- Poor flexibility at higher coating thicknesses
- More expensive than most other coating systems
- Hydroscopic material leading to increased cathodic protection demand as pipeline ages.

15.10.3 Coating application

Dual-layer FBE is applied almost in the same fashion as single-layer FBE. After proper surface cleaning to SA 2½, FBE is applied through electrostatic spray application in a booth where the first few guns spray the FBE base coat and the rest of the guns spray FBE simultaneously during the melt stage of the first layer. This results in an intimate chemical bond between the two layers. A significant advantage of multilayer FBE technology is that unique characteristics can be developed by selecting specific properties for each coating layer. Each layer is designed to impart specific characteristics that synergistically combine to produce performance results that significantly exceed those of a single coating.

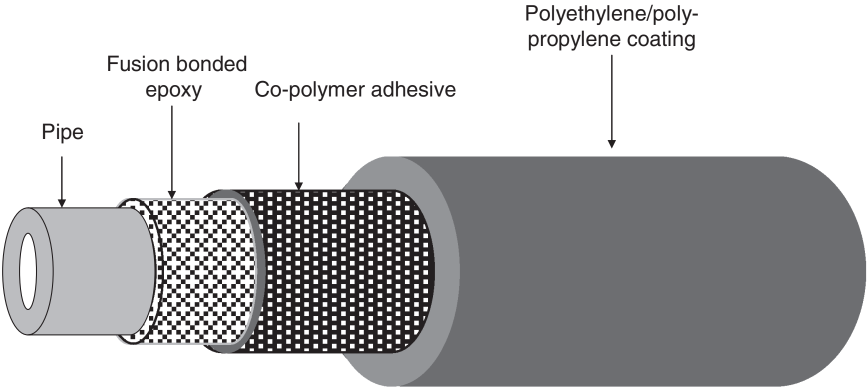
15.11 Three-layer polyethylene/polypropylene coatings

The three-layer polyolefin system offers corrosion protection with an epoxy primer layer, which is usually a thin layer, and mechanical protection through a polyolefin top coat. Since unmodified polyolefins do not adhere to FBE, an adhesive middle layer is also used, making it a three-layer system. The polyolefin coating can be either polyethylene or polypropylene as top coat. Three-layer coatings have been used both offshore and onshore for the last 40 years. Special multilayer systems are available according to requirements. These include systems with high glass transition temperatures, with modified polypropylene for high temperature operation, and with increased polyolefin thickness for directional drilling. Three-layer polyethylene coating systems consist of the following:

- First layer: FBE primer
- Second layer: adhesive primer (tie layer)
- Third layer: polyethylene/polypropylene.

A diagram of a three-layer polyethylene/polypropylene coating is shown as Fig. 15.3.

A three-layer PE mainline coating consists of an FBE primer layer 75–150 microns thick, an intermediate olefin copolymer adhesive of around 250 microns, and a polyethylene outer layer of approximately 2500 microns. These are all applied in-shop. The FBE represents the foundation for the system, providing a primary base, which when applied properly, adheres well to the steel substrate. This is essential, because polyethylenes are non-polar and do not readily bond to steel. The benefit of FBE as a primary layer is its low oxygen permeation rate compared with polyethylene. The middle layer serves as a bridge between the low-surface-energy polyolefin and the FBE base layer. Middle layer adhesives are typically acid copolymers or polyethylene modified with polar end groups grafted on to the



15.3 Three-layer PE/PP coating.

polymer backbone. The polar groups in turn react with and chemically bond to the FBE. The polyolefin adhesive is also compatible with and fuses with the unmodified polyolefin topcoat. The top layer of the structure is the polyolefin, which provides a high degree of damage tolerance or impact resistance because of its thickness. In addition, polyethylene exhibits low moisture permeability. For polyethylene (PE), as density increases so does permeability resistance. With both polyethylene and polypropylene (PP) increasing thickness improves permeability resistance. This trait is particularly useful at elevated operating temperatures. Polypropylene, with its high softening point, is especially suited for high-temperature pipeline applications. Epoxy primer is the true anti-corrosion member, often measured by the cathodic disbondment resistance test. Cathodic disbondment is a function of:

- Type of epoxy or FBE powder grade
- Thickness of film
- Application temperature as defined by the supplier and controlled by the applicator
- Steel surface anchor pattern
- Pre-treatment used to ensure cleanliness.

FBE is the best material component for oxygen barrier properties. Keeping both oxygen and moisture away from the steel surface, a three-layer PE/PP coating will impede any corrosion over time. Thus the synergistic effect of all three components plays a role in the performance of the final coating. The exterior multilayer high density polyethylene coating is a passive anti-corrosion system for new pipelines typically designed for greater than 30 years of service life for transporting oil or gas. Material components play a role and each has a purpose here which, when combined, offer a synergistic approach to corrosion protection. Polyethylene is one of the best moisture barrier resins and the best UV-resistant plastic material. Copolymer adhesive is the tie layer between the PE top coat and epoxy primer components. It must be fully compatible with these components so as to chemically bond to the epoxy groups prior to crosslinking and to melt blend with the PE topcoat while still molten. The adhesion level must be greater than any soil stress or handling stress associated with the coating system environment. The failure mode can be either 'adhesive' or 'cohesive' but failure should never occur between the steel and the epoxy primer.

Based on the experience gained during the last 40 years, there is a shift in industry to using high density polyethylene from low density polyethylene for the following reasons:

- It has high penetration, abrasion and impact resistance.
- There is less moisture permeation, which offers better disbondment resistance.
- It results in using less top coat thickness.
- Pipelines can be easily operated at high temperature.
- There is less damage and hence less repair cost.

In the changing scenario of the present time, pipeline owners are giving more emphasis to value-added coatings, low maintenance and low installation cost of pipelines, and demanding high performance that will ultimately result in a long design life and a short payback period. This has led to the use of powder material for adhesive systems and high density polyethylene top coat systems coupled with improved epoxy powder with higher thickness. More emphasis is given to better adhesion, improved cathodic disbondment, better water immersion values and higher service temperature.

15.11.1 Benefits of three-layer PE/PP coatings

Compared to other coatings, three-layer polyethylene/polypropylene coatings have a number of advantages and some are enumerated below:

- Excellent barrier to oxygen
- Superior adhesion
- Excellent chemical properties
- Moisture barrier
- Superior mechanical and thermal properties
- High dielectric resistance
- Good chemical resistance
- UV resistance

- Minimum damage during transportation and handling
- Excellent low temperature flexibility and impact resistance
- Excellent corrosion resistance.

15.11.2 Limitations of three-layer PE/PP coatings

Three-layer PE/PP coatings also have some limitations. Some are as given below:

- Shielding of cathodic protection current in case of coating disbondment
- No fail-safe coating
- Prone to thinning across raised weld seams
- High cost compared to other coatings
- Repair is costly and difficult
- Sensitive to steel surface preparation and operating condition
- Difficult to have meaningful quality test.

15.11.3 Application of three-layer PE/PP coatings

The steel surface condition is one of the most critical areas of the coating, having most influence on adhesion and cathodic disbondment resistance values. The steel surface should first be blast cleaned to a near white metal surface with anchor profile of 50–75 microns. Pre-treatment is the preferred option, but it must be applied immediately before primary heating. The aqueous solution is evenly applied on the steel surface, which must be dry before the FBE powder is applied. The advantages of chromate treatment are well known. The beneficial effect becomes especially evident during high temperature wet tests, such as the hot water soak and elevated temperature cathodic disbondment test.

Epoxy powders used for single-layer FBE differ substantially when employed as primers for three-layer PE/PP coatings. The chemical and physical properties, as well as the powder ingredients themselves, are suited to provide a desired combination of application temperature, gel time and cure time. The powder application temperature and the distance to next unit operation, combined with line speed, become the most critical factors in producing a high quality three-layer PE/PP coating.

The thickness of the primer coating is normally 75 microns but many specifications are now recommending a thickness from 100 to 250 microns to enhance the adhesion and cathodic disbondment properties. The purpose of the adhesive is to provide an intermediate layer between the epoxy primer and the polyethylene outer coating. The adhesive has a number of polar groups which bond chemically to epoxy, provided that the epoxy is not fully cured yet. At the same time, the adhesive layer provides a strong bond to the polyethylene outer layer due to the chemical affinity of adhesive and polyethylene.

Application of the adhesive must follow FBE primer very closely to optimize the chemical bond between the primer and the adhesive. The time lapse between the two should never exceed 15 seconds. There are several different kinds of polyolefin which can be used as an outer coat for three-layer PE/PP coating. Historically the oldest and still commonly used is low density polyethylene, followed by medium and high density polyethylene. Polypropylene can be used for applications in excess of 100°C. Polyethylene is extruded on to the pipe in a co-extrusion die, together with the polymeric adhesive. Co-extrusion offers the largest degree of adhesion between the intermediate and outer layers, as it virtually squeezes both layers together in a molten state, causing them to adhere under high pressure and high temperature. At the same time, it does not allow air to penetrate between the adhesive and polyethylene layers, which sometimes occur in non-extrusion processes. A polyolefin rough coat or rough finish consisting of polyolefin powder applied during shop application has also been used to improve the friction between the polyolefin outer coating and the cement weight coating. The three-layer PE/PP system provides extremely effective defense against the hazards of transportation and installation, the stresses of temperature change, and action by water, organic acids, alkalis and bacteria, as well as galvanic action. The chemical bonding between the layers provides very high peel strength adhesion. Three-layer PE/PP coatings are thick coatings, which not only provide the anti-corrosion properties of the FBE that is the first layer (primer), but also provide mechanical protection due to the thick layer of either polyethylene or polypropylene. A three-layer polyethylene coating is rated for low temperature services, whereas three-layer polypropylene coatings are rated for services up to 120°C.

15.12 Surface preparation and its importance in coating

The performance of the coating can be improved by proper surface cleaning of line pipe. Coal-tar epoxy (CTE) coatings require less sophisticated surface cleaning, while FBE and three-layer PE/PP require thorough surface preparation. For CTE coating, the following procedure is adopted:

1. The pipe is heated to eliminate humidity.
2. The surface is shot-blasted to remove scale and rust.
3. Primer is applied to improve adhesion.
4. The coal-tar enamel is applied.

In the case of FBE coating, dual-layer FBE coating and three-layer PE/PP coating, the first layer is always FBE, so surface preparations are more or less the same for all three coatings. In coating application generally, the following steps are performed:

1. Surface cleaning preparation
2. Abrasive cleaning
3. Final cleaning and inspection
4. Acid wash and chromate treatment of pipe
5. Preheating of pipe
6. FBE coating application and cooling for standalone FBE coated pipe
7. Application of adhesive and outer layer of polyethylene or polypropylene
8. Final inspection.

15.12.1 Surface cleaning preparation

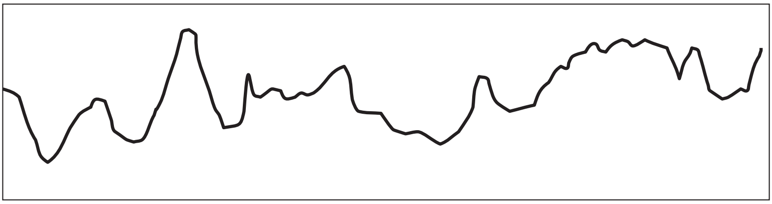
Pre-abrasive cleaning preparation includes removal of surface contamination and elimination of mill scale. Pipes are often contaminated with salt, soil, grease and mill scale. All these need to be removed before the first abrasive cleaning operation, otherwise there could be excessive contamination of the abrasive medium. Salts and soil can be removed effectively with fresh water at high pressure, and organic contaminants by application of hydrocarbon solvent. To remove moisture, it is necessary to preheat the pipe in the temperature range 60–80°C. Electrical induction heating is a good method of preheating.

15.12.2 Abrasive cleaning

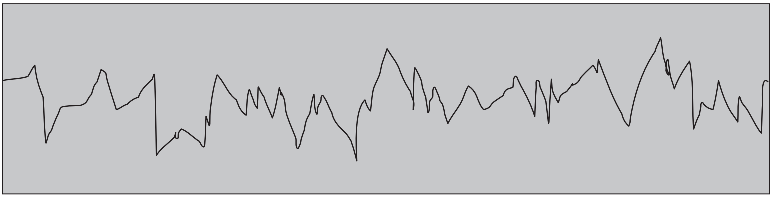
Abrasive cleaning helps in obtaining a surface profile of 50 to 100 microns. The surface cleanliness should meet a minimum of near white surface as per SSPC and NACE standards, which can be achieved by centrifugal-type blast cleaning equipment using steel shot and steel grit as the abrasive media. The use of various sizes of abrasive shot and grit will depend upon the steel grade used for making the pipe. To obtain an adequate cleanliness and anchor pattern, a second abrasive cleaning process is preferred.

15.12.3 Final cleaning and inspection

Final cleanliness of the pipe should be checked occasionally by tightly pressing the surface with adhesive tape, and then examining the tape underside for dirt particles. The specification for pipe coating requires a near white metal blast quality. This is essential to achieve the required anchor pattern. The profile should be angular with no undercuts that can result from overblasting. The profile can be measured by Elcometer Surface



15.4 Round and dished surface profile.



15.5 Angular, dense surface profile.

Profile Gauge. Diagrams showing Round and Dished as well as Angular and Dense surface profiles are shown as Figs. 15.4 and 15.5 respectively.

15.12.4 Acid wash and chromate treatment of pipe

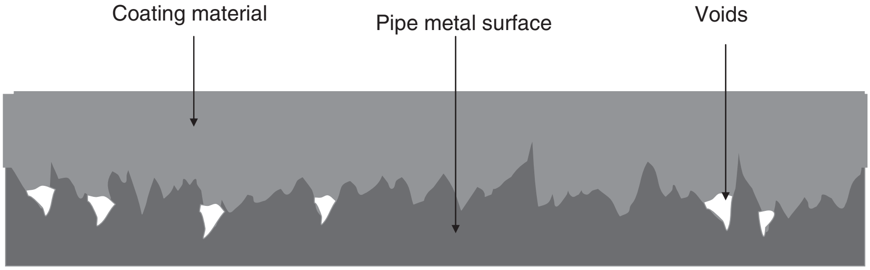
Line pipe surface treatment is required for superior coating adhesion. Pipe can be washed with weak phosphoric acid solution in water and further with only treated water having hardness less than 200 ppm. This treatment becomes essential in case an uncoated pipe has been undergoing corrosion in the presence of chloride or sulfate ions.

15.12.5 Preheating of pipe

For successful application of coating on pipe, the steel temperature required is based on a particular pipe size, line speed, and coating specifications. The metal temperature should not exceed 275°C, as this may cause metallurgical or surface defects. The heating source can be gas-fired radiant heat or electrical induction. For best results, a uniform metal temperature should be maintained. Tempsticks or infra-red pyrometers can be utilized for this purpose. A diagram showing the effect of low temperature on coating flow is shown as Fig. 15.6.

15.12.6 FBE coating application and cooling for standalone FBE

The powder application is performed by electrostatic spraying. Spray guns should be properly set up. Sufficient time should be given before quenching



15.6 Improper coating application: effect of low temperature on coating flow.

the pipe with water in order to achieve a film with optimum resistance properties. This minimum requirement depends on the preheating temperature, the pipe size and the steel mass.

15.12.7 Application of adhesive and outer layer of polyethylene/polypropylene

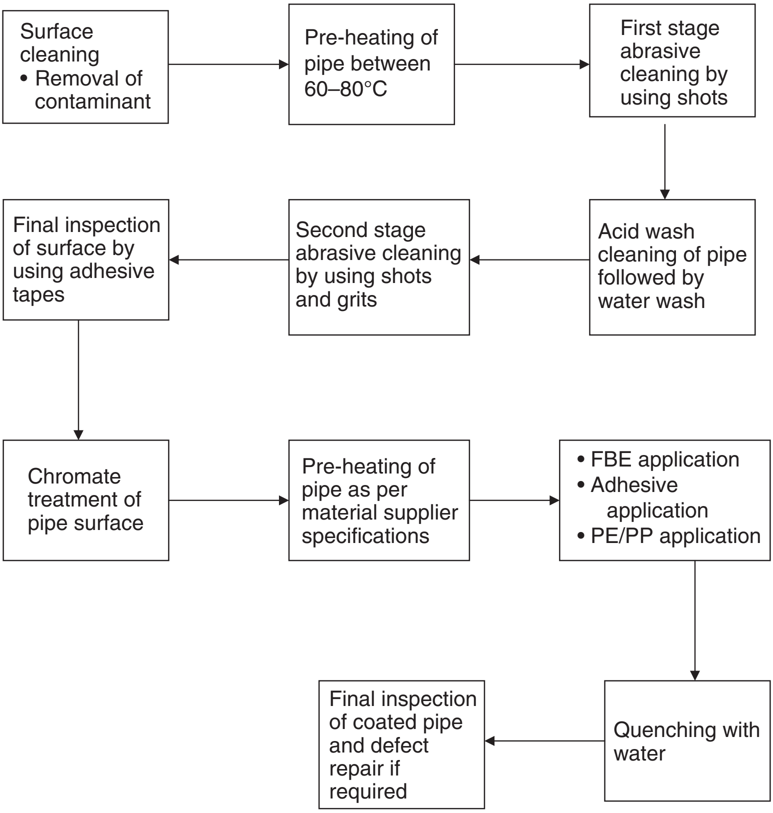
To obtain better peel strength, it is preferable to apply the adhesive before the epoxy coat gels. This is required for giving sufficient reaction time between the chemical groups on the epoxy and the adhesive. If the adhesive is applied too late, the peel strength will be very low and the peel will reveal a smooth coat of epoxy with failure between the adhesive and epoxy. In case of extruded adhesive, the epoxy needs to have achieved a level of mobility to support the extruded film without skidding. The outer layer of polyethylene or polypropylene is generally applied by side extrusion, crosshead extrusion or according to client requirements.

15.12.8 Cooling of three-layer coated pipe

Cooling of the pipe should only be carried out after complete curing of the coating has taken place. This helps in getting optimum resistance properties. This minimum time requirement depends on the preheating temperature, the pipe size, the steel mass and the three-layer system specification. The specification of the three-layer film affects the cooling phase, since the insulation properties of the outer layers will enable the epoxy to continue the curing process after the water quenching has started.

15.12.9 Final inspection

For achieving best quality coating, a thorough inspection and coordination is required. Inspection should be considered as a means of process control rather than of acceptance or rejection. If each processing stage was done



15.7 Surface preparation and coating sequence.

correctly, a high quality coating will be only a natural consequence. A regular quality control test to be carried out during application includes film thickness check, holiday detection, the peel test and cure test. The curing of the epoxy layer is usually assessed on a section of the pipe coated without the adhesive layer. The peel test is important in assessing the cure and the intercoat adhesion. Failure during the peel test should be within the adhesive film, leaving some adhesive attached to the epoxy and some attached to the outer coat, which is known as cohesive failure. A block diagram showing the various steps involved in applying coatings to pipelines is shown in Fig. 15.7.

15.13 Comparison of various coatings

As seen in earlier sections, no coating is perfect. Every coating has some favorable characteristics and some inherent limitations. A comparison of

Table 15.1 Comparison of coating coal-tar, FBE and three-layer PE/PP coatings

Property	CTE	FBE	Dual FBE	Three-layer PE/PP
Electrical resistance	Good	Good	Good	Excellent
Water absorption with time	Low	High	High	Low
Maintenance of dielectric strength with time	Poor	Fair	Fair	Excellent
Adhesion	Poor	Good in dry, poor in wet environments	Good in dry, poor in wet environments	Excellent
Water absorption	Very low	High	High	Very low
Impact resistance	Good	Good	Excellent	Excellent
Type of damage	Large	Pinpoint	Pinpoint	Pinpoint or splitting
Abrasion resistance	Poor	Good	Excellent	Excellent
Cathodic disbondment	Low	Very low	Very low	Very low
Chemical degradation	High	Low	Low	Low
Retention of physical characteristics	Poor, degrades	Good but absorbs water	Good but absorbs water	Excellent, but PE may disbond
Field joints system	Easy and cheap	Difficult and costly	Difficult and costly	Difficult and costly
Integrity of joints	Good	Good	Good	Good
Repair system	Easy	Easy	Easy	Difficult
Integrity of repair	Good	Good	Good	Good
Testing	Easy	Easy	Difficult	Difficult

different coating materials with respect to the required properties is given in Table 15.1.

While FBE coatings have good corrosion and water resistance, oxygen barrier properties, comparable cheap cost and compatibility with CP system, they have limitations of handling on site, soft backfill material requirements and lack of suitability for directional drill pipes. Similarly, three-layer polyethylene coatings have excellent physical and corrosion properties but limitations in terms of temperature use, CP shielding and problems related to quality tests, as well as high cost. Coal-tar coatings are cheap and absorb less moisture but have less impact resistance.

15.14 Coatings and cathodic protection

Corrosion protection with the help of coatings is known as a passive method of corrosion protection. Although coatings are extremely successful as a corrosion protection system for underground pipelines, there are some inherent limitations in each coating that make it difficult to provide total corrosion protection. To overcome this problem, a supplementary system, which is known as an active protection system, i.e. cathodic protection, is used along with the coating system. The best way to prevent pipeline corrosion is by a combination of coating and cathodic protection.

The ideal pipeline coating may well be perceived quite differently by different agencies or persons depending upon one's point of view. A perfect pipeline coating system can be defined as the system which economically meets the pipeline corrosion protection requirement. Cathodic protection is an integral part of any pipeline corrosion protection system. However, corrosion engineers often look at cathodic protection and coatings as separate responsibilities. It is essential that both disciplines are done in concert. A well-designed cathodic protection system in conjunction with the appropriate coating system ensures leak-free pipeline operation in the most economical fashion. Desirable characteristics of coatings with respect to cathodic protection are:

- Effective high quality insulator
- Effective moisture barrier
- Good adhesion to pipe surface receiving cathodic protection
- Ability to resist development of holidays
- Ability to maintain substantially constant electrical resistivity with time.

By applying a high quality coating to a cathodically protected structure, the required cathodic protection current density is substantially reduced. The advantages of a high quality coating can be summarized as follows:

- Low required current density
- Low power consumption
- Low wear of anodes
- Larger spacing between CP stations and hence less CP cost
- Interference problems minimized.

The concept of shielding of cathodic protection by coating is a controversial topic. If dielectrically strong coating disbonds from the pipe and electrolyte enters this area, the cathodic protection current may be shielded from reaching any active corrosion cell. This can be avoided by proper coating selection and design. Cathodic protection for underground pipelines is normally designed for 20 to 30 years. The cathodic protection current design requirement depends on the type of coating used over the pipeline and the precautions taken during the laying of the pipeline to avoid holidays in the coating.

15.15 Coating failures

A number of coating failures on underground cross-country pipelines have been reported from many countries, that are neither area-specific nor coating-specific. Coating failures have occurred in the USA, UK, Middle East, Iran, India, Pakistan, etc. The main causes of coating failures have been inadequate specifications, poorly prepared substrates, incorrect application, use of unqualified personnel and bad construction practice. Good quality of pipeline coating can be achieved by:

- Proper surface preparation
- Adequate coating specifications
- Total control of coating application in plant
- Pre-qualification of all coating materials and coating processes
- Production of a meaningful quality and inspection, testing plans
- Independent, trained and knowledgeable coating inspectors
- Coating specifications inline with CP requirements.

15.16 Future trends

Although the present coating systems are able to reduce corrosion to a large extent on buried pipelines, each system has its own limitations. These limitations need to be eliminated by making improvements in each coating system. An extremely promising field is open to those coating manufacturers who can accept these challenges. The following are the areas that need further improvement in coatings for underground pipelines:

- Shielding of cathodic protection current on three-layer polyethylene/polypropylene coatings
- Disbondment of three-layer PE/PP coatings within a short span of time
- Improvements in SCC prone coating
- Coatings for high temperature use
- High thickness coatings and suitability to bend
- Effectiveness of coating with less prepared surface
- Substituting for non-environmentally friendly coatings
- Standardization of coating standards.

15.17 Coating standards

There are many standards for coal-tar, FBE and three-layer polyolefin coatings for underground pipelines. Proper surface preparation is important in pipeline coating applications. There are also many standards related to surface preparation of line pipes. Universally accepted coating standards and surface preparation standards are as given below:

- NACE Standards
- ISO Standards
- Canadian Standards
- American Standards
- European Standards
- AWWA Standards
- Indian Standards
- Australian Standards
- British Standards
- German Standards

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16

Organic coatings for marine and shipping applications

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16.1 Introduction

Since the maritime environment is strongly aggressive, coatings needed to protect steel can be classified as 'heavy duty coatings'. In most maritime applications because of maintenance difficulties a long service life is generally required. This, together with safety and environmental issues, demands high requisites in performance and reliability.

On top of performance and reliability requirements for long-term protection, there are often also conflicting interests between the desire of a ship owner or operator for a well-built, long-lasting structure with minimal operating cost (long-term financial interest) and the short delivery time or shipyard's production line. Depending on the ship building market demand at the time of contract, the owner may have to accept a compromise against his better technical judgement and operating know-how. The extra cost for the desired system may be exorbitant, seen from the owner's or operator's point of view, and the standard guarantee for a ship is only one year from delivery, so the yard will rarely face a claim for coating failure if the coating application is reasonably well done. While this may recoup some financial gain in terms of the time-to-delivery of a new structure, there might be a more significant negative impact to the owner or operator in terms of cost of early and on-going maintenance and repairs over the lifetime of the structure. The relative costs of coating systems are minor compared to replacement of steel during operational life. However, costs for staging and steel preparation needed to apply those coatings rise swiftly with increasing surface area. Correct selection of coating materials and their specification at the design stage may yield financial benefits in the longer term.

Although there are coatings available on the market that perform satisfactorily, and provide long-term protection against corrosion, their reliability is dependent on a strict control of the application, type and thickness of the coating as well as operating conditions. Furthermore, the past 10 to 15 years have shown significant changes in the coating industry. Because of the awareness for the consequences for human health and for the environment, nowadays many regulations and restrictions have been decreed concerning the application, content and removal (waste) of coatings. Many traditional anticorrosive coatings are now no longer acceptable due to their potentially toxic and carcinogenic nature, e.g. red lead, coal-tar pitch, and more. In addition, requirements to reduce emissions to the atmosphere of potential ozone-depleting materials have resulted in a reduction in volatile organic content (VOC) of paints and coatings. Novel coatings should also keep their properties and flexibility during harsh sea conditions and elevated temperatures at which ships may operate.

This chapter will deal with the types of coatings and degradation mechanisms as well as mitigation of degradation of coatings in marine environments and shipping applications in particular.

16.2 Types of application

16.2.1 Introduction

From the point of view of coating properties and requirements the most important application area for marine coatings is shipping. Protection of the ship against corrosion is mainly a matter of safety and reliability. Optimal performance of protective measures is essential and may involve maintenance operations and high costs.

A number of parts with totally different operating conditions and requirements are typical for the shipping application area. In the case of the hull, deck and ballast tanks seawater corrosion has to be taken into account. For other parts such as drinking water, sewage and fuel tanks together with the corrosion protection coatings have to be compatible with the load. The underwater part of the hull requires even more attention because of the natural process of marine growth. This 'fouling' has to be completely avoided, because it reduces the speed, in other words increases the fuel consumption, and hinders the manoeuvrability of the ship. Moreover it can influence and even damage the anticorrosion measures such as the coatings and the cathodic protection. To combat fouling, a so-called antifouling coating as top layer above the anticorrosive coating is required. For anticorrosion coatings for shipping normally a lifetime of 15 years is expected, in which period inspections and maintenance are foreseen. Antifouling coatings have a short lifetime, up to a few years depending on the type of application and sea-going practice.

An overview of typical coating systems currently used in different critical areas of ship painting is presented in Table 16.1 [1–3]. Please note that in Table 16.1 coating systems designed for the underwater hull area are not incorporated. The specific aspects of the main marine degradation

Table 16.1 Examples of typical anti-corrosive paint systems currently used in different critical areas of ship painting [1–3]

Critical areas in ship painting	Main requirements	Typical paint systems
Hull and superstructures	Anticorrosive protection in seawater Compatibility with cathodic protection UV resistance Washability Compatibility with antifouling (top)coat	Pure or modified epoxy primer/ epoxy topcoat Aliphatic polyurethane Aliphatic polyurethane/acrylic Polysiloxane/epoxy hybrid (anti-rust stain topcoat may be applied)
Decks	Appearance Anticorrosive protection UV resistance Non-slip	Zinc silicate followed by two-pack epoxy/ polyurethane system Trowel- or roller-applied elastomer (1–3 mm) over high build primer Topcoat should include aggregates, e.g. aluminium oxide, silica or others to provide non-slip properties
Tanks Ballast Fuel Sewage Drinking water	Resistance to alternating contact with sea water and with transported products Compatibility with cathodic protection (in the case of seawater)	Modified epoxy Aluminium-pigmented pure epoxy Solvent-free epoxy Special waterborne asphaltic emulsion Cement-reinforced acrylic
Cargo Crude or petroleum oils or hydrocarbons Very aggressive products	Resistance to contact with specific cargo types	High-solid or solvent-free polyamine-cured epoxy High-solid polyamine epoxy Epoxy-cyclosilicone

mechanisms of corrosion and fouling, specifically for underwater applications, are considered to be of major importance and are dealt with in greater depth in Sections 16.3 and 16.4. In this Section 16.2, considerations and dedicated coating systems for other specific ship areas (cargo tanks, ballast tanks, potable water tanks, decks, superstructures, boot top, and steam pipes and pipelines respectively) are presented.

16.2.2 Cargo tanks

The internal coating of a ship's cargo tanks is a common and necessary way to protect steel surfaces against corrosion, to avoid cargo contamination, and to facilitate cleaning. In product and light chemical carriers, for example, full coating of internal tank surfaces is necessary to avoid corrosion damage and possible cargo contamination, since a smooth coating facilitates tank cleaning between cargoes and helps prevent contamination from rust or leftover cargo deposits. Therefore, proper tank coating is essential for effective and profitable ship management.

For the right choice of coating system and proper handling of cargoes, a basic knowledge of the chemical properties of the most common cargoes is advisable, since the behaviour of products within the same groups of organic compounds may vary to a great extent. For instance, methanol will soften most organic coatings, but alcohols with higher molecular weight are far less aggressive. Compounds of lower molecular weight usually are more aggressive than their higher homologues. For instance, pure epoxy coatings are not suitable for long-term contact with acetone, other lower ketones (e.g., methyl ethyl ketone), or the lower esters such as methylacetate. They are, however, suitable for higher homologues such as methyl isobutyl ketone and dibutylphthalate.

This difference in behaviour towards coatings depends mainly on the steric hindrance (3D structure) of individual molecules. It is easier for smaller and linear molecules to penetrate the polymeric structures. Other factors influencing the solvent power of non-hydrocarbon compounds on polymers are functional groups, polarity of molecules, and hydrogen bonds. All of today's organic coatings for cargo tanks are two-component types, resulting in a chemically crosslinked film that cannot be redissolved. However, strong solvents can soften cured coatings, causing swelling and, in some cases, even scaling from the substrate. An additional factor affecting coating suitability is the water solubility of solvents. Most organic coatings used for cargo tank protection can tolerate a certain degree of softening from solvent absorption, provided they are given sufficient time for the absorbed solvent to evaporate and to regain their original hardness. However, if the retained solvent is water-soluble and tanks are washed with water or loaded with an aqueous cargo before the film has completely dried, blistering due to osmosis may occur.

During the last 40 years, several types of coatings have been used for tank lining service in the sea trade: vinyls, polyesters, epoxies, epoxy phenolics, epoxy isocyanates, polyurethanes, alkaline zinc silicates, and ethyl zinc silicates. Some of these coating materials have stopped being used for tank linings. Vinyls, being thermoplastic, had limited solvent resistance. Glass-reinforced polyesters, used for transportation of acid cargoes, were replaced by stainless steel tanks. Polyurethanes, loudly advertised in the 1980s for their wide resistance to different types of cargoes, showed some application problems and unsatisfactory resistance to ballast water. Today's state-of-the-art coatings basically fall into the following categories: pure epoxy, epoxy phenolic, epoxy isocyanate, alkaline zinc silicate, ethyl zinc silicate, and cyclosilicon epoxy [4–6].

16.2.3 Ballast tanks

Coating systems for ballast tanks should be resistant to (polluted) seawater, corrosion inhibiting, free from pores, and resistant to the side-effects of cathodic protection. According to the classification societies, one of the most life-determining factors for a ship is the condition of its ballast tanks. The inner water ballast tank area of a ship can be extremely large. For a single-hull very large crude carrier (VLCC), the water ballast tank area might be 140 000–160 000 m^2; for a modern double-hull design, it could be 240 000–280 000 m^2 or even larger.

Besides exposure to a corrosive environment during service, the ballast tank coating is subjected to various sources of stress that may lead to cracking of the coating:

- Mechanical stress due to vibration and movement of the ship
- Thermal variations due to loading and unloading of ballast water or product in adjacent cargo tanks
- Wet/dry cycles due to loading and unloading of ballast water
- Reverse impact from ice trading, tug boats, fenders, collision or loading of cargo in adjacent cargo holds
- Internal stress due to curing shrinkage and solvent evaporation.

International regulations have had a clear and positive effect on the structural protection of ships. They deal with the duty to coat ballast tanks (with light-coloured, hard coatings combined with cathodic protection), the minimum width of double hulls, the height of double bottom tanks, the deletion of the allowance for reduced scantlings when tanks are coated with an approved system, and a harmonized system of survey and certification from the classification societies.

Modern systems for ballast tanks normally consist of at least two coats of straight, modified or solvent-free epoxies with a total dry film thickness of at least 250 μm for straight and modified epoxies and 300–350 μm for solvent-free epoxies. Reinforcement of an epoxy coating with (synthetic) fibres helps to significantly improve mechanical coating properties and reduce possible cracking in water ballast tanks in ships [4, 7].

16.2.4 Potable water tanks

Compared to water cargo tanks or ballast tanks, drinking water tanks on ships are relatively small. Cargo ships usually have two or three tanks with an overall volume of about 100 m^3, while passenger ships require larger tanks. A suitable coating for potable water tanks should last, with minimal maintenance, for the service life of the ship, up to 25 years without problems of corrosion or water quality. Coatings applied to potable water tanks are usually two-component pure epoxies, either solvent-free (100% solids) or solvent-borne. Most pure epoxy coatings that are suitable for immersion service are also suitable for potable water contact, provided they do not contain pigments with heavy metal compounds such as chromates. Before accepting a coating for use on board ships, classification societies require certification from a recognized laboratory that the coating is suitable for prolonged contact with drinking water. There are several standards for testing such coatings, but all test criteria address water taste and extraction of possible harmful substances. Most epoxy coatings, if formulated properly, will pass these test criteria. There are usually no significant differences between solvent-borne and solvent-free coatings during laboratory testing, because test panels are prepared under controlled conditions that avoid possible solvent entrapment. However, under field conditions, solvent entrapment may play a major role in coating performance. Therefore, solvent-free coatings are better suited for potable water tanks than those containing solvents, which require careful ventilation and proper thermo-hygrometric conditions to avoid solvent retention. Also, small percentages of solvent retained in a coating system for potable water tanks may be a serious problem, since they can affect water taste and smell. Moreover, once solvent has been entrapped, it might be impossible to remove without reblasting and recoating the tank [8].

16.2.5 Decks

Paint systems for decks should be very resistant to corrosion and the influences of weather. They should be non-slip (even when the decks are wet) and resistant to UV, impact, scratching and abrasion, as well as resistant to (sea) water, fuel oils, lubricating greases, cleaning agents and cargo spills. To minimize damage that may occur to a deck coating before delivery, the best procedure may be to apply a recoatable epoxy holding primer during construction and the final coating system as soon as possible before delivery. The most common deck coating systems are two-component epoxies, polyurethanes and zinc silicates with a dry film thickness of 250–300 μm for epoxy/polyurethane systems and 75–100 μm for zinc silicates. Epoxy/polyurethane systems often consist of a primer, a thick midcoat, and an easily recoatable topcoat, preferably all high-solid products. The topcoat can be made anti-skid by adding an aggregate such as non-sparking silica, pumice powder or aluminium oxide. Due to their limited resistance to acids and alkalis, zinc silicates should not be used on the decks of chemical tankers. Special, heavy-duty systems based on thick, solvent-free elastomeric coatings applied by trowel or roller over a thin primer to a dry film thickness of 1–3 mm also are available. In addition, water-borne systems consisting of an alkali zinc silicate primer and an epoxy emulsion mid- and topcoat are used for decks [3, 9].

16.2.6 Superstructure

For the topside and superstructure, an aesthetic topcoat of aliphatic polyurethane or aliphatic polyurethane/acrylic may be used. Isocyanate-free alternatives include epoxy/acrylic or other modified epoxy coatings, although they generally have reduced gloss and colour retention compared to polyurethanes. Silicon-based inorganic coatings are much more resistant to these degradation mechanisms, and polysiloxane coatings offer significantly enhanced durability when compared with conventional polyurethane coatings. Polysiloxane coatings must, however, be modified to the right extent with organic resins to enable other coating performance properties such as flexibility, toughness, adhesion to primers and cost to be obtained while, at the same time, not detracting from the polysiloxane properties. By carefully choosing the organic modification of the polysiloxane polymer, e.g. acrylic, these materials can provide an inorganic backbone that provides not only enhanced finish coat aesthetics but also long-term durability against coating breakdown caused by weathering and exposure to aggressive environments. Polysiloxane epoxy hybrid coatings also can be used as aesthetic topcoats.

A special antirust-stain finish may be applied to the topside and superstructures. This finish contains an active pigment that chemically combines with rust to produce a colourless, water-soluble material. As a result, rust stains are not visible. Although not often mentioned in painting specifications, water-borne coatings based on alkali zinc silicate, styrene acrylate dispersion, or epoxy or alkyd emulsion are suitable for the topside and superstructure. However, their use generally is limited to the mid- and topcoat layers. Suitable products include acrylic dispersions and epoxy acrylic or (silicone) alkyd emulsions. However, their gloss levels are usually lower than those of solvent- borne paints. Water-borne systems can be successfully applied, especially for ships built completely under cover. However, this requires at least moderate temperature and humidity levels and strict planning. Also, painters experienced in applying water-borne paints are needed [3].

16.2.7 Boot top area

Modern paint systems typically include a two-pack epoxy primer. Polyurethanes and coal-tar epoxy have been banned for environmental reasons. Apart from good photostability and surface tolerance, they generally should have long maximum overcoat times and good recoatability. Total dry film thickness of boot top systems ranges from 250 to 400 μm. Anticorrosive properties are obtained by barrier protection, which means that the water vapour transmission of the system should be very low. Increasing use of glass flake in coatings for underwater hulls and especially for boot top areas is evident. Epoxy-based glass-flake coatings are the most commonly used protective coatings in these extremely aggressive areas and are hard, tough materials with good chemical, solvent and abrasion resistance. They can also be used in association with cathodic protection systems [3].

16.2.8 Steam pipes and pipelines

The problem of protecting deck steam lines and pipelines from corrosion has plagued operators, owners and coating suppliers for years. While taking up a very small space, these components of the vessel's engineering system are vital to the operation of the ship. Steam is used to power deck winches in some older vessels and to heat coils in the cargo tanks of vessels carrying liquid product. Failure to heat the liquid cargo increases its viscosity to the point where it is too thick to pump or transfer. This condition is unacceptable. Steam lines and deck pipelines have traditionally been an enigma to protect because of their unique environment. In addition to the obvious problem of heat, which often can range from 150 to 180°C, depending on the pressure of the system, the line can be constantly awash with cooling salt water or salt spray. In addition to the obvious corrosion problem this causes, it creates a thermal expansion and contraction cycle that puts significant stress on the coating material. Thus, many factors affect the protective system on the pipes. In the past, concoctions of enamel paints and oils were used to provide an inexpensive topcoat that offered some protection and was easy to apply. Today, a common method of maintaining the deck lines is to constantly repaint them with a heat-resistant aluminium coating, as time and schedule permit, and then to replace the coatings as they fail. Another approach is to use surface-tolerant epoxies, but because of the heat, they offer only short-term protection [10].

16.2.9 Surface preparation

The aim of surface preparation is to remove any surface contamination such as mill scale, corrosion products, old coatings, grease and detritus and salt contamination, thereby presenting a clean (and ideally profiled) surface on which to apply the paint system. The principal methods of surface preparation are:

- Mechanical preparation using hand or power tools. These methods are the most basic but least efficient means of preparation; however, factors such as access, prohibition of blasting or simply cost may dictate their use.
- Dry abrasive blasting using a variety of abrasive types (e.g. grit, shot, sand, garnet, etc). The most common method in use today, dry blasting offers efficient removal of contaminants to present a good profiled surface appropriate to the paint specification. Drawbacks include noise, removal of spent abrasive, and requirements for containment on site.
- Use of water as a blast medium is still increasing, either as wet abrasive slurry blasting, or ultra high pressure (UHP) water jetting. UHP jetting offers very efficient removal of contaminants, especially water-soluble salts, though it will not create a profile in steel although it will reveal any previously created profile.
- Flame cleaning and acid pickling are older-style methods, but are still used in specific instances. Chemical strippers can be useful for small areas where blasting is impractical.

According to Almeida *et al.* [1], the anti-corrosive protection of steel ships starts in the shipyard, which is now normally equipped with automatic blasting and painting plants for both steel plates [11] and steel profiles. Here, the different steel surfaces are blasted and painted with shop primer, in accordance with the ship's construction schedule [12, 13]. Following a suitable drying time, the prepainted plates and profiles pass on to the plate shop where, depending on the ship's design, they are subjected to various operations such as marking, forming, cutting and welding. In most cases, practicalities prevent full blasting of the join-up welds and these tend to be ground and power-disked [14]. After this, they are mounted, firstly in unitary blocks or pre-blocks, and later in large blocks or superblocks, which are then transported to the site where the ship is under construction. Finally, appropriate surface treatments and painting procedures are applied to each of the ship's specific exposure/operating areas. Nowadays these blocks can be treated and fitted out in blasting/painting cabins, after which they are transported to the construction site [1].

Fabricators using this process work very much on a production line basis: each coated block must be in the right place, at the right time, and there can be no hold-ups, a number of vessels are in the dry-dock at any one time, and progress on all of these must be synchronized to allow flooding. In many cases, to ensure production schedules are met, coating application is directed at being absolutely certain that required dry film thicknesses are met, even at the risk of over-application and over-usage of paint. This, together with the use of stripe coats on welds/edges, etc., can lead to extremely thick areas up to 3–4 times the specified dry film thickness [14].

16.3 Coatings for corrosion protection

16.3.1 Coating failure and corrosion mechanisms

The corrosion protection of metal substrates by organic coatings is attributed to a barrier mechanism, resistance inhibition, and/or an active inhibitive mechanism. Each of these mechanisms is discussed extensively in the literature [15, 16] and in preceding chapters in this book. This paragraph deals with the mechanisms of corrosion and protection against corrosion in marine environments.

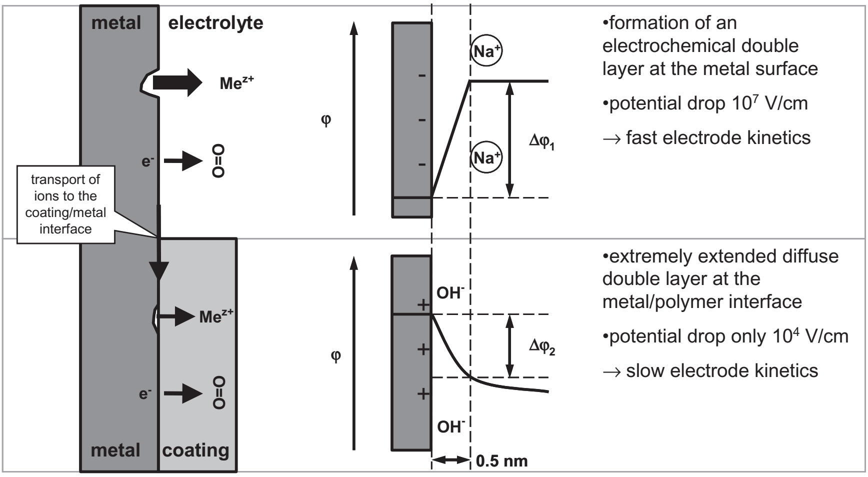
Formation of conductive pathways

For coated materials, water uptake is often mentioned as the first step of the degradation process. This process causes the opening of conductive pathways in the coating, allowing ions to reach the metal surface (Fig. 16.1).

Nguyen and Hubbard [17] assume that the formation of conductive pathways in an initially intact organic coating during water uptake (Fig. 16.2: step 1; note that the consecutive steps are indicated by the circled numbers) is due to an attack by water in the hydrophilic regions in the film, followed by interconnections of these regions.

The presence of macroscopic defects such as craters and pinholes, air bubble inclusions, poor wetting between pigment and binder, or mechanical damage in the coatings would accelerate the pathway connections. Swelling, stress relaxation and conformational changes in the coatings during exposure may all contribute to the formation and enlargements of such pathways.

Hydrophilic regions contain low molecular weight/low-crosslinked (LMW/LC) materials. Ionogenic groups, like soluble pigment components and ionizable resin functional groups, facilitate the formation of the conductive pathways. These materials take up large amounts of water, have a low resistance to ion transport and are susceptible to water attack e.g. hydrolysis and dissolution.

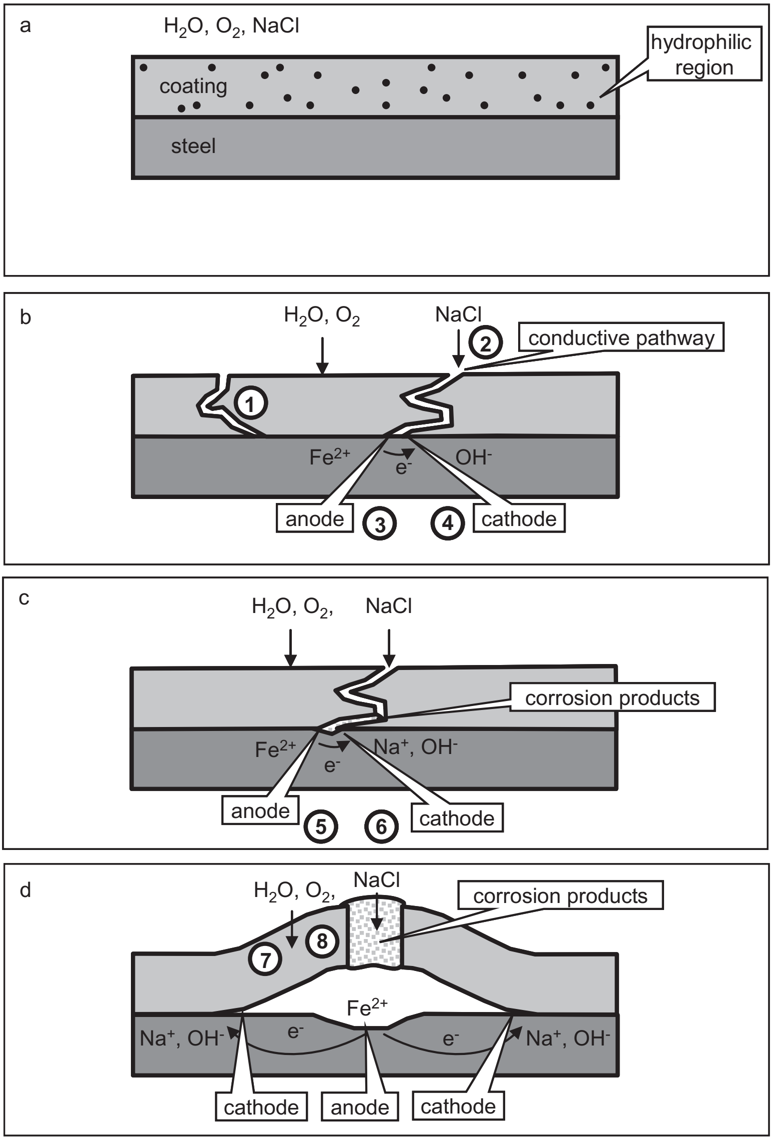


16.1 Schematics of the characteristics of the double layer for electrolyte covered metal (top) and polymer-coated metal (bottom) [15].

Transport of corrosive species to the metal surface

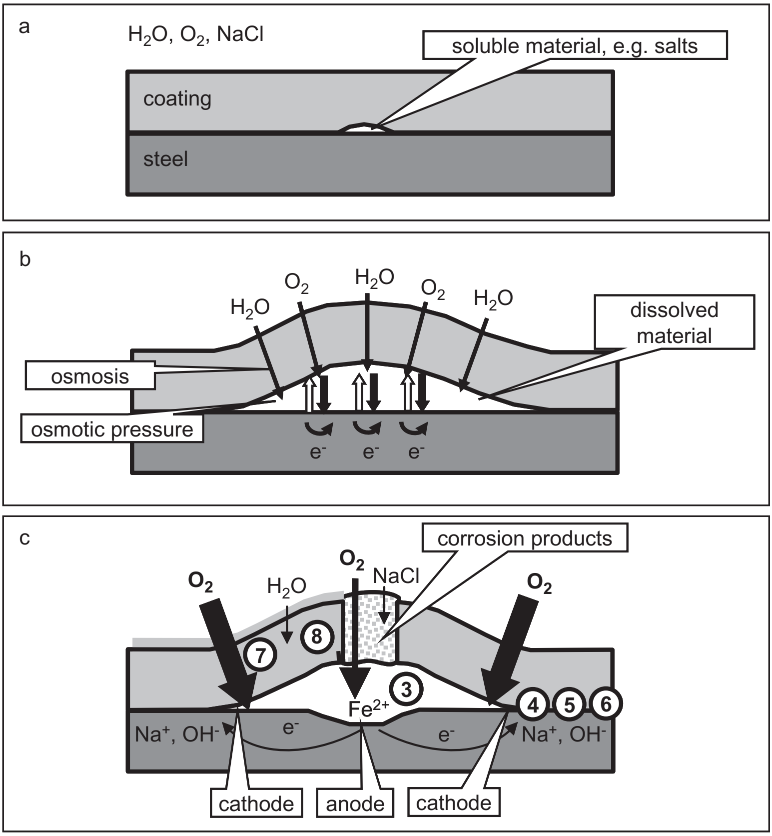
Following the pathway formation, the next step in the degradation of coated steel is the transport (Fig. 16.2: step 2) of water oxygen and ions from the environment to the metal surface. Although both water and electrolyte can penetrate films, electrolyte tends to penetrate films only locally by formation of conductive pathways. The regions of direct electrolyte penetration have indeed been shown to be small, localized and randomly distributed. Furthermore, these regions have been demonstrated to correspond to initial sites of corrosion. The molecular origin of the direct electrolyte penetration regions is not entirely clear, but in some cases, they have been associated with inhomogeneous crosslinking.

As stated earlier in this chapter, typical organic films are permeable to water and oxygen to such a degree that the transport of the materials is not rate controlling. In case of the presence of soluble materials under the coating, water uptake may be accelerated due to osmosis (Fig. 16.3a, b). One source of underfilm electrolytes could be salts embedded in rust deposits, not removed prior to the paint application. At this stage, all ingredients for corrosion are present in the blister: anodic species (substrate material), cathodic species (water and oxygen) and an aqueous film in which the electrochemical double layer is formed. At the initiation of corrosion, the anodic and cathodic sites on the metal will be randomly distributed and constantly changing over the metal surface (Fig. 16.3b). The build-up of osmotic pressure may eventually lead to collapse of the blister (Fig. 16.3c) leading to a similar situation as depicted in Fig. 16.2d.



16.2 Model for the degradation of an initially intact organic coating on steel in a neutral NaCl solution [17].

Regardless of the rate-controlling step, the transport of ions from the environment to the metal surface is through discrete, least resistant, conductive pathways in the coating. This view is supported by the fact that the solubility of ions in a polymer matrix is extremely low, approximately 10^{-8} mol/l in equilibrium with one molar electrolyte. Ion transport through



16.3 Model for the degradation of an organic coating on steel in a neutral NaCl solution initiated by osmosis.

conductive pathways is in agreement with the impedance equivalent circuit models, which generally consists of the coating capacitance shorted by a resistive element, representing the presence of ionically conductive pathways through coatings.

Based on this conceptual model, the steps (circled numbers in Fig. 16.2) involved in the degradation of an organic-coated steel panel containing no apparent defects exposed to a neutral NaCl electrolyte may be summarized as follows:

1. Conductive pathways develop by water attack in the hydrophilic regions of the film, followed by the interconnection of these regions; macroscopic defects (in the coatings) accelerate this process.
2. Ions migrate through conductive pathways to the metal surface.
3. Anodes develop on the metal surface at the base of the pathways.

4. Cathodic contacts develop under the coating at the periphery of the pathways.
5. Sodium ions migrate along the coating/metal interface from the defect to the cathodic sites to neutralize the hydroxyl ions; this transport process is the rate-determining step.
6. Alkalinity of NaOH solution at cathodic sites causes disbondment (cathodic delamination).
7. Hygroscopic NaOH materials at cathodic sites produce a water activity difference between the environment and interface, setting up an osmotic pressure gradient; water is driven to cathodic sites through the coatings by an osmotic pressure.
8. For some coatings, blisters develop, enlarge (probably facilitated by mechanical stresses) and eventually coalesce, resulting in total delamination.

It has been shown that pore-free polymers initially provide a rather good corrosion protection, due to low solubility of ions within the polymer. If, however, part of the polymer is destroyed (formation of pores, or conductive pathways) or mechanically removed, then the electrolyte has direct access to the metallic substrate. At the borderline of the defect an interesting electrochemical situation occurs. At the defect a rapid metal dissolution is possible (active electrode), whereas below the adherent coating the dissolution reaction is strongly inhibited (passive electrode) [18].

16.3.2 Mechanisms and techniques of corrosion protection

Additional to the corrosion protection provided by organic coatings, protection to steel marine and ship structures can be improved by cathodic protection. The conventional basis for cathodic protection relies on inducing a negative steel potential shift which reduces the tendency for iron to dissolve as positive ions. Key factors that determine what is required for fully effective cathodic protection in seawater are:

- Seawater salinity and resistivity – these have a strong influence upon the required current density at the protected surface and the current available from the specific anode geometry and anode distribution.
- Dissolved oxygen – with the corrosion of steel under cathodic control, the required current density is directly proportional to the product of the oxygen concentration and the oxygen diffusion coefficient in seawater.
- Temperature – this affects electrochemical charge transfer and diffusion kinetics, the solubility of the calcareous deposits and the electrochemical capacity of sacrificial anode materials.
- The formation of calcareous deposits – these reduce the current demand in the long term and improve the spread of protection.

The principle of cathodic protection is in connecting an external anode to the metal to be protected. The external anode may be a galvanic anode, where the current is a result of the potential difference between the two metals, or it may be an impressed current anode, where the current is impressed from an external DC power source.

Galvanic anode systems use reactive metals that are directly electrically connected to the steel. Commonly used metals are aluminium, zinc and magnesium. Impressed current systems employ inert (zero or low dissolution) anodes and use an external source of d.c. power to impress a current from an external anode to the cathodic surface. Cathodic protection is commonly applied to a coated structure to provide corrosion control to areas where the coating may be damaged. It may be applied to existing structures to prolong their life. In practice its main use is to protect steel structures buried in soil or immersed in water. Among other purposes cathodic protection is generally used for ship hulls and tanks, but is functional only when immersed.

The provision of an organic coating to the structure will greatly reduce the current demanded for cathodic protection of the metallic surface (approximately 110 mA/m^2 for unprotected structure and 5 mA/m^2 for protected structure, a factor of 22). The use of a well-applied and suitable coating increases the effective spread of cathodic protection current. A combination of both a coating and cathodic protection will normally result in the most practical and economic overall protection system. Ideally, the coating has a high electrical resistance, is continuous and will adhere strongly to the surface to be protected. Compatibility with the alkaline environment, such as epoxy binders provide, created or enhanced by cathodic protection is desirable.

In the case of critical areas with the danger of damage or failure of the coating, additional cathodic protection is applied. This is always the case for the underwater part of the hull of a ship and for offshore constructions, pipelines and seawater ballast tanks. Due to the cathodic protection, at the coating–metal interface, in the vicinity of damage, conditions of high pH will be created, which will cause detachment of the coating. Modern protective coatings for these kinds of applications are designed to tolerate normal required protection for unalloyed steel: 200 to 300 mV lower than the open corrosion potential.

16.4 Coatings for antifouling protection

16.4.1 Introduction

Since ships are used for transport, the use of all kinds of 'antifouling' products is also well established. Depending on availability, technical possibilities and knowledge of the effects on the environment, many different products have been applied: wax, tar, asphalt, pitch, shielding with copper or lead. Coatings used early in the last century were based on linseed oil, shellac or rosin, containing all kinds of toxic elements: copper, arsenic or mercury oxide mixes.

In the latter half of the last century a new technology was originated: organometallic compounds. There were developed and applied as antifouling compounds in paints: organo-arsenic, organo-lead and in the 1970s organotin. This last group, in particular tributyltin (TBT), was very successful, because of its:

- effectiveness (in combination with copper oxide it covers the whole range of the marine growths concerned)
- combination with the acrylic binder which gives self-polishing properties, making a new effective surface continuously available, moreover decreasing drag resistance by smoothing the surface
- compatibility with anticorrosive systems
- relative long lifetime, up to five years
- acceptable price.

However, because of the high toxicity of TBT to oysters, molluscs and crustaceans and their bioaccumulation, the application has been banned globally by IMO since January 2003. Moreover, from 1 January 2008 no coating on ship hulls containing organotin may be in contact with seawater.

Since the first signs of the environmental problems caused by organotin much research for alternatives has been started, though because of the 'excellent technical suitability' of organotin-based antifoulings it is an almost impossible challenge to develop similar products. Furthermore, another practical barrier is raised in the development and application of new antifouling agents: for their admission, production and use in the US and EU, approval of the respective authorities is needed (the US Environmental Protection Agency, and the various directives issued in the EU resulting in the actual REACH – Registration Evaluation and Authorisation of Chemicals). The procedure for approval is costly and risky; for this reason, despite the various initiatives, including those looking for new compounds 'learning from nature', few novel products have reached the market during the last decade. For example, in Europe much research was conducted to copy active compounds (secondary metabolites) from sponges retaining antifouling properties and to produce them synthetically [19, 20]. These projects were successful from a research point of view: three different compounds have been developed. From the practical or commercial point of view they have not been successful: they have not been taken into consideration for development because of the registration costs and risks.

16.4.2 Current and future developments in antifouling

Antifouling techniques can be subdivided into the following principles:

- *Chemical*. Chemical compounds acting as active, mainly toxic agents. Coatings containing these compounds form the largest group in practice. Metal cladding and release of toxic metal ions also belongs to this principle.
- *Physical*. Low energy surface (silicone or fluoropolymer based) coatings: in this case organisms can attach, but they are easily removed during sailing. Application of gels can also be attributed to this group.
- *Biological*. Interfering with the metabolites of marine organisms, for example with enzymes. Predation by other marine organisms can also be considered as a biological technique.
- *Electrical.* Using direct current, electrical pulses or electrolysis of the seawater.
- *Mechanical.* Mechanical cleaning of the surface (Fig. 16.4).

In practice, for the protection of the hulls of ships against fouling, mainly coatings based on the chemical principle are used (estimated at 90%) and the remainder are mainly low energy surface coatings (Fouling Release Coatings, FRCs).

Due to the restrictions for environmental reasons, paint manufacturers have been forced to commercialize environmentally less harmful products. In antifouling coatings based on the chemical protection principle, alternatives to TBT-based antifoulings are nowadays available. Almeida *et al*. [1], Table 16.2, gives a complete overview of the products actually available that replace the organotin antifouling [1, 21–31]. The principal antifouling

16.4 Mechanical cleaning of fouling.

Table 16.2 Overview of the main alternatives for TBT based antifouling available on the market [1, 21–31]

Type of paint	Company	Product designation	Basic known components	Proposed mechanisms	Reference
Controlled depletion paints (CDPs) (increase of soluble matrix technology with use of new resins)	Chugoku Marine Paints	TFA-10/30		CDP. Hydration	
		Sea Tender 10/12/15		CDP. Hydration	
	Kansai Paint	New Crest		CDP. Hydration	
	International Marine Coatings	Interspeed 340 Interclean 245		CDP Contact leaching	
	Transocean M.P.A.	Optima 2.30–2.36		CDP	
Tin-free self-polishing systems (TF-SPCs) (identical mechanism to self-polishing technology but without tin)	Ameron	ABC-1a4		SP. Hydrolysis	
	Chugoku	Sea Granprix 500/700 (2nd generation)	Zinc or copper acrylate-based binder integrating biocides and others	SP. Zinc acrylate. Hydrolysis	[29–31]
		Sea Granprix 1000/2000 (3rd generation)	Silyl-acrylate-based binder integrating biocides and others	SP. Silyl-acrylate. Hydrolysis	[29–31]

Hempel	Globic Series	Synthetic colophony substitutes with reduction of co-binder (plasticizer) reinforced with mineral fibres and product 81900–81970 as potential biocide, or sea. nine/Cu pyrithione	SP. Ion exchange. Fibres $\mathrm{R{-}COO{-}Zn{-}OOCR + 2Na^{+} \leftrightarrow 2R{-}COO{-}Na^{+}\ (s) + Zn2^{+}\ (aq)}$	[21–28]
	Oceanic Series		SP. Ion exchange. Fibres	
	Olympic Series		SP. Ion exchange. Fibres	
International Marine Coatings and Nippon Paint	Intersmooth Ecoflex SPC	Acrylic matrix bonded to copper salts of an unrevealed organic chain. Potential biocide zinc pyrithione	$\mathrm{P{-}COO{-}CuOOCR\ (s) + Na^{+} \leftrightarrow P{-}COO{-}Na^{+}\ (s) + RCOO{-}Na^{+}(aq)}$ + basic copper carbonate	[21–28]

(*Continued*)

Table 16.2 Continued

Type of paint	Company	Product designation	Basic known components	Proposed mechanisms	Reference
	Jotun	Sea Quantum (Plus, Classic, Ultra, FB) SeaQueen SeaPrince SeaGuardian	Potential biocide Cu pyrithione	SP. Silyl-acrylate. Hydrolysis SP. Copolymer binder SP. Copolymer binder SP. Copolymer binder	
	Kansai Paint	Exion Nu Trim		SP. Zinc acrylate. Ion exchange SP. Hydrolysis	
	Sigma Coatings	Alphagen 10–20–50 Sigmaplane Ecol (also HA)	Potential biocide isothiazolone Potential biocide isothiazolone	SP. Hydrolysis and ion exchange SP. Hydrodissolution	
Hybrid systems (CDPs/SPCs)	International Marine Coatings	Interswift 655	Potential biocide Zineb or Cu pyrithione	Hybrid of CDP + SPC	
	Hempel	Combic Series		SP + saponification	

mechanism of almost all these products is obtained by copper oxides or salts. In addition other active compounds with toxic properties for specific organisms not covered by copper are added. As far as is known and also from the authors' experience, some alternatives are performing satisfactorily; however, their efficacy and lifetime do not meet those of the TBT-based antifoulings.

Fouling Release Coatings (FRCs) are free from biocides, so they can be considered as one of the most environmentally friendly solutions. Their development and optimization, however, is more difficult. The adherence with the substrate is critical and requires a 'sealer' or tie coat. Moreover, the mechanical properties during utilization are delicate. Application and repair demand particular expertise. This all makes the coating rather expensive as compared to conventional antifouling coatings. Finally, these coatings do not really prevent fouling, but lower the adherence of the marine organism to the coating. Nowadays all known antifouling paint manufacturers offer also Fouling Release Coatings. Their application in practice is satisfactory, at least for certain types of vessels: those with a limited 'non-sailing time' and with the possibility of sailing faster than 15 knots. Development is still on-going and particular attention is also being given of the possibility of lowering the drag resistance by adapting the surface profile of these coatings in practice.

16.5 Inspection, monitoring and maintenance

16.5.1 Protection against corrosion

Introduction

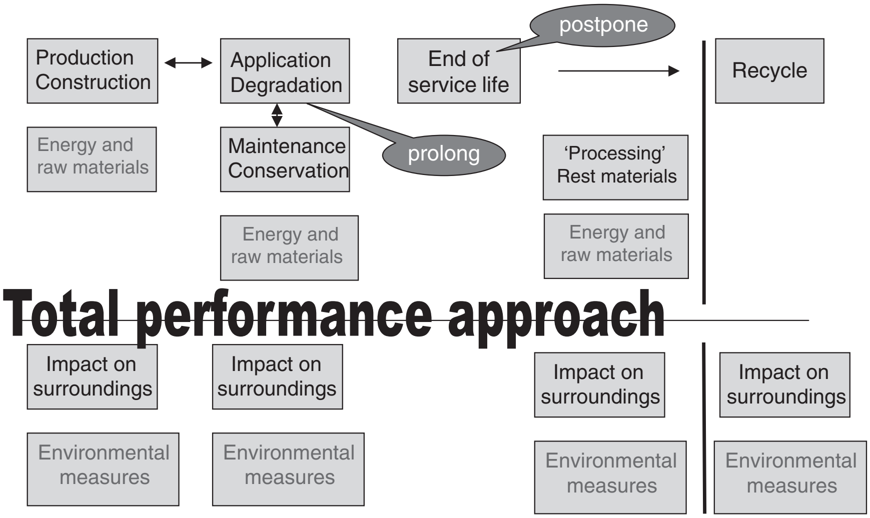
When discussing the effectiveness of the protective action against corrosion of coating systems, it is imperative that design objectives of these systems for durable performance and the actual performance under practical conditions are realistically compared. Of course, this would normally only be possible after quite some years of exposure to practical conditions. It would be unacceptable and costly to conclude only after say five years that the coating system is not suitable for the chosen application. Therefore we need inspection and monitoring methods with an early warning capability and, on the other hand, accelerated testing and evaluation procedures that can reliably predict long-term behaviour based on laboratory experimental data.

In ideal cases the testing methods used for monitoring can also be used under careful control for laboratory experimentation with predictive properties. In these cases the measuring techniques are so sensitive that information on very limited degradation not resulting from accelerated testing, but obtained under mild exposure conditions similar to those found in practice, becomes quantitatively available such that under well-defined conditions extrapolation to long-term behaviour becomes possible. These techniques, such as electrochemical impedance spectroscopy, electrochemical noise and mechanical delamination testing, although available in principle, have yet to be improved to be adopted for general use as lifetime predictive tools [32].

Design for lifetime

Design for lifetime prediction, reaching out for durable coating systems, should always be part of a total performance approach as given in Fig. 16.5. In this chapter we will focus on the second step in this system: we aim at application of the coating such that its lifetime is optimized (within the limitations of the lifetime of the total structure), while monitoring its potential degradation and taking the appropriate maintenance measures if needed. In most cases the normal lifetime of a coating system is lower than that of its protected structure. This means that we can focus on the extension of the lifetime of the coating in use based on proper knowledge of the coating's performance-related parameters such as adhesion, thickness, porosity, ionic transport properties, barrier action, permittivity, water uptake, blistering, etc.

Often the service life of a construction is not specified. It is then implicit by referring to specifications using standards for raw materials, metal alloy type, generic coating type, cover thickness, curing conditions and allowable



16.5 The concept of the total performance approach.

crack width: a long service life is assumed to result. If long-term proven records of similar structures exist this may work well. Then testing and service life calculations are not needed. In other cases it may lead to unacceptable early failure.

Explicit design for service life using performance-based design has become more important nowadays. First, better comparison of different material classes becomes possible, while also product standards do not necessarily apply in new and different ambient conditions (Middle and Far East vs. Europe; Europe vs. Florida; etc.). Also a great variety of new materials, including new combinations, has arisen in the last 15 years, while environmental issues render some materials obsolete. Last but not least, the responsibility for product performance has shifted to the manufacturer, which increases awareness. For performance based design we need proper data based on practical experience with materials and constructions, either from exposure sites or directly from practice. Alternatively we need representative testing results, either as a result of monitoring under conditions in use, or as a result of accelerated testing or refined sensitive testing procedures in the laboratory.

Assessment of performance

In Section 16.3 we described the various damage and degradation scenarios encompassing blistering and cathodic delamination. Different degradation processes demand different measuring techniques for proper evaluation of the coating properties. In this subsection we will give a short summary.

The most reliable way of studying the suitability of a coating for a specific substrate and environment is to actually expose coated substrates to the environment in which the coating will ultimately be applied [15, 16, 34–40]. This is generally done by mounting coated panels to exposure rigs as shown in Fig. 16.6. Although long-term exposure to the actual environment offers a good representation of the actual service life, 'natural' degradation of modern protective coating systems is extremely slow. Outdoor exposure tests frequently require 10–20 years before reliable conclusions can be drawn. Consequently, results are not provided in a commercially acceptable time period [35, 38, 39, 42–44]. A second drawback to this approach is the variability of the 'natural' environment. No time period or location is the same as any other and thus exposed materials are degrading in constantly changing rates and fashions. This greatly influences the accuracy of the service life prediction [35, 43–45].

Many researchers have attempted to speed up the natural coating degradation process by increasing the physical and chemical stresses (e.g. by altering temperature, humidity, pH, salt concentrations and the intensity of UV radiation) in so-called accelerated tests. Ideally, the stresses only cause

16.6 Typical setup for outdoor exposure of coated panels in a coastal environment.

the system to fail faster than it normally would, while the mechanism of failure remains the same as in the non-accelerated conditions [36, 46–49]. The ability to relate the performance of a coating exposed in such tests to the field performance is a universal need. If such a linkage can be made, then it should be possible to greatly reduce the time-to-market for new products by substituting short-term laboratory exposure results for results from long-term field exposures [35, 50–53].

The most widely used accelerated test for coating evaluation is the salt spray test [35, 54–58]. This has been true despite severe criticisms this type of testing has received [35, 48, 52–64]. Salt spray tests are cabinet tests where a salt solution is pumped into a nozzle where it meets a jet of humidified compressed air, forming a droplet spray. The standardized pH-neutral salt spray tests ASTM B117 and ISO 9227 continuously subject test specimens to a fog of salt particles (5 wt% NaCl) at an elevated temperature of 35°C. The justification for these extreme conditions has always been that a coating system that will resist these test conditions should also perform well in aggressive service environments. The assumption was that the mechanisms of corrosion and degradation in service would be similar to those in the test cabinet [54]. However, many examples can be found in the literature suggesting that little, if any, correlation exists between the results from salt spray tests and in-service performance. Most remarkably, negative correlations have been observed quite regularly [37, 57, 61–66].

To overcome the deficiencies of continuous salt spray tests, cyclic weathering tests were developed. Incorporation of cycling steps seems intuitively justified, considering that coatings exposed to the outdoor environment undergo similar effects on a frequent basis [39]. Indeed, many have claimed the superiority of cyclic tests over conventional salt spray tests, as these tests produce failures more representative of field results, with better correlation to actual environments [33, 35, 56, 62, 64, 67]. Test chambers in which specimens are exposed to ultraviolet radiation (UV) are widely used to obtain weathering data for a wide range of polymer products, including coatings. Commercially available UV chambers already began to appear in about 1920 and since then numerous modifications in have been made [68].

While cyclic testing was seen as an important advance, it was also suspected that ultraviolet radiation (UV) plays an important role in natural weathering of coated metals. This led Skerry and his co-workers to investigate the influence of an added UV weathering cycle. The results indicated that the corrosion performance characteristics of organic coatings were markedly affected by the UV-weathering factors in the test [58]. Furthermore, the combined cyclic salt fog/UV test showed an improved reproduction of coating performance ranking and failure modes observed in practice [36, 48, 52, 54, 58, 59]. In this respect, this cyclic salt fog/UV test is superior to continuous salt fog, or even cyclic salt fog alone. In Table 16.3 the most important test methods are summarized. Testing should be encompassed by proper evaluation methods. Coating degradation is usually evaluated using standardized methods; the common methods are given in Table 16.4. Unfortunately the majority of these methods are based on visual observation [69], rendering them rather subjective. There has been considerable effort to develop evaluation methods for organic coatings that are numerical, reproducible and accurate [70–72]. The use of electrochemical techniques, in particular electrochemical impedance spectroscopy (EIS), has been shown to be very valuable. EIS not only provides results in a short time but the obtained data can give indications on the actual corrosion mechanisms. In addition, corrosion and coating damage may be determined prior to its visual manifestation [33, 41, 49, 63, 73–80]. This coincides with the present trend towards the development of methods which enable early prediction of coating performance, even before the occurrence of any substantial changes in its appearance [33, 41, 73, 76–78, 80].

Electrochemical noise measurement (ENM) for corrosion studies was first described by Iverson in 1968 [81]. Eden and Skerry were the first to apply ENM to the study of organic coatings [82] and were soon joined by other laboratories. It was found that changes of the noise resistance with time were in general agreement with the known performance of several coating systems. However, Mansfeld and co-workers emphasized the need for analysis of noise data not only in the time domain, but also in the frequency domain in order to obtain mechanistic information [83]. Therefore, the spectral noise resistance, obtained through Fast Fourier Transforms

Table 16.3 Overview of some (standardized) accelerated tests

Test method	Conditions
Continuous salt spray tests	
ASTM B117[a] ISO 9227 (NSS)[b] DIN 50021 SS[c]JIS Z 2371 (NSS)[d]	Continuous, pH-neutral salt spray (5% NaCl at 35 °C).
Immersion test	
ASTM D870[a]	Coated specimens are partially or completely immersed in distilled or demineralized water at ambient or elevated temperatures.
Humidity tests	
ASTM D2247[a] ISO 6270[b]	Coated specimens are exposed to atmosphere maintained at approximately 100% relative humidity with the intention that condensation forms on the test specimens.
Cyclic tests	
ASTM G85 Annex 5[a]	Wet and dry cycling (1 h of fog (0.05 wt% NaCl + 0.35 wt% $(NH_4)_2SO_4$) at ambient temperature and 1 h of drying at 35°C).
ASTM G 154[a] ISO 4892–3[b]	Coated specimens are exposed to alternating UV/condensation cycles.
Advanced cyclic tests	
ASTM D5894[a] ISO 20340[b]	Alternating UV/condensation cycles and wet/dry salt-spray cycles. ISO 20340 includes an optional freeze cycle.
Automotive tests	
GM 9540P/B (General Motors)[e]	Wet/dry and humidity cycling. Electrolytic solution: 0.9% NaCl, 0.1% $CaCl_2$, 0.25% $NaHCO_3$, pH: 6–8. Total cycle time: 24 h. The typical duration of the test is 80 cycles (1920 h).
CCT-I, IV (Nissan)[e]	Wet/dry and humidity cycling. Electrolytic solution: 5% NaCl. The typical duration of the test is 200 cycles (1600 h) for CCT-I and 50 cycles (1200 h) for CCT-IV.
VDA 621-415[e]	Wet/dry and humidity cycling. High time-of-wetness, poor correlation for zinc pigments and galvanized steel. Also used for testing heavy infrastructure paints.

Table 16.3 Continued

Test method	Conditions
HCT (Hoogovens Cyclic Test)[e]	Based on actual weathering conditions in the Netherlands. The test simulates two years of exposure including daily and seasonal variations in 1680 hours. The temperature and relative humidity are varied from respectively 25 to 50°C and 50 to 98%. Test specimens are periodically dipped in an electrolyte. The composition of the electrolyte differs during winter and summer simulations.
VICT (Volvo Indoor Corrosion Test)[e]	Different variants exist. Stresses used are temperature, humidity and salt solution (spray or submerged). Tends to produce filiform corrosion at scribes. The typical duration of the test is 12 weeks.
SAE J2334[f]	24 h cycle consisting of: 6 h 100% relative humidity at 50°C, 15 min salt application (0.5% NaCl + 0.1% $CaCl_2$ + 0.075% $NaHCO_3$) and 17 h 45 min drying at 60°C and 50% relative humidity. The typical duration of the test is 60 days.
Other tests	
Kesternich: ASTM G87[a] ISO 3231[b] DIN 50018[c]	8 h exposure to water vapour and sulphur dioxide at elevated temperature and humidity levels, followed by 16 h of ambient laboratory conditions. Test originally designed for bare metals exposed to a polluted industrial environment.
SCAB (Simulated Corrosion Atmospheric Breakdown) test: ISO 11474[b]	Accelerated outdoor corrosion test. Test specimens exposed outdoors are periodically sprayed with a salt solution.

[a] ASTM International – American Society for Testing and Materials
[b] ISO – International Organization for Standardization
[c] DIN – Deutsches Institut für Normung e.V
[d] JIS – Japanese Standards Association
[e] Corporate standard
[f] SAE International – Society of Automotive Engineers

(FFT) of potential and current fluctuations, was introduced. This method not only allows one to evaluate the frequency dependence of noise data, but also enables a direct comparison with the modulus of impedance obtained with EIS. This practice has been successfully applied by several workers [82–84]. ENM and related analysis methods are only starting to

Table 16.4 Common standardized evaluation methods of specimens subjected to accelerated tests

Standard	Aspect	Description
ISO 4628-2, ASTM D714	Blistering	These standards describe a method for assessing the degree of blistering of coatings by comparison with pictorial standards. The ISO standard has adopted the pictorial standards from ASTM and includes the correlation between the ISO and ASTM rating systems.
ISO 4628-3, ASTM D610	Rusting	These standards describe a method for assessing the degree of rusting of coated steel surfaces by comparison with pictorial standards. The ISO standard includes the correlation between the ISO and ASTM rating systems.
ISO 4628-4, ASTM D661	Cracking	These standards describe a method for assessing the degree of cracking of coatings by comparison with pictorial standards.
ISO 4628-5, ASTM D772	Flaking	These standards describe a method for assessing the degree of flaking (scaling) of coatings by comparison with pictorial standards.
ISO 4628-6, ISO 4628-7, ASTM D42148	Chalking	These standards describe methods for assessing the degree of chalking of coatings by comparison with pictorial standards.
ISO 4628-8, ASTM D1654	Delamination and corrosion	These standards specify methods for assessing delamination and corrosion around a scribe in a coating on a test panel or other test specimens. The ISO standard describes one method which involves the use of pictorial standards. Both standards include numerical rating of failure.

mature, but this technique appears very promising for the study of organic coatings.

Maintenance and repair

Maintenance and repair are extremely important in achieving design lifetime. However, it is a field in itself and somewhat out of the scope of this chapter. Therefore we restrict ourselves to the objectives and we give some important issues to reflect on. The objectives of maintenance and repair are:

- Prevention of needless corrective measures during service life, e.g. by proper and regular cleaning procedures
- Repairing in the best possible way, as quickly as possible, at the lowest costs, with little inconvenience to users
- Optimizing maintenance costs, minimizing non-operational time, optimizing life-cycle costs of the structure.

Important issues are:

- Accessibility to inspection and action
- Built-in, easy to apply test devices (intelligent pig, corrosion samples/electrodes, capacity sensor)
- Maintenance manuals
- Expert diagnosis.

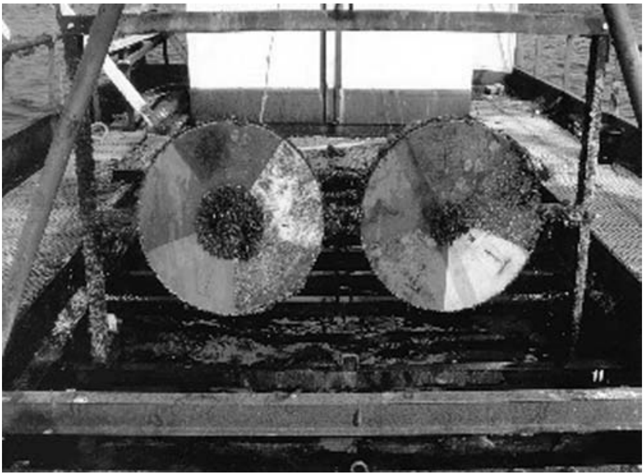
16.5.2 Protection against fouling

Assessment of performance

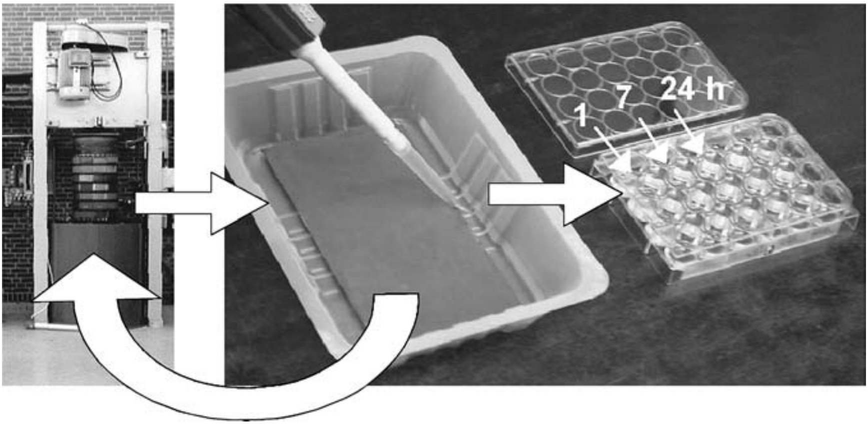
The most common way to determine the performance of antifouling coatings is to expose panels with antifouling in a natural sea location (Fig. 16.7). However, this is time consuming, especially if long-term activity is expected, and not suitable for development purposes. On the other hand, because of the quiescent situation, this test can be considered as more severe than in conditions encountered in practice. A practical test is the use of test patches on ships. This test is suitable for products that are already developed.

For development purposes and prediction of performance a number of laboratory tests have been developed. For example, rotor tests according to ASTM D4939–89 are used to determine erosion rates of self-polishing coatings in natural seawater under different conditions (5–25 knots and at a temperature of 10–35°C). The erosion rate is a measure of biocide release, giving reliable indications for long-term performance. The same equipment is used for accelerated ageing of coated panels, which can then be subjected to bioassays with barnacle larvae or raft exposure. In this way additional information on long-term performance of coatings is obtained (Fig. 16.8).

As stated in Section 16.4, Fouling Release Coatings are non-toxic coatings that do not prevent settlement but provide fouling organisms a bad surface to adhere to. For such coatings static immersion testing is inadequate. For example, ASTM D5618-94 is a standard test method for measurement of barnacle adhesion strength in shear that is used for efficacy determination. Comparison of adhesion strengths on newly coated and (raft) aged panels gives valuable information on long-term coating perfor-

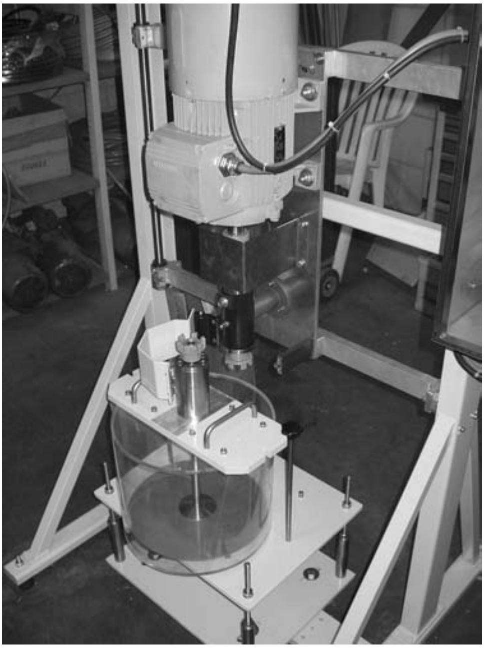


16.7 Test discs on the raft in a natural sea location: the harbour of Den Helder, The Netherlands.



16.8 Combined rotor and bioassay test to assess the ageing and efficacy.

mance. Another criterion for efficacy assessment of FRC is the critical speed at which fouling organisms detach from the surface. Such critical speeds can be determined using rotary equipment with coated panels or discs that are subjected to various rotation times and regimes. Figure 16.9 shows an example of a rotary apparatus suitable for measuring critical speed and drag in resistance. Combining this with ageing procedures gives valuable information on long-term performance of FRC.



16.9 Instrument for drag resistance measurements.

16.6 Conclusions and future trends

This chapter describes the mechanisms of corrosion and fouling protection as well as failure mechanisms of coating systems in marine and shipping applications. The ideal status is a truly durably protected structure, while costs are minimized over the lifetime. In order to achieve this situation proper design of protected structures is needed, while maintenance and eventual repair remain important.

Environmental issues nowadays rightfully require new approaches in coating technology, but they also make market introduction of new coatings cumbersome. Assessment of the performance of coatings under development and in practical conditions is vital, but sometimes extremely difficult. Accelerated testing remains a field with a huge potential for improvement, especially important for the development of new coatings. Two approaches can be followed in principle: acceleration of the degradation process by enhancing the aggressiveness of the medium, with a risk of changing the degradation mechanism leading to false conclusions, or enhancing the sensitivity of the test method under normal conditions, ensuring the mechanism remains unchanged. The second approach is the better one, but requires much R&D to cover the various degradation mechanisms. The authors expect that the development of sensitive testing methods will be the major tool for design of new coating applications together with fundamental studies on the adhesion of coatings to metallic substrates at the molecular level.

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17

Organic coil coating of metal

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17.1 Introduction

Coil coating is a metal anticorrosive protection technology developed to promote the use of steel and aluminium in the most varied environmental conditions such as roof and wall elements in the building industry, casings for household appliances and internal parts or bodywork structures for the automotive industry.

The process was started in the middle of the twentieth century in North America by Joseph Hunter who designed his line to assist local manufacturers of blinds (Drufke, 2006). With this process high performance liquid coatings could be applied to flat metal sheets or strips packaged in rolls or coils, like pre-painting, in a range of colours, cured in seconds and recoiled. The main metal substrates used in the coil coating process are galvanised steel, cold-rolled steel, electrogalvanised steel and aluminium. In addition, coil coated metal can be formed without any loss in surface quality or appearance. Usually, coil coated products have been most dominant in the building market. However, the use of this technology has increased and coil coated products also appear in our homes and workplace as casings for domestic appliances such as microwaves, refrigerators and washing machines. Characteristics such as the reproducible manufacturing process, lower cost and reduced environmental impact have contributed to increase use of the coil coating process (Seija, 2007).

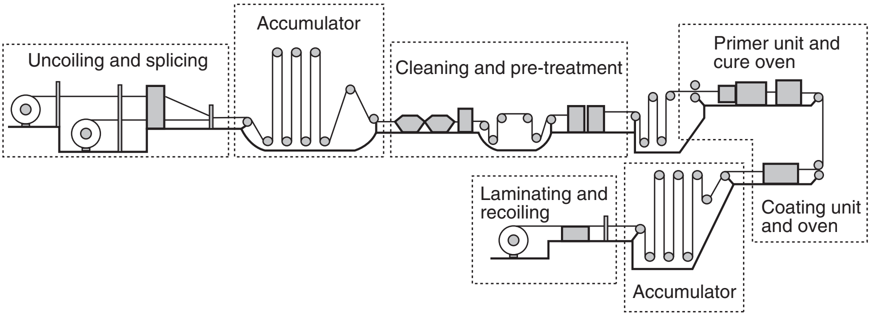
In this chapter the coil coating technology will be explored. At first the process will be explained, together with the procedures involved in it and some information about the development of coil coating. The different applications and end uses of coil coatings will be shown. Lastly, coil coating tendencies and progress will be explored in order to exemplify and reinforce the importance of the coil coating process nowadays.

17.2 Understanding the coil coating process

Metal coil surfacing, known as coil coating, is a continuous process by which protective or decorative organic coatings are applied to flat metals in rolls or coils. The metal substrate is delivered in coil form from the rolling mills. The metal coil is placed at the beginning of the line, and then unrolled at a constant speed, passing through various pre-treatment and coating processes before being recoiled. Figure 17.1 presents a diagram to give a better understanding of the process. In some installations, the wet section contains an electrogalvanising operation. Most coil coating lines have accumulators at the entry and exit that permit continuous metal strip movement through the coating process while a new coating is mounted at the entry and/or a full coil removed at the exit. Some important aspects that could be observed in a coil line are that production gives minimal pollution with little waste product, productivity is improved with reduced processing time, wastage of raw materials is decreased, and bottlenecks are substantially reduced or totally eliminated. Coil lines typically run 24 hours a day, five to seven days a week, and are more than capable of coating over 4.5×10^6 kg of steel or 2.2×10^6 kg of aluminium per week. In addition, the process complies with the most demanding conditions of pollution control regulations (Drufke, 2006).

Coil coating in general is dependent on several factors, such as the nature of the substrate, the properties of the coating materials, the speed of application, the roll pressure and the temperature and humidity in the application area. A fundamental principle of coil coated material is that the material travels through the various process sections in a continuous manner without ever stopping or changing speed. As a result, consistent properties are obtained in the coated material (Drufke, 2005b).

One of the advantages of the coil coating process is the cleaning and treating section. Because the metal is in a flat form and in a suspended position, the cleaning and treating are done thoroughly. This is a unique



17.1 Coil coating flow diagram.

quality of the coil coating operation and is a central reason why coil coated products perform in such a superior manner (Froehlich, 1998).

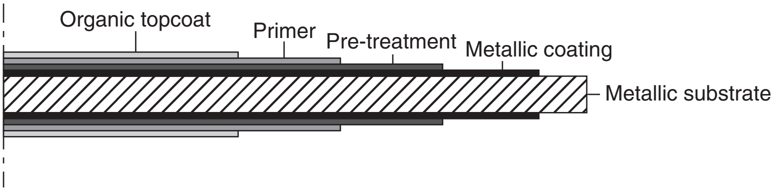
Although the physical configurations of coil coating lines are different from one installation to another, the operations generally follow a set model of common steps or processes: uncoiling the bare metal, cleaning, treating, painting, curing, cooling and rewinding the same coil for shipment or further process. Some of these steps will be explained in detail in sequence.

17.2.1 Cleaning and pre-treatment

These procedures are the first on any coil coating line. The purpose of this section is to create an oil-free surface that enables better fixation of a subsequent organic coating. The metal moves through a sequence of tanks that serve to both clean and treat the surface by chemical conversion. Generally a freshwater rinse tank follows each cleaning tank, which is usually equipped with a high pressure pump feeding a series of spray bars that clean both sides of the metal. Variable solutions are used in these tanks: alkaline and acid solutions, electrolytic solutions, sometimes steam and mechanical brushing rolls within the tanks contribute to the cleaning. The chemical treatments of the metal surface start after cleaning. Chemical treatments are useful to inhibit rust and to promote coating adhesion to the metal surface. One of several different chemical formulas is used in this step, each being specially designed for the particular metal substrate, application technique and planned end use (Froehlich, 1998). Nevertheless some of these chemical conversion coatings use hexavalent chromium, which is strictly regulated due to the toxicity of its compounds and suspected carcinogenicity. Hence coil coaters, chemical suppliers and researchers are working on eliminating chromium from their process and waste streams (Duarte *et al.*, 2005; Drufke, 2005b). In this respect, many different new treatments have been proposed, for example pigments based on phosphates, zinc compounds or barrier coatings without inhibitive pigments (Deflorian *et al.*, 2000).

17.2.2 Coating application

There are several general classes of coil coating lines; the choice of system depends on a combination of life expectancy and commercial considerations. There are a number of coater designs depending on the configuration of the coil line, types of coatings being used and types of metal being coated. In almost every case, however, the coater is equipped with a vessel, a steel or ceramic pickup roll and a rubber-covered coating roll. The coating is circulated in the paint vessel. A rotating pickup roll is partially immersed in the coating and rotates in a counter-clockwise direction. The coating is



17.2 Coil coated metal cross-sectioned.

then transferred onto the coating roll which is rotating in the reverse direction to the roll coating, from where it is applied to the substrate. By adjusting the pressure between the transfer roll and the coating roll, the film thickness can be controlled (Graziano, 2002). To promote coating curing, the coated strip is heated in an oven at a temperature in the range 300–500°C. The dwell time of the coil coating is from 15 to 60 seconds and the upper limit for the metal temperature is 250°C, known as the Pick Metal Temperature (TMP), above which organic material might oxidise (Korhonen *et al.*, 2003).

A two-coat paint system is normally used. Lines for this are called tandem lines and can apply a primer and a top coat in a single pass (Drufke, 2005b). The primer is usually applied directly onto the pre-treated metal surface and will probably contain anti-corrosive pigments to protect the metal substrate from corrosion and also to prevent the undercutting of paint, safeguarding the durability of the product and overall quality. Various primers can be selected to help create an industry-specific coating system that maximises the performance of the product for special end-use applications. Primers are used on galvanised and cold-rolled steel for exterior exposure or when water-borne finishes are applied to steel or aluminium. Epoxy esters are mainly used for more demanding applications (Paul, 1996). The second coat of finishing paint provides the colour and appearance of the final coated system, and plays a large part in the system's weathering and mechanical performance. Figure 17.2 illustrates a coil coated metal. The dry film thickness of the coatings is usually 5 to 35 microns for a primer and 15 to 200 microns for a topcoat, and is determined by the quality of the paint chosen and the pre-coated metal's final usage.

17.2.3 Curing

The curing section of coil coating lines is an important step during the process. Although the ovens may look the same from the outside, there are important differences that have a substantial effect on the actual process of removing solvents and curing the coating. The industry usually utilises a natural gas convection oven with control of solvent concentration in order to improved energy efficiency. The ovens are also equipped with appropriate incineration technology to ensure that solvent emissions are destroyed before being emitted to the atmosphere (Froehlich, 1998). Some coatings require a very high curing temperature and high impingement flotation ovens become necessary; these kinds of ovens have increased line speeds because of better energy transfers. In the case of water-based coatings, electrical and gas-fired IR ovens could be used, once these ovens benefit from reduced maintenance costs.

The degree of cure of the system is of fundamental importance, since it influences the mechanical and adhesive properties of the resulting coating. Undercured systems lead to soft, weak films with poor durability. In contrast, degradation of the coating can also occur for overcured systems, which leads to problems of brittleness (Perruchot *et al*., 2003).

17.2.4 Quality control

The pre-painting process is designed to produce highly uniform and perfect quality coatings. The coatings are precisely applied with special equipment that provides a high-quality finish, which permits various processing procedures such as cutting, punching, parting, perforating, bending and sketch to be executed with the organic coating already applied to the metal surface. To avoid damaging the paint, the tools used need to be in very good condition and extreme care must be taken during the processing work (Seija, 2007). Manufacturers using coil coating metals will find consistent colour, texture, thickness and performance in their finished products. Moreover, the coatings are strongly bonded to the metal and frequently are applied to both sides of the metal and could be available in various degrees of gloss, colour, texture, flexibility and combinations of them. In addition, products must conform to exacting specifications agreed to by the supplier, coater and end-user.

In order to ensure the best results, numerous quality control tests are performed during the coil coating process. Usually, samples are removed at various stages of manufacture, and the factory mixing sheets are usually designed to show the results on intermediate and final tests on a batch of paint (Morgans, 1990). First of all, before coating, the physical performance of the paints and the metal substrates is tested. Properties like colour, viscosity and gloss are investigated. The uniformity of viscosity is essential for modern production where continuity of supply is involved. During the entire coating process the surface treatment is tested and adjusted; this procedure ensures a high-quality finish. Likewise, the paint thickness, curing temperature and production line speed are controlled and measured (Seija, 2007).

Although protection is generally the first priority, the appearance of the finished structure is also of importance. Accordingly, after production, some coated parts are taken away to test laboratories in order to investigate the coating performance, including characteristics like gloss, colour, hardness, adhesion, and resistance to cracking and damage.

In the case of coil coating, flexibility is a very important property, which is estimated on the film attached to a substrate by some kind of bending or flexing operation. Another important property related to the performance of paint films is adhesion, which is influenced by a number of factors, among them the nature of the coating and of the surface. The durability of coil coated material is dependent on good adhesion throughout its lifetime. Some of the tests used to measure surface-coating adhesion are the scratch test and the peel test, both destructive methods (Paul, 1996). ASTM reference standards can be used to study certain properties such as surface hardness (ASTM D-3363), impact resistance (ASTM D-2794) and the ability to be bent or deformed as a cured coating (ASTM D-522 and ASTM D-4145).

Besides that, pre-painted parts are examined for corrosion resistance, heat resistance, accelerated ultraviolet and environmental exposure. Other tests conducted on coil coated parts include stain resistance, welding capability, and resistance to abrasion. Some end-uses require additional test procedures including chemical resistance properties. Although paint formulations are designed to meet strict requirements for salt spray, humidity resistance and durability, coupons cut from the coil stock may also be subjected to these tests as an ongoing quality control programme (Graziano, 2002).

17.3 Substrates and paints

With a coil coating process a range of substrates could be painted such as aluminium, carbon steel, galvanised steel, galvalume®, stainless steel and zinc-aluminium alloys. In fact, practically any type of flat material can be coated on either or both sides and at the edges; moreover the coated materials can be handled in sheets or coils. The choice of substrate used depends mostly on physical dimensions and mechanical properties, such as the corrosion resistance and chemical resistance required, with respect to the product's eventual use and location.

The current European market for coil stock is some 8×10^8 m^2, of which approximately 80% is steel and the remainder is coated aluminium (Lavaste *et al.*, 2000). This difference could be related to the mechanical properties of these two materials associated with the cost-effectiveness of steel. The mechanical properties of steel provide ideal conditions for optimal crashworthiness, superior formability and weldability if we are thinking of the automotive industry. The elastic modulus of steel is almost three times that of aluminium, related to the stamping performance; aluminium will possess higher springback than steels (Ashby and Jones, 1996). In roofing applications steel also has more advantages than aluminium, because of its inherent strength and dent resistance. Because of their low tensile strength and high degree of thermal expansion and contraction due to temperature variations, aluminium flat pan architectural roofing panels often exhibit an unacceptably high degree of waviness and distortion. The low melting point of aluminium could be another obstacle to its use in structures or buildings. Aluminium melts quickly in a fire, much quicker than steel, which causes safety issues in structural designs. Despite these differences, both substrates need to be flat with a thickness of about 0.25 to 2.0 mm and are able to support stamp processes. In this respect, steel and aluminium could both be coil coated on a large scale as substrate. The next consideration is which coating should be used.

Some properties are very important for coatings that will be applied in the coil process. The first refers to application: the coating should be easily applicable and give uniform appearance and defect-free films even on the fastest production lines. Another factor is cure time which must be very short, in order not to damage the pigment colours. The time spent in the oven can vary from 6 to 60 seconds depending on the line; the substrate temperature is between 210°C and 250°C according to the paint used. Lastly, flexibility enables the coated metal to be bent without cracking or loss of adhesion of the paint film (Drufke, 2005c, 2006). The key properties for a successful coating are that it must confer good corrosion resistance, and an appropriate level of adhesion to the substrate which allows good formability of the coated coil stock, allowing complex components to be manufactured without damaging the coating (Crunkhorn *et al*., 2005). An important characteristic of coil coatings is that the coating must be able to be applied at up to 3.5 m/s, flowing equally at this speed without any evidence of blister, sags or leaks (Drufke, 2006). This way, the basic parameters for coil coating formulations provide package solids in the range of 50% by weight and viscosities of 100–150 s^{-1} (Graziano, 2002).

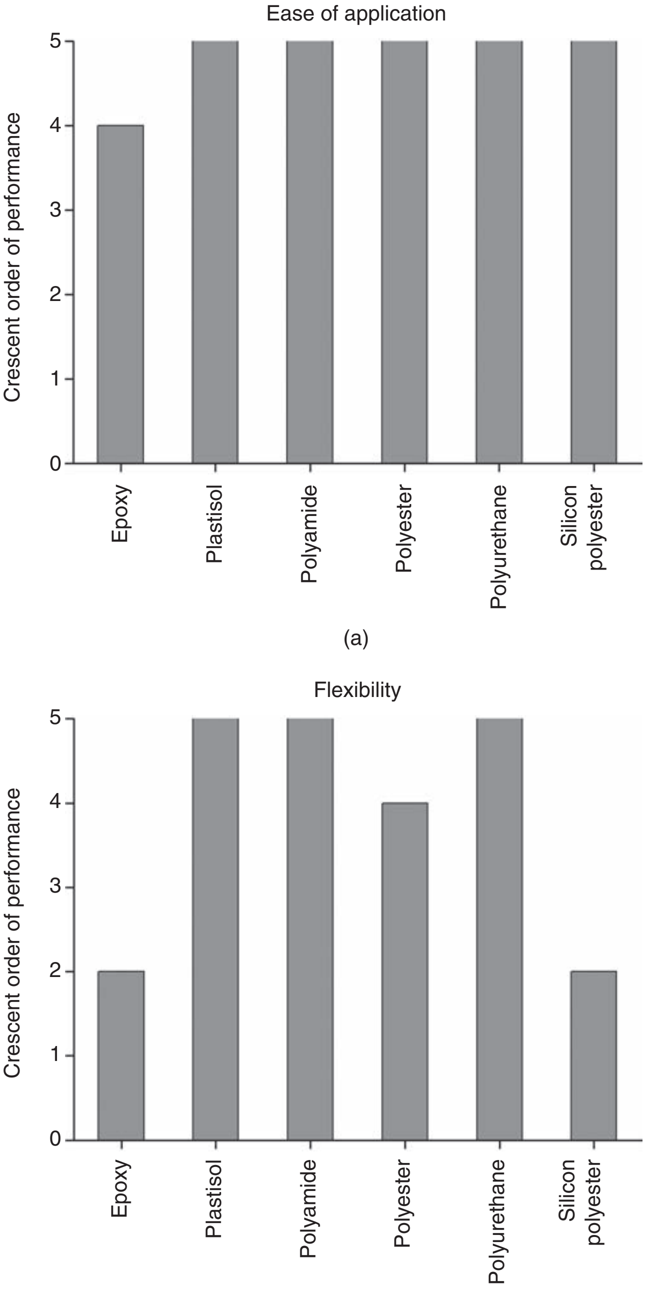
Thermoset resins are rarely used for commercial coating applications without the incorporation of other materials, since a successful coating requires properties which cannot be obtained by any one component alone. Generally the coatings consist of a combination of catalysts, hardeners, fillers and additives. Catalysts and accelerators are used to reduce the processing time. Hardeners modify the reaction rate, and in addition change the final properties of the thermoset resin, such as its network structure and dynamic mechanical properties. Fillers are useful to provide or enhance physical properties such as modulus, thermal expansion and dimensional stability, thermal and electrical conductivity, and also help to reduce costs.

Thermal stability is obtained by additives that can also improve the burning characteristics of the resins (Korhonen *et al.*, 2003). The variety of coatings available is almost unlimited and includes polyesters, polyurethanes, epoxies, vinyls, plastisols, acrylics, waterborne emulsions, zinc-rich coatings, fluorocarbons, dry lubricants, and treatment and primer combinations. About 85% of the coatings used are organic solvent-based and have solvent contents ranging from near 0 to 80% v/v, with the prevalent range being 40–60% v/v. Most of the remaining 15% of coatings are waterborne, but they contain organic solvent in the range 2–15 vol%. These volatile organic compounds (VOC) are the major pollutants emitted from coil coating operations (Anon, 1995).

Moreover, product quality is continually improving as a result of new industry-specific coatings that are regularly coming onto the market and advanced testing performed throughout the coil coating process. An estimate of some relative properties of the main types of coil coatings is presented in Fig. 17.3a–d; these data were obtained from the Becker site. Polyester resins are the most commonly used system for internal and external applications, and are increasingly used in combination with polyurethane resins. Combinations of polyester resins with amine resins or polyurethane base resins dominate the scene of coil coating paints with a share of about 60% (Korhonen *et al.*, 2006). Increased understanding of the mechanics of breakdown at the molecular level has enabled the performance of polyesters to be progressively improved. The polyester coatings were cheaper and had a greater range of thicknesses. A secondary but significant effect is that the coaters were finding that they had a reduction in oven fires and explosions because of the higher volume solids found with the polyesters. Many people believe that the introduction of polyesters in coil coating is the single biggest reason for its rapid development. Polyesters allowed the coaters to dramatically expand their pallet of colour and gloss offerings (Drufke, 2005c).

Another resin used when a high-performance external coating is desired is polyvinylidene (PVDF), which has an exceptional weathering stability and produces the most durable formulations for coil coating. PVDF is extremely resistant to UV-induced radical attack, although it exhibits poor adhesion that could be improved by applying it onto an epoxy primer, which is highly susceptible to UV attack (Hatcher, 2001).

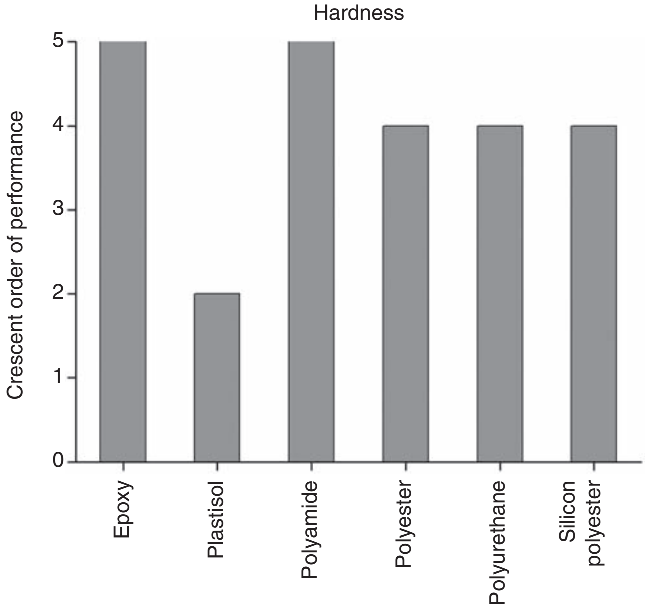
In environments where corrosion is a prime requirement, PVC plastisol is largely used, e.g. in marine coatings. Vinyl resins are widely used in surface coatings and exhibit good colour, flexibility and chemical resistance. On the other hand, these resins are very vulnerable to heat, UV radiation and oxidising agents, evolving hydrogen chloride. Therefore, it is essential to add appropriate stabilisers to obtain satisfactory long-term properties (Paul, 1996).



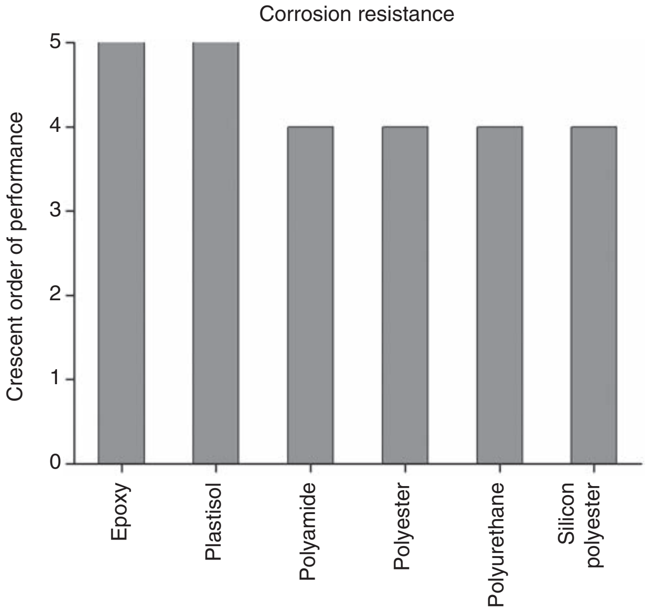
(a)

(b)

17.3 Performance in terms of (a) ease of application, (b) flexibility, (c) hardness, and (d) corrosion resistance of some coatings used in the coil coating process.



(c)



(d)

17.3 Continued.

Fluorocarbon resins present very good performance with respect to exterior weathering properties, particularly colour and gloss retention. Because of these properties and performance, these fluorocarbon coatings have become the choice of architects. These fluorocarbon resin and paints cure on the coil coating line under heat by a chemical reaction, not simply a heat fusion (Ballway, 2007).

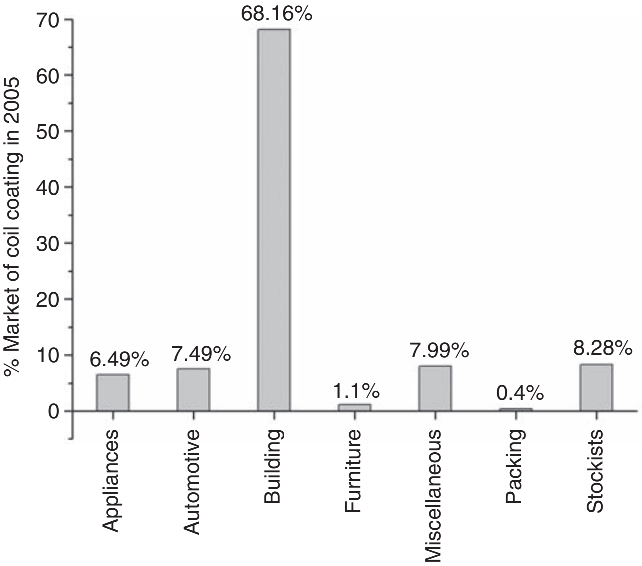
For many years, silicone resins have been used to improve the weather resistance of organic coatings. The chemical combination of silicone and organic resins gave a higher degree of compatibility, allowing a broader range of organic resins to be used. According to Easton and Poultney (2006), the success of silicone-alkyds in naval and military applications led to the evaluation of silicone-organic copolymers in coil coatings for residential and commercial aluminium sidings. Other organic resins could be modified by silicone such as polyesters and acrylics, giving better weather resistance of exterior coatings (Easton and Poultney, 2006).

17.4 Coil coating uses

Today, coil coatings are used extensively in at least three markets: building, transport and furniture. Thousands of products in different industries are made more efficiently with pre-painted metal and new applications make the switch every year.

With regard to construction, it is known that architectural applications make up the largest customer demand for coil coating. This is justified by the use of pre-painted metal as an extremely practical and functional solution in a wide range of situations and locations, such as in roofing, exterior and interior panels, garage doors, etc., from farms to factories, from stations to stadiums. In its turn, the transport market includes the automotive industry in which pre-painted metal has been used for body panels, in fuel tanks, bumpers and other components. Coil coating is also used in other forms of transportation, such as railway carriages and tube trains. For example, pre-painted aluminium is often used for the exterior coatings of caravans, mobile homes and lorry containers because it is light, corrosion-resistant and flexible. Coil coatings have been extensively used by household electrical goods manufacturers, since it removes the painting process from the factory, improves productivity and reduces processing costs. The segments of products are various: washing machines, ovens, microwaves, refrigerators, air conditioners, computers, small electrical appliances like mixers and toasters, not to mention office and school furniture, storage and shelving systems, light fittings and extractor hoods. Figure 17.4 shows the main coil coating market in 2005.

Today, more than 800 million tons of coil coated steel and aluminium are produced and shipped in North America alone each year. Industry



17.4 Main coil coatings markets in 2005 (steel and aluminium).

leaders using coil coated metal include GE, Whirlpool, Trane, Mercedes Benz, Nordyne and Steelcase, to name just a few (Seija, 2007).

The use of coil coating metals has grown in numerous applications for many reasons. In some applications pre-painted metal can offer superior coating performance when compared to metal painted after fabrication. Another point is that modern coil lines can produce as much metal coil pre-painted and the final material could be obtained as laminates, coined, printed or lubricated with coatings of oil or wax in the same line operation. Multilayer materials can also be obtained from the same coil coating line, just by changing the paint to adhesives/polymers and another plate, with adequate programming of the equipment. These multilayer composites with various viscoelastic cores among layers of metal are designed specifically to meet the damping, temperature, stiffness and operating environment needs of their intended component (Vaskevicius, 2005). Consequently a variety of decorative and functional items such as skins for humidifiers, kitchenware, automotive gaskets, and sound-damped composites could be produced in this manner.

There are very many end-uses for coil coating and researches are being conducted continuously in order to develop new products. This fact has played a significant role in the growth of coil coating and is likely to continue to maintain its impact in the future.

Much information concerning coil coating and its applications is available on the internet. On the website of the National Coil Coating Association

(NCCA), some e-learning modules and online videos are used to give information about the process and how to pre-clean, pre-prime, pre-treat, and/or pre-paint metal effectively, for beautiful and economical results (http://www.coilcoating.org/). The website of the European Coil Coating Association (ECCA) presents information about the history, type of coatings, end uses and advantages of the coil coating process (http://www.eccacoil.com/). To know about regulatory and pollution prevention information for businesses engaged in painting and coating, consult the website of the Paint and Coatings Resource Center (PCRC) (http://www.paintcenter.org/). To learn about coating innovations the Specialchem site gives much information in the domain of speciality chemicals, including the industry platform *Coating & Inks – Innovation & Solutions*, with technical letters and industry news (http://www.specialchem4coatings.com/). Some industries have in their websites complimentary information about the coil coating process, kinds of substrates and paint that they use, and applications of their products, such as Becker Industrial Coatings (BIC), the industrial paint division of AB Wilh.Becker (http://www.beckers-bic.com) and Companhia Siderúrgica Nacional (CSN) (http://www.csn.com.br).

17.5 Future of coil coating

In recent years coil coating production has been increasing, exceeding the growth rates of both steel and aluminium production, although its growth rate is inherent to the success or failure of the new products that have been introduced (Drufke, 2005d). The advantages of pre-painted metal could be held to be responsible for the constant enlargement of this technology, such as the reproducible manufacturing process, lower cost and reduced environmental impact.

New coating and process development is the way ahead for the evolution of coil coating. Many efforts have been made to find new applications and markets for coil coating products, diversifying their end-uses. Investigations of new resins and improvements in their properties such as cure temperature, corrosion and scratch resistance and abrasion have been made by various researchers (Lange *et al.*, 1999; Chico *et al.*, 2003; Perruchot *et al.*, 2003; Rossi *et al.*, 2007). These activities reinforce the perspectives about the evolution of coil coating products and their uses.

Concern about environmental impact is another factor that has been the subject of much attention by researchers in coil coating industries and institutes. They have been working on the production of new surface pretreatments and painting cycles with better environmental compatibility. Toxic pigments, for example chromates, used in organic coating formulations are being progressively replaced by chromium-free ones, inasmuch as they exhibit sufficient corrosion protection properties without a negative impact on the environment (Bittner and Heubach, 1989; Duarte *et al.*, 2005).

Reducing the amount of solvents that are eliminated from coil lines is another challenge for the coil coating industry and researchers. Curing with UV light appears to be a solution to providing environmental safety; in addition, low temperatures are required, reducing the costs of the process. In this process, the solvent acts as a reactive thinner during the curing process, with the result that there are no significant VOC emissions (Spyrou, 2006). The possibilities provided by this technology are particularly promising for coil coating.

In view of what has been described in this chapter, it is possible to observe that for a manufacturer using painted steel, aluminium or other metals in the production process, coil coating can considerably improve productivity, associated with a reduction in processing costs, quality improvement and fewer environmental concerns, all at the same time. So, the advantages of coil coating metal are many, and a number of opportunities for the world of coating companies are obvious. From the standpoint of Drufke (2005a), both the major and niche producers need to take a serious look at the next generation of products with new technologies and new methods of application. Those chemical and coatings companies that are working in partnership with the coil coaters will certainly ensure that their companies do not fall behind in these exciting times of growth and innovation.

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18

High-performance organic coatings for wastewater treatment plants

D DHAGE, EWAC Alloys Ltd., India

18.1 Introduction

High-performance coatings can be defined as coatings that are applied at high film build, in order to provide exceptional resistance and durability, particularly to aggressive environments. High-performance coatings perform under harsh exposure conditions such as extremely polluted industrial environments, marine environments, splash zones and spillage areas. High-performance coatings show resistance over a wide range of pH, strong resistance to acids and solvents, and also properties of high electrical resistance, strong adhesion to the substrate and resistance to marine organisms. Typical applications where high-performance coatings are extensively used are storage tanks, pipelines, scrubbers, ducts, marine constructions, harbour facilities, etc.

The high-performance anticorrosion coatings that are designed today are able to achieve longer service life with consistent performance over 15 years. These coatings are used to protect metals, concrete structures, tanks, pipes and processing equipment from deterioration, caused by exposure to corrosive environments. This chapter deals with the application of high-performance glassflake reinforced coating systems to combat corrosion in wastewater treatment plants.

In recent years, a lot of attention has been given to reducing the effect of waste material on the natural environment and to recover resources from it. Clean water is essential for everyday activities, personal health and industrial usage. These activities result in production of unwanted or undesired materials generally called waste. Wastewater travels from collection systems to wastewater treatment plants where it is treated and discharged to rivers, lakes and streams.

In India, nearly 27.022 million litres of sewage waste is generated per day across the country. The current wastewater treatment plants are capable of treating only 18.6% of the total amount. In Mumbai, 50% of the sewage goes untreated into the Arabian Sea. With such marginal sewage treatment, many Indian rivers are heading towards environmental disaster [1].

Wastewater treatment plants control processes and equipment to remove or destroy harmful substances, chemical compounds, and microorganisms in the water. The waste exists in different forms, viz., solid, liquid and gas. With increase of industrial activity and the various complex processes involved, the complexity of the waste has increased manifold in waste treatment plants.

A total investment of Rs 7655 crore is estimated for treating the entire sewage waste throughout India. Often, the present treatment plants are running beyond their capacities, in turn demanding higher life for waste treatment plants in the future.

18.2 Categories of waste treatment plants

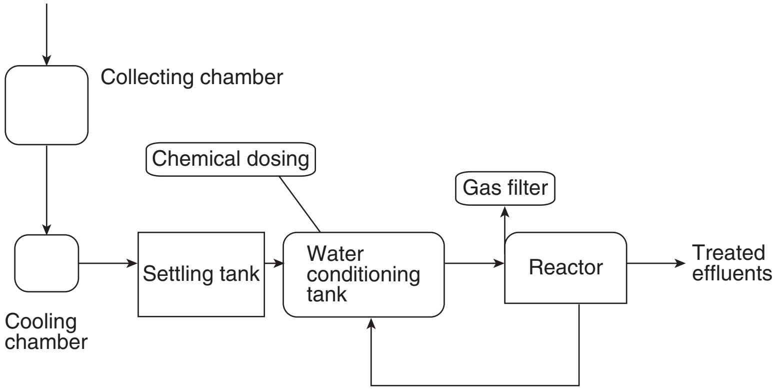
Waste treatment plants can be categorized as below:

- Industrial waste treatment plants
- Common effluent treatment plants
- Municipal waste treatment plants.

18.2.1 Industrial wastewater treatment plants

Industrial wastewater treatment plants treat water that has been generated in various industrial processes by contamination due to industrial activities, before releasing it into the environment or reusing it. The various industries that generate wastes are as follows:

- *Iron and steel industry*. The iron and steel industry waste involves contaminated products like ammonia, cyanide gasification products such as benzene, naphthalene, phenols, cresols and range of organic hydrocarbons in waste streams. Wastewater also includes pickling acids and soluble oils.
- *Mining industry*. In the mining industry, the waste is in the form of quarries and slurries. The contaminants are fine particulate haematite, surfactants and oils, especially hydraulic oils.
- *Food and beverage industry*. Waste from the food and beverage industry has a high biological oxygen demand (BOD) and much suspended solids. The waste is often very complex due to its wide range of pH. The waste also includes insecticides, antibiotics, flavouring and colouring materials with acids and alkalis.
- *Chemicals industry*. Chemical industries like pesticides, pharmaceuticals, dyes, petrochemicals, detergents, etc., involve various complex processes. Therefore the resultant waste is also more complex. The waste consists of material in dissolved or particulate form, cleaning agents and solvents.



18.1 Typical industrial wastewater treatment plant.

- *Nuclear industry*. Nuclear waste is generated from fuel that contains small amounts of uranium and thorium. A high level of waste is generated from nuclear reactors containing transuranic elements.

Treatment of industrial wastewater

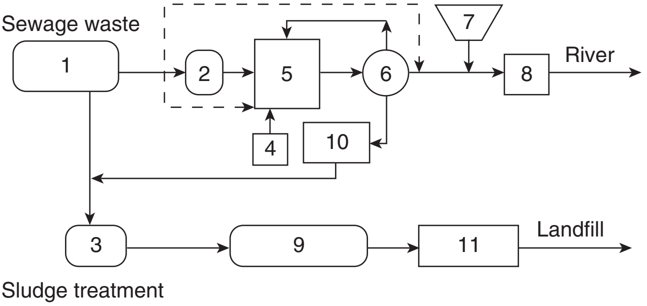
Industrial wastewater treatment plants require different procedures for treating their waste and are specific to their industry. A typical industrial wastewater treatment plant is shown in Fig. 18.1.

18.2.2 Common effluent treatment plants

With exponential increase in small-scale industrial units, a need for affordable and cost-effective waste treatment measures for treating the waste is foreseen. Setting up individual waste treatment plants may not be a feasible solution for small-scale units. Under such circumstances common effluent treatment plants facilitate the proper management of effluent as per the standard norms. Common effluent treatment plants cater for more than one kind of industry and so segregation and pretreatment of the effluent is imperative.

18.2.3 Municipal waste treatment plants

These are generally sewage treatment plants or domestic wastewater treatment plants containing physical, chemical, organic, inorganic and mainly biological contaminants. Municipal wastewater treatment plants face a more aggressive corrosive environment than do industrial waste treatment plants. In industrial wastewater treament plants, the corrosion is often



18.2 Typical sewage treatment plant (see text for description of each numbered part).

below the waterline and predictable. In municipal waste treatment plants, the corrosion is above the waterline and highly unpredictable. Corrosion is mostly induced by biological organisms. Also there are various chemicals in the system that cause severe corrosion.

A typical municipal wastewater treatment plant is shown in Fig. 18.2. In a typical municipal wastewater treatment plant, waste is treated as follows:

1. *Preliminary chamber*. Raw sewage passes through bar screens and grit classifiers.
2. *Bioroughing chambers*. Ultra high-rate trickling filters assist in BOD removal.
3. *Sludge holding tanks*. Biosolids are removed in the primary and secondary processes and blended prior to further treatment.
4. *Aerating plants*. These generate pure oxygen for biological growth.
5. *Secondary aeration reactor*. This mixes oxygen and returns sludge to activate organisms for decomposition of pollutants.
6. *Chemical dosing*. Bleaching agent is mixed with water and injected into the final effluent.
7. *Dechlorination*. The remaining bleach is removed by adding sodium bisulphite.
8. *Effluent pump station*. Treated effluents are finally pumped out.
9. *Sludge thickening and treatment*. This process uses polymer and dissolved air to reduce water content in the wasted secondary biosolids. Biosolids are removed in the primary and secondary processes and blended prior to further treatment.
10. *Sludge solidification*. This treats sludge to reduce water content in the wasted secondary biosolids.
11. *Dewatering systems*. Sludge is conditioned by vacuum filters followed by landfilling.

18.3 Materials of construction and their deterioration

Concrete is the state-of-the-art construction material for wastewater treatment plants. The primary effluent chamber, collecting chambers, structures like dry sludge beds, clarifiers, vessels, trenches and other structures are made of concrete. Even though the concrete used is as per the design, specification and standard, it deteriorates mainly due to the hydrogen sulphide and sulphuric acid generated by microbial activity and various other chemicals present in the treatment plants. Due to the omnipresent nature of microbes and the available nutrients in aqueous environments, there exists microbially induced corrosion and its by-products. These agents ensure loss in concrete and the metal surface of treatment plants.

Hydrogen sulphide generation in municipal wastewater treatment plants has always been associated with severe deterioration of concrete. The biological species are classified in two categories based on the corrosion they engender:

- Anaerobic microbially induced corrosion
- Aerobic microbially induced corrosion.

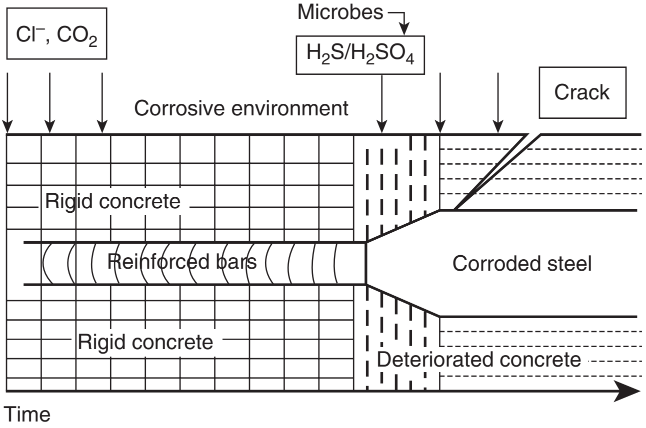
Sulphate-reducing bacteria (SRB), a type of anaerobic bacteria, have a high growth rate of reproduction. Large colonies are formed over shorter periods, which becomes potential sites for the onset of corrosion.

In aerobic conditions, the SRB that are present in submerged structures convert the natural sulphates to H_2S. This process lowers pH, encouraging growth of *Thiobacillus* bacteria. The gaseous H_2S, methane and CO_2 become condensed on wet surfaces in the presence of sulphate-oxidizing bacteria (SOB). These SOBs oxidize H_2S to H_2SO_4 and other mild acids as their waste products. This mechanism makes the surrounding environment highly acidic, resulting in rapid corrosion [2].

Deterioration of concrete in highly aggressive media leads to the corrosion of reinforced bars inside the concrete structure. Coupled with microbial activity and carbon dioxide gases from the environment, there is breakdown of passivity by neutralization of concrete. Associated with this, if ingress of chlorides crosses the threshold value, pitting corrosion of rebars starts, resulting in degradation of the steel reinforced structures embedded in the concrete [3]. Rebar corrosion inside the concrete structure over a period of time is shown in Fig. 18.3.

18.3.1 Corrosion prevention

Concrete corrosion costs crores of rupees every year in repairs. Corrosion reduces the life expectancy of concrete structures and sometimes results in



18.3 Corrosion of reinforced bars embedded in concrete structure.

catastrophic failures. There are various ways to combat corrosion, which are as follows:

- Application of protective coating
- Application of cathodic/anodic protection
- Use of inhibitors and chemical additives.

Protective coatings are not the only means by which corrosion can be prevented, but they are the most important, often the most economic and sometimes the only appropriate method for protecting the structure against corrosion. The performance of a coating depends on the bond between the substrate and the concrete where the concrete should have high surface strength. Concrete having pH between 6 and 9, tensile strength greater than 1.5 N/mm^2, cured and aged at a temperature of 24°C for a minimum of 30 days is recommended for coating [4].

Coating performs the role of a barrier, thereby preventing the external environment from reaching the substrate and thus inhibiting corrosion. Since over the service life the environment penetrates and reacts with the coating, the porosity of the coating is a major factor governing the corrosion of the steel inside. The effect of the environment is evident from changes in the properties of the coating such as resistivity, alkalinity, carbonation and diffusion of chlorides, sulphates, etc. The properties of the steel, such as composition, mechanical working and deformation pattern, also influence the corrosion rates.

Protective coatings do not require inhibitive or sacrificial pigments to provide protection. Coatings provide protection by becoming a physical barrier, or shield and isolate the steel substrate from its immediate environment. A barrier coating must prevent aggressive liquids and gases from passing through it and reaching out to the steel substrate. One important property of a barrier coating is called permeability. The permeability of a barrier coating layer depends on its moisture vapour transmission rate. A lower rate of permeability yields better barrier properties to the coating. Along with this, the basic resin chemistry of coatings also plays an important role. The higher degree of resin crosslinking results in lower permeability and better adhesive bond of the coating to the surface [5].

18.4 Protection by coatings

The purpose of the coating is to act as a barrier between the environment and the substrate metal, as described above, and is a combination of:

- A physical barrier – a non-porous, flawless, defect-free, insoluble coating
- A barrier providing resistance to chemical attack
- An electrical resistor: it offers high resistance to the flow of ions and electrons.

The reactants necessary for corrosion to proceed in normal environments are water, oxygen and sulphur dioxide (SO_2). Aggressive ions (Cl^- ions) can also influence the rate of corrosion by formation of soluble corrosion products.

Concrete corrosion in effluent treatment plants due to the H_2S environment is well established. A couple of decades ago, the concentration of H_2S in the municipal sewerage system was marginal. Presently, the average H_2S concentration reported is about 2–7 ppm. In most of the system headspaces, sulphuric acid concentration has increased from 1% to 7%. Increase of industrial activity, with more complex processes involved therein, and also growing concern with environmental protection activity with the enforcement of stringent laws such as the environmental protection acts of 1986, prohibiting the release of pollutants, heavy metals and creating more headspaces for odour control measures in the environment, have increased the H_2S concentration many times. The resultant effect is a severe increase in the corrosion rate in the treatment plants.

Protective coatings such as coal-tar epoxies have been largely used to protect waste treatment plants against corrosion over the years. But in recent years there has been tremendous change in the exposure conditions of wastewater treatment plants with higher sulphuric acid and H_2S concentration. These changes in exposure should be taken into account when selecting a coating system.

Conventional coating systems such as coal-tar epoxy and amine-cured epoxy with proper surface preparation were providing protection for 10–12 years. But in changed exposure conditions these conventional coating systems are showing premature failure within six months to two years. These failures can be attributed to the insufficient resistance of the coating to acid and the high permeation level to gaseous environments [6].

18.4.1 Criteria for selecting coatings for wastewater treatment plants

Due to changes in exposure conditions, the following criteria should be considered for protecting the concrete and structures in closed and exposed conditions:

- Resistance to higher sulphuric acid concentration
- Resistance to hydrogen sulphide
- Low permeation to water vapour transmission
- High coating build-up
- High adhesive/bond strength.

Other physical properties of the coating, e.g. abrasion resistance and coefficient of linear thermal expansion, should be taken into consideration for selecting the coating.

18.5 Glassflake-filled coating systems

Over the years, the most universally adopted practice for corrosion prevention is to use anticorrosion coatings, since they provide a practical and economical solution. If all corrosive ions were prevented from reaching the substrate, corrosion would never occur. However, in practice an impermeable barrier may not be possible to achieve. It is impossible to form a totally impermeable barrier to corrosive ions with organic materials, and sufficient permeation through the coating allows corrosion to take place.

Conventional coatings consist of an inhibitive prime coat followed by a barrier coat system. The primer is intended to protect the corroding material by either passivation or sacrificial means, but the effectiveness can never be permanent because the inhibitive pigments are consumed in preventing corrosion. Topcoats in the system have the purpose of protecting the primer from chemical attack, providing a barrier from the environment, and reducing permeation of corrosive ions to a level that can be coped with by the primer. When the topcoat system is effective in reducing permeation, the primer will consume rapidly and corrosion will result. Electrical influence accelerates transport of corrosion ions, thereby increasing the permeation rate.

There are two ways of looking at a problem of utilizing coatings for corrosion protection:

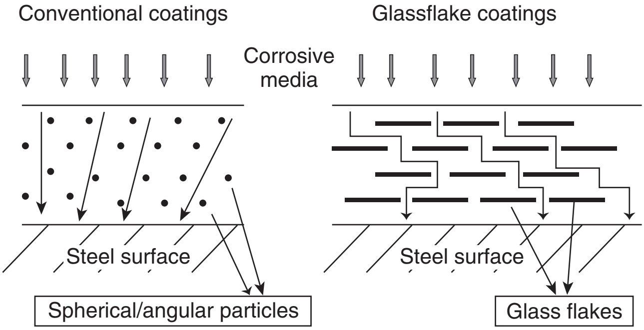
- either reduce permeation of corrosive species to a level where corrosion is stopped or becomes insignificant, or
- use an adequate inhibitive system with good topcoat barrier.

A glassflake coating system falls into the first category. Organic coatings are permeable to water vapour because of their molecular structure. No polymer is impermeable in itself, but with fillers the permeability can be brought to a lower level. The permeability depends upon various factors, including the resin chemistry and the fillers that are incorporated in the polymer matrix. Glassflake coating forms the best barrier on the surface with approximately 100 layers of flake for every millimetre of coating thickness applied.

Glassflakes in a coating matrix, due to their high aspect ratio, align parallel and overlap over each other, thereby forming a barrier in the coating system for gaseous molecules and increasing the path of corrosive media to reach the substrate. This effect increases the path for corrosive ions – known as the 'tortuous path' effect. In conventional coating systems, the particles or barrier material are granular or spherical in nature and cannot overlap, thereby offering limited resistance [7]. Glassflake alignment in the coating matrix is represented in Fig. 18.4.

The principle lies in providing a longer tortuous path through the resin binder in order that corrosive ions travelling through the permeable binder will have to travel a much longer distance. The tortuous path property gives theoretically 20 times longer path length than unfilled binder, but in practice 9–11 times longer path length can be achieved due to difficulty in obtaining symmetry of flakes despite the use of leafing agents and physical orientation. The distance travelled by corrosion ions will depend upon:

- Thickness of flakes, which determines the number of layers that can be achieved in any given thickness of coating



18.4 Glassflake alignment in coating matrix.

- Size of flakes, which determines the lateral distance the corrosive ions have to travel before descending to the next layer
- Symmetry of flakes within the binder. The longer path through the binder can be achieved with a flake of high aspect ratio.

There are several flake materials, which are available in flake form and can be used as good filler in an organic coating film. However, many of these have disadvantages in their own right in spite of specific advantages. Corrosion resistant glass offers the best all-round properties of a flake. If the glassflake and resins are blended correctly, the compound expansion is similar to the expansion of low carbon steel. This does not occur in the same way with granular fillers. The following are the three main properties of glassflake-filled coatings:

- Low permeation
- Low surface stress
- Coefficient of thermal expansion similar to low carbon steel.

These three properties lead to the fourth and fifth properties:

- Extremely high resistance to undercutting
- Abrasion resistance.

Abrasion resistance and low permeation rate are achieved due to the high aspect ratio of glass which, unlike granular fillers, protects the resin from being eroded around it. For example, if the abrasion is due to particles of much larger size than the filler used, the resin will be reloaded around the filler or even the filler particle can be taken away along with the abrasive particle [8].

In the case of a glassflake-filled coating, even if the resin is eroded, glassflakes being harder and difficult to erode protect the further layers of the coating from eroding. This results in good abrasion resistance, much closer to that of glass filler than that of binder. The high proportion of flakes reinforcement within the resin achieves dimensional stability. This property is important when coatings need machining. Another property is good resistance to cathodic disbonding, which is due to high electrical resistivity and low permeation. Typical specifications of glassflakes used in coatings are:

- Composition – borosilicate glass
- Thickness – 1 to 7 μm
- Particle width variation – trowelling compounds normally use 3.2 mm, while high build spray applied coatings use 0.4 mm (1/64″). Micronized glass is used in spray-applied coatings that are typically 45 μm build.

The following coating systems have been established as having all of these required properties:

- Styrene based vinyl ester resin
- Styrene based bisphenol-A polyester resin
- Styrene based isophthalic polyester resin
- Special epoxy system.

Based on the above resin systems, various glassflake-filled coatings are available for several applications. However, until recently their use was more confined to very high-build coatings for specialized applications in vessel linings and immersion systems. Glassflake coatings can be formulated for a wide spectrum of end-usages and are suitable for application where extreme corrosion resistance and abrasion resistance with excellent mechanical properties are required.

Glassflake pigmentation is a primary weapon in formulations, which can be incorporated in a range of high-performance binder systems to produce coatings that offer the following:

- VOC compliance
- Easy application over a wide range of specified film thickness
- Superior resistance to water ingress
- Good mechanical properties, especially adhesion, abrasion resistance and flexibility
- Compatible with cathodically protected steel on immersed structures
- Capable of withstanding a wide range of chemical resistance and high temperature conditions, depending on the binder system used.

Glassflake is a high aspect ratio reinforcement additive. Unlike granular or fibre fillers, glassflake imparts unique properties as a reinforcing agent. Glassflake is manufactured from a modified 'C' glass composition in a range of flake thicknesses and particle size distribution. Its performance advantages include:

- Directional reinforcement
- Enhanced fire resistance performance
- Increased heat distortion temperatures
- High dimensional stability
- Good weld strength
- Reduced mould shrinkage and warpage
- Excellent thermal, UV and colour stability
- Increased flexural modules
- Added isotropic properties
- Glassflake can be used in conjunction with other fillers and additives.
- Glassflake is compatible with a number of adhesion promoters to enhance bonding.
- Glassflake is a natural electrical and thermal insulator.
- Glassflake offers a low coefficient of thermal expansion.

18.6 Different resin systems for glassflake coatings

Glassflake coatings with various resin systems have been in use for various applications. The various resin systems are epoxies, polyesters and vinyl esters.

18.6.1 Epoxies

The properties of epoxies enable them to be formulated into coatings to provide protection over a wide range of specification requirements, including:

- Excellent corrosion protection for subsea, splash zone and atmospheric environments
- Excellent resistance to cathodic disbondment
- Tough and abrasion resistant
- No catalyst storage problems.

However, there are also disadvantages, such as:

- Maximum immersion temperature typically 60°C, and maximum dry heat resistance typically 120°C
- Chalking and colour retention problems on atmospheric exposure
- Generally poor acid resistance.

18.6.2 Polyesters

Polyesters offer faster curing rates than high solids epoxies, although applicators need to be sufficiently aware of the relative short pot life and of the safety aspects of the catalyst. Isophthalic or bisphenol polyester resins cured with organic peroxide catalyst offer improvement in performance over epoxy in terms of mechanical properties and temperature resistance.

- Maximum immersion temperature is typically 80°C, and maximum dry heat resistance is typically 140°C
- Isophthalic polyesters are more resistant to chalking and offer superior colour retention on atmospheric exposure compared to epoxies.

18.6.3 Vinyl esters

Vinyl esters offer the ultimate performance in terms of chemical and temperature resistance. Maximum immersion temperature is typically 120°C, and maximum dry heat resistance is typically 150°C.

18.7 Application of various resins

Vinyl ester based products have been established for chemical resistance with good tensile strength at higher temperatures of 100–120°C for immersed and 160°C for non-immersed conditions. These products are suitable for a wide range of chemical environments including strong acids, strong alkalis, petrochemical service environment and demineralized drinking water. For less aggressive media bisphenol-A resin systems are most suitable. These are normally used for seawater application, sweet crude oil service and moderate chemical environments.

Epoxy solvent-free systems give long-term protection against moderate chemical attack with desired physical properties. Some fillers used are stainless steel, silicon carbide and metallic filler to give high abrasion resistance. A very special product, unsaturated ester resinous surface coating, is available to reduce fluid friction and micro-turbulence in water transport systems, thereby increasing efficiency and often reducing power requirements. This coating system is effective in reducing surface roughness and has a hydrophobic nature. When compared to metallic surfaces that are highly attractive to water molecules, the hydrophobic nature of such coatings gives a low surface attraction and repels water, resulting in lower frictional losses.

The reason for the success of glassflake systems has primarily been their low permeability. The new series of glassflake linings now offer a very high level of improvement in this area without loss of other physical properties such as abrasion and impact resistance, flexibility, ease of application, etc.

18.8 Formulation issues

The theory of glassflake pigment particles aligning without an applied coating film to give an extended difficult pathway through the film is well known, as is the reinforcement nature of the lamellar pigment. There are, however, possibilities that the particles of glass can end up misaligned in the film, and if these particles have a length greater than the film thickness, they can create a potential fault within the coating, leading to accelerated permeation through the film. This effect can lead to the necessity of applying very thick films or multi-coat applications to compensate for these defects.

Recent developments have shown increasing promise in the use of polyester/acrylic and vinyl ester/acrylic copolymer binders with 0.4 mm to 3–4 μm thick glassflakes. Formulators have arranged the glassflakes to lie parallel to the substrate, thus offering excellent resistance to permeation, corrosion, abrasion, physical abuse and thermal shock. In each 1 mm thickness of lining there are multiple layers of overlapping glassflakes. The minimum 1 mm lining thickness can be derived from two coats of 500 µm each. A single coat of 750 µm can also be applied.

18.8.1 Micronized glass

It is accepted that the lower aspect ratio of the micronized flake does not give the same potential diffusion pathway as large flake sizes. Tests have shown that micronized flake pigmented systems show higher rates of water absorption and vapour permeability compared with the larger flake. However, in epoxy systems combination of the micronized flake with other lamellar fillers and zinc phosphate gives a synergistic effect, which offers similar permeability to large flake pigment, reducing the permeability of the vinyl ester system. However, in the vinyl ester system zinc phosphate cannot be incorporated due to its effect on the curing mechanism of the resin system. These combinations offer:

- Ease of application using smaller spray tips than standard Glassflakes allow
- Film thickness variable from 200 µm to 1000 µm depending on end-use requirements
- Retention of mechanical properties, abrasion resistance and cathodic disbondment, coupled with outstanding corrosion resistance.

18.8.2 Glassflake levels

There are no official standards governing glassflake coatings as there are for zinc phosphate coatings, zinc-rich coatings and several others. Factors that should be taken into consideration when deciding on levels of glassflakes in a coating are as follows.

- *Steric effects of glassflake*. Overloading will cause physical interference between flakes, which may in turn give rise to film defects.
- *Viscosity increase*. Higher levels of glassflake cause increased viscosity, which will eventually affect application characteristics.

There is no principle governing the optimum loading of glassflake. The type of glassflake and its level of incorporation are to be decided with the end application in mind. To give an example, an epoxy formulation intended for anticorrosive protection of structural or immersed steel will be quite different in terms of the type and content of glassflake from a vinyl ester chemical resistant vessel lining. Increasing glassflake levels improves cathodic disbondment performance. However, it is the zinc phosphate contents that are the major contributory factor in cathodic disbondment of epoxy glassflakes. Micronized glassflakes do not perform well in polyester or vinyl ester systems in terms of cathodic disbondment. Dry film thickness remains a critical factor in the performance of these systems.

18.8.3 Primers

In the case of glassflake epoxy materials formulated on a blend of glassflake and zinc phosphate, a separate primer coat is not necessary from the viewpoint of anticorrosive performance. In the case of polyester and vinyl ester specifications, a vinyl ester based holding primer is suggested to maintain the integrity of the blaster substrate prior to the application of the glassflake coating. Epoxy primers for use under glassflake polyester or vinyl ester in immersion service are not available.

There are several products that are formulated from chemically resistant glassflakes and a wide range of chemically resistant resins to produce coatings and lining systems with excellent performance characteristics. Using different sizes of glassflakes and varying the addition percentage produce coating systems that are applied by brush, airless spray or trowel. The heavy duty lining versions will outperform conventional linings, often at lower cost. Special systems formulated from higher chemical resistant resins and inert fillers reinforced with woven glass fabric or woven synthetic fibres give maximum protection. In addition to glassflakes, carbon flakes and mica flakes are also used. Aggressive chemicals are prevented from penetration through to the substrate, and these systems therefore provide a viable alternative to acid-proof brick and tiles.

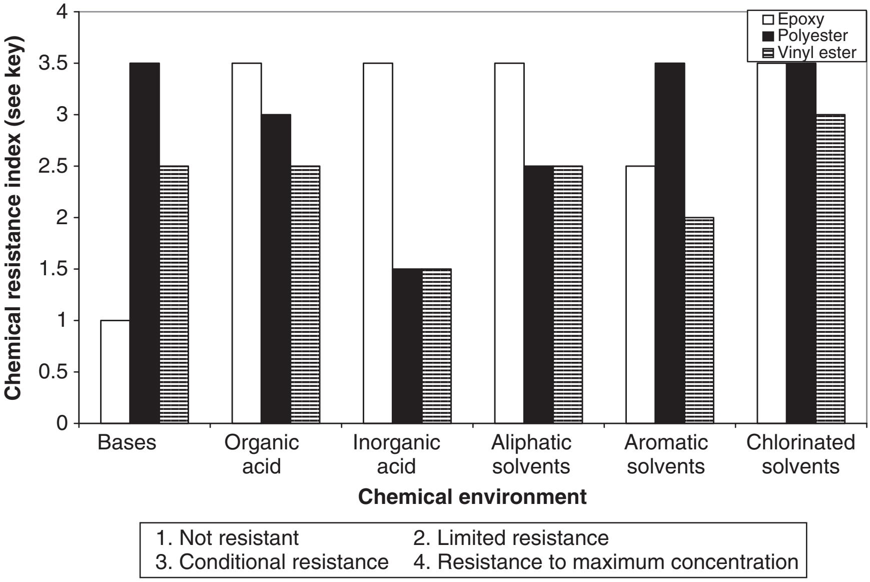
18.9 Advantages of glassflake coatings

The incorporation of glassflake in the polymer resin with proper formulation techniques offers:

- outstanding corrosion resistance to a wide range of inorganic and organic chemicals and fumes
- low permeation to chemicals and fumes
- low coefficient of expansion
- low shrinkage, leading to stress-free curing
- formation of monolithic coatings
- easy repairability
- resistance to undercutting corrosion.

18.9.1 Chemical resistance

With advancements in coating chemistry, a wide range of coating formulations are available today. These coating systems are based on resin systems



18.5 Resistance of resins to chemical environment.

such as polyester, vinyl esters and epoxies [9]. Their resistance to different chemicals is listed in Fig. 18.5. Figure 18.5 illustrates that epoxies are susceptible to alkaline environments but are highly resistant to inorganic acids and solvents. Coating systems formulated using vinyl ester resins and their modifications are known for their superior chemical resistance, but because of suitability in installation, epoxy resin based coating systems are the most widely used for the concrete surface.

The versatility of the resin chemistry allows formulators today to formulate products to achieve chemical resistance and physical properties to meet the requirements of aggressive conditions. ASTM G 20 should be used to determine the chemical resistance of the coatings.

18.9.2 Low permeability and water absorption

Organic coatings should be evaluated for their permeability. The ASTM D 1653 standard should be used to characterize the coating, based on its permeability level. The lower the permeability value, the better is the resistance of the coating system.

18.9.3 Bond strength and abrasion resistance

The bond strength of the coating should be evaluated as per ASTM D 4541 standard with adhesion to steel surface. These data should be evaluated for

Table 18.1 Typical performance characteristics of glassflake coatings

Characteristics	Test method	Results
Coefficient of linear thermal expansion	ASTM D 696	10–15 × 10^{-6}/°C
Volume solid	ASTM-2697	100% reactive
Temperature resistance		115°C (immersed), 175°C (non-immersed)
Adhesive strength to steel	ASTM C 633	200–250 kg/cm^2
Shear strength	ASTM D 1002	150 kg/cm^2
Tensile strength	ASTM C 638	220 kg/cm^2
% Elongation at break	ASTM C 638	0.4%
Compressive strength	ASTM D 695	850–900 kg/cm^2
Abrasion resistance	ASTM D 4060	<200 mg (CS-17 wheel)
Hardness	ASTM D 2240	>80 Shore D
Water vapour permeability	ASTM D 1653	0.06 gm/m^2 day mil
Salt spray resistance	ASTM B117	0 under film corrosion

comparison purposes as the strength of coating may exceed the cohesive strength of the concrete. ASTM D 4060 should be used to evaluate the coatings for their abrasion resistance [10]. Typical performance characteristics of glassflake coatings are given in Table 18.1.

18.10 Performance of glassflake-filled coating against conventional coatings

Studies done by R. Nixon, on the exposure of various coatings to a hydrogen sulphide environment in wastewater, relate the permeability of the coating and the concentration of gaseous H_2S in the environment to the time in service before blistering or failure in the coating was observed. The study showed that cycloaliphatic amine-cured epoxy with water vapour permeance of 0.54 perms and average H_2S concentration of 35 ppm showed failures after 14 months of exposure. Coal-tar epoxy with water vapour permeance of 0.62 perms and average H_2S concentration of 37 ppm showed failures after 12 months of exposure. On the other hand, glassflake-filled coating with water vapour permeance of 0.02 perm and H_2S concentration of 50 ppm showed failures after 15 months of exposure [11].

18.11 Application of glassflake coating to wastewater treatment plants

Traditionally glassflake coatings were required to be specified at dry film thickness of around 500 to 1000 microns due to constraints caused by their application characteristics. However, this thickness may be required in some but not all environments. For example, in atmospheric anticorrosive protection of structural steel, such a thickness can be over-engineered and uneconomic. A range of glassflake coatings are available, at film thicknesses that give the required protection without the need to apply more coating than is necessary. ISO 12944 standards can therefore be made applicable for such specifications. The proper installation of the coating system for forming a barrier is of paramount importance in achieving the service life of the product.

Three types of coating system can be recommended for wastewater treatment plants depending upon the structure/equipment and medium they handle [12]. These are spray-applied, glasscloth-reinforced and glass mat coatings.

18.11.1 Spray-applied glassflake coating

Structures in waste treatment plants such as primary effluent collecting chambers, effluent channels, anaerobic chambers and common effluent channels should be treated with spray-applied glassflake coating to a thickness of about 1000–1500 microns, depending upon the service medium handled.

18.11.2 Glasscloth-reinforced glassflake coating

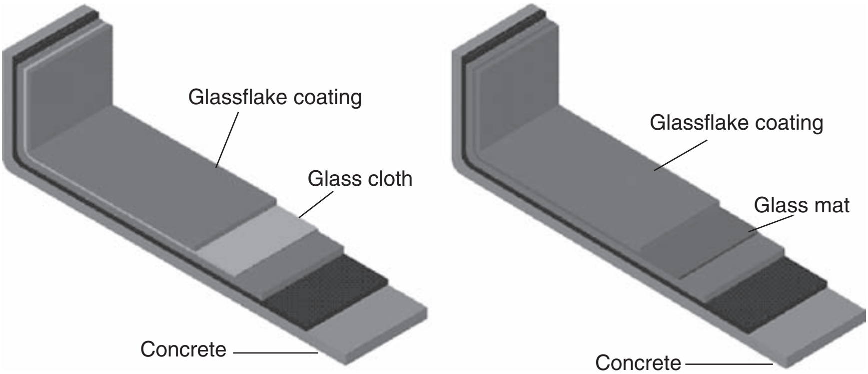
In grit chambers, common effluent boxes, common inlet channels and clarifiers where there is high abrasion, glasscloth reinforcement is recommended. The coating system should be with a base coat of glassflake coating, followed by glasscloth reinforcement and a top coat of glassflake coating with 1000–1500 microns thickness.

18.11.3 Glass mat glassflake coating

In structures such as sludge dry beds, junction boxes and crack filling areas, where there is strain experienced by a chemical-resistant top coating, a glass mat saturated with resin should be applied over the base glassflake coating. These glass mat layers isolate the top chemical-resistant glassflake coating and provide the higher tensile strength required in the crack area. The coating system is shown in Fig. 18.6.

18.12 Conclusions

Glassflake coating with proper formulation technique can achieve low permeability and high resistance to gaseous environments of high concentration of H_2SO_4 and H_2S in wastewater treatment facilities. With proper



18.6 Glass cloth and glass mat with glassflake coating installation system.

installation procedures such as surface preparation and quality control measures, glassflake coating can provide a lifetime of over 15 years against corrosion in wastewater treatment plants.

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19

Anticorrosion organic coatings for the automotive industry

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19.1 Introduction: automotive coatings

A boom in the automotive industry is a boon for the automotive coatings industry. The automotive coatings industry plays a major role in sustaining the boom, since many customers give more importance to the color of their car than the rest of the factors which help in its smooth running. Selecting the right color that would attract customers is a major challenge for coatings suppliers and manufacturers, since they have to satisfy a diverse customer base [1].

There are color watchdogs like the UK-based International Color Authority and Global Color Research, and the US-based Color Marketing Group (CMG) which conduct surveys on various car colors. Some companies like DuPont have their own research survey teams which rate various colors on the basis of sales and responses from various customers they had interviewed during their survey. Once the surveying is done, the paint suppliers and manufacturers sit together and decide on the possible colors based on the sales, chemistries, demography, etc. Chemistry is a very important factor here since the paint costs are related to the body of the car. For instance, a pearl finish would be costlier than a metallic/mica finish. Paint suppliers also have to cater to the whims and wishes of their customers. An executive class color should be exclusively for that class and Ferrari enthusiasts would want a bright red car.

If Ferrari's success was driven by Schumacher, there should be another Schumacher who must be driving the automotive coatings market. The main driver for this market currently is technology and innovations brought about by the paint manufacturers, without which survival becomes a challenge. Coatings manufacturers have to make sure that their coatings look great and at the same time perform. A variety of new approaches are being researched and nano-technology and UV-cured technology have been the latest solution to the ever-increasing problems. The environmentally friendly technologies are the ones hunted for nowadays and these technologies are aimed at meeting environmental demands and in addition providing improved corrosion resistance and protection. Automotive coatings manufacturers have started shifting to these technologies with environmental regulations becoming more stringent in Asia. The resin suppliers too are fueling this advancement with formulator-tailored resins that offer better adhesion and resistance.

The automotive coatings market is the single largest application for the radiation cured resins market and nano-technology is fast catching up. The market is expected to experience double-digit growth rates in the future with China supporting the cause and India and the rest of Asia helping it out.

This total systems concept has made the Nippon Paint name synonymous with premium quality amongst automobile manufacturers worldwide. Nippon's comprehensive product range responds to market demands for beauty and protection, simultaneously setting new industry standards with specially developed paints and coats that enhance vehicle performance and life span. Vehicles have very specific demands in terms of paints and coatings. Nippon Paint's end-to-end paint systems provide the long-lasting durability and hardness that is required of automotive paints, while adding new dimensions of aesthetics and function to automobiles.

Now it is the turn of the carmaker to sell the color, and companies like GM display some of the chosen colors to some random customers who are brought to the production plants. Now the car manufacturers are confident about the colors they have chosen from the above process and paint suppliers produce the desired color based on the chemistries and budgets. Even after such a safe process some colors get a lukewarm response and these colors are shifted to other models which are produced simultaneously.

How often do you see a Mercedes Benz, a Fiat or a GM car on Asian roads? Even though their sales have increased and many new models have been unveiled, the Asian automotive manufacturers are giving stiff competition to their foreign counterparts. The rise of Hyundai, Maruti and other local manufacturers has certainly made the foreign manufacturers reform their strategies to gain leadership in the market where they had a monopoly before.

The automotive coatings manufacturers also want to grab a piece of the pie when available, and global giants like DuPont and PPG have kicked off their investments in Asia through joint ventures (JVs). Recently, DuPont set up a JV with Beijing Red Lion Coatings Ltd, called DuPont Red Lion, with an annual capacity of 20000 tons, and to top it all DuPont is planning to increase its stake. The automotive coatings market looks very bright, especially in China and India.

UV-cured technology and nano-technology may be catering to the diverse needs of formulating companies but they also have their own drawbacks.

With manufacturers coming up with complex structures for their automobiles, the onus falls on the coatings companies as they have to meet the ever-increasing demands.

The manufacturers are trimming costs to widen their customer base, and coatings manufacturers also have to come up with cheaper methods and at the same time should bring about technical innovations. With more technological innovations the specialty content of the raw material is increasing and the commodity type is on the downhill. Technological advancements require huge investments in R&D and coatings suppliers have to keep this in mind before investing.

To conclude, automotive coatings suppliers have a bright future provided they constantly improve their technology. Catering to a wide customer base should not be done at the cost of performance, and coatings manufacturers have to strike a balance and draw a line somewhere. Kudos to Charles Darwin whose 'Survival of the Fittest' theory fits in aptly here, the fittest being the one who comes up with technical innovations at low cost. Thus optimum surface protection and an attractive appearance are now the most important requirements of vehicle coatings.

19.2 Types of automotive coating

Despite advances in the technology of surface coatings, metallurgy of steel, design of motor vehicles, materials of construction and assembly operations, priming remains a fundamental stage in the defense against corrosion, whether of cosmetic or perforation type [2]. To the ever-increasing emphasis on safety, serviceability and after-sales value of a motor vehicle, protection against any form of corrosion and maintenance of the paint film integrity is and will be of paramount importance. Automotive systems of the past, such as low solids enamels, low and medium solids dispersion lacquers and medium solids enamels, required more solvents than today's paints. They also were not as resistant to harsh conditions such as acid rain, bright sun, sand and salt spray. Today's high solids enamels, high solids and waterborne basecoat/clearcoats and urethane clearcoat paint systems greatly reduce the use of solvents while offering improved durability, greater corrosion resistance and better finish than earlier materials.

19.2.1 Natural

The coating materials of the first cars consisted of air-drying binder systems based on table oils and resins, rosin and copals. Copals are semi-fossil rosins of trees which grew in the tropics. In England, this coating technology, based on the combination of vegetable oils and copals in a hot blend process, was developed to a high quality. For the coating process 20 separately painted coat layers are required and up to three weeks' working time. In the 1920s the demand for cars increased rapidly and production assembly lines were invented and developed. Topcoats based on cellulose nitrate as a film building vehicle were used. Cellulose nitrate was combined with plasticizers, and the coating systems that consisted of this combination performed best, drying at ambient conditions and retaining good appearance.

19.2.2 Synthetic

- Self-crosslinking: two components when mixed result in a chemical reaction and hardening. Mainly consist of unsaturated polyester resins and polyurethane resins.
- Thermoplastic: softens easily at higher temperatures and also dissolves in solvents. Mainly consist of vinyl resins and acrylic resins. Examples are nitrocellulose and cellulose acetate butyrate.
- Thermosetting: heat and chemically reactive resins. These are chemically resistant. Mainly consist of melamine and epoxy resins.

19.2.3 Alkyds

Alkyds are a form of polyesters containing mainly phthalic esters of different polyalcohols and are modified with monocarboxylic acid, normally with unsaturated fatty acids from vegetable oils (linseed oil, tung oil, soybean oil), which gives this resin group the opportunity to dry and build films by crosslinking with atmospheric oxygen. Alkyds became the most important group of synthetic resins for many different types of paints and coating systems over many years until the present time. Today there are different lines of repair topcoats on the market which are based on fast-drying alkyds.

19.2.4 Melamine formaldehyde (MF)

Melamine formaldehyde is the current standard crosslinking agent used in surfacer formulation and most other technologies based on polyesters. The technology is extremely well established and there are a wide range of commercially available products. In addition, they are relatively cheap. Reactivity varies depending on the degree and type of alkylation (normally butylation). Ratios of resin to crosslinker generally range from 80:20 to 70:30 depending on required properties and the baking schedule available. Stoving temperatures are recommended to ensure a complete reaction at a typical stoving time of 20 minutes. Technologies of two or more MFs blended with differing reactivities are often used to achieve crosslinking over a range of temperatures to help anti-sagging properties of the partially cured coating.

19.2.5 Thermosetting acrylics

In the 1950s acrylic resins started to be used in automotive topcoats. Copolymers of different esters of methacrylic acid with rather high molecular weights are one class of acrylic resins, which dry physically. They are still used in repaint topcoats. In the 1960s coating systems were introduced based on the combination of –OH-functional copolymer esters of acrylic and methacrylic acids with amino resins for automotive topcoats.

19.2.6 Epoxies

Epoxy resins have been used in surfacers, in one form or another, for a number of years because of their inherent strengths of adhesion, toughness and corrosion resistance. They are still present in current polyester products to improve adhesion to bare steel and to provide a degree of corrosion protection. In some cases stone-chip performance is upgraded.

19.2.7 Polyurethanes [3]

Two-component topcoats came on the market, based on –OH-functional polymers (polyesters or acrylic resins) and crosslinked by polyfunctional isocyanates. In this case the content of the paint is delivered in two separate parts, so that the curing reaction can take place chemically when they are mixed and be applied to the substrate to be painted.

19.2.8 Hardeners for two-component systems

Paints use various types of isocyanates in different types of coatings. Primers mainly use highly reactive toluene diisocyanate. Being aromatic in nature, the yellowing tendency will not affect the appearance. Topcoats mainly use hexamethylene diisocyanate and isophorone diisocyanate, which do not yellow but have a lower reactivity rate.

19.3 Sequence for coating automobile body shells

19.3.1 Pretreatments of metallic substrate

Pretreatment chemicals used in the automotive industry are essential to prepare substrates prior to topcoat application and to provide corrosion resistance, promote good paint adhesion, and bond/seal automotive bodies.

In a typical automotive assembly process, a vehicle body is pretreated to prepare the substrate surface for paint adhesion and corrosion resistance. The body is then electrocoated with cationic primer to provide primary corrosion resistance, especially on interior or recessed areas.

Primer surfacer may also be applied using the electrocoat process. Structural adhesives and sealants are applied at various stages of the assembly process to bond and reinforce components during vehicle fabrication, to provide sound deadening, and to seal seams and joints. This finish adds value through improving appearance, paint adhesion, and the overall corrosion protection of the vehicle.

Automotive pretreatment exhibits a wide array of benefits, including:

- Superior corrosion protection
- Improved metal cleanliness
- Excellent paint adhesion
- Increased uniform metal appearance.

19.3.2 Electrodeposition [4]

The metal frame of a car or light truck has an extremely complex shape. Many areas are hidden from a direct line of sight. It is virtually impossible to coat such a complex shape with conventional spray-applied paint. In order to achieve maximum coverage and therefore maximum corrosion resistance, this first coating layer is applied in a process known as electrodeposition. The metal body is electrically charged, then immersed in a bath containing oppositely charged paint particles. These particles are attracted to the metal surface, are neutralized, and can then be baked into a coherent, tough film. Current practice favors making the vehicle body the cathode in this process (this minimizes corrosion for steel). These products are called cathodic electrocoats.

The requirements are as follows. Electrocoat products must exhibit high throw power (the ability to penetrate deeply into crevices) as well as excellent corrosion resistance. The electrocoat products need to be applicable on all substrates used in the automotive industry (steel, zinc-coated steel, aluminum alloy, etc.). The baking requirements must be compatible with the different customer needs, and the products must provide a smooth appearance. A new environmental requirement requires that the electrocoats must function without the addition of heavy metals such as lead and in some areas in Europe also without tin.

The coating industry has been providing electrocoat products to the automotive industry for over 40 years, protecting over 300 million vehicles in this time. A full line of cathodic dip primers used by all major automobile manufacturers worldwide would include the following steps:

- Degreasing
- Acid treatment
- Ultrafiltration of paint to increase efficiency
- Phosphating
- Water rinsing
- Passivation.

19.3.3 Primers [5]

The primer layer is the coating layer that joins a corrosion-protected substrate to the topcoat. It functions to smooth out surface irregularities and improve stone-chip performance, and helps to protect the substrate from visible and UV light. The primer must be capable of reliable and uniform application, and should contribute a minimal environment footprint. Today's primers include solventborne, waterborne and powder forms. Color-keyed primers are often used to allow minimum basecoat film thickness, to optimize the painting process and to minimize defects related to stone-chip damage.

19.3.4 Basecoats [5]

Basecoat is the coating layer that provides color and aesthetic effects. Basecoat must provide uniform appearance initially and for many years without fading. Modern requirements for appealing vehicles often require micas, aluminum flakes and other pigmentation effects. These can be incorporated in one basecoat layer or in a separate layer (for example in two-tones). If two basecoat layers are used, the sandwich with the clearcoat is called a tricoat topcoat.

19.3.5 Clearcoats [5]

The clearcoat is the coating layer that forms the last interface to the environment. It carries the biggest part of the technological performance and must be able to resist environmental etch, bird droppings, car wash machines and other outside influences. To improve performance against all these influences, OEM coating systems move from colored topcoats to basecoat/clearcoat systems. The clearcoat in combination with the basecoat forms the automotive topcoat, which gives the vehicle its appearance. One- and two-component (known as 1K and 2K) clearcoats are applied over both solventborne and waterborne basecoats.

The driving forces for clearcoat development are cost of material and process, appearance, etch and scratch resistance and the environmental footprint. Environmental pressures have led to intensified development of super high solids, waterborne and powder clearcoats. Worldwide, approximately 80% of all passenger cars are coated with 1K clearcoats, and the remainder with 2K clearcoats. The 1K clearcoats are subdivided into solventborne acrylic melamine systems, clearcoats with enhanced etch resistance, high-solid systems, waterborne systems and powder versions. The 2K clearcoats include solventborne, super-high-solids and waterborne versions.

19.4 Detailed methodology of primers, basecoats and topcoats and metallic finishes

19.4.1 Introduction

Solventborne 2K epoxy/amine chemistry has been used in the anticorrosion primer market for general industry coatings, particularly when ambient temperature cure is needed. These systems are chosen for many reasons, including the excellent chemical resistance achieved from a crosslinked coating film and excellent adhesion to various substrates (especially metals) due to low volume shrinkage during cure. The key to the performance of 2K epoxy systems is in the epoxy/amine crosslinking reactions.

A primary polyamine can react with epoxy. The resulting secondary amine can react with the epoxy ring. The key to achieving low volume shrinkage are these ring-opening reactions (unlike many other crosslinking reactions). The final reaction illustrates that there still remains the potential for epoxy reaction(s) between the –OH groups to further contribute to the development of a highly crosslinked coating.

Formulation of anticorrosion primers

Waterborne products (mainly those based on solid resin dispersions) have an even better adhesion level compared to solventborne products [6]. A critical method to verify anticorrosion performance is to employ a crosshatch tape test after the salt fog or humidity chamber exposure. With this test method it was found that on critical substrates, like galvanized steel or aluminum, the adhesion level is significantly influenced by the amount of hardener used in the formulation. The main reason for this finding is likely to be the fact that crosslinking reactions between epoxy groups of the dispersion and the active hydrogens of the amine hardener in waterborne systems are not reaching the same level as in solventborne or solvent-free systems. In this scenario, there would remain a level of non-reacted (hydrophilic) amine hardener left in the film, resulting in increased polarity of the coating film. These polar sites would allow interaction with ions and water. It seems reasonable that the best results with a specific waterborne epoxy/amine system in salt spray or humidity chamber exposure are obtained with a lower level of amine hardener than is suggested by stoichiometry alone.

19.4.2 Basecoat technology

Applying a basecoat is a process for producing color in a paint or creating a special effect for two-layer coatings on substrates. The process mainly comprises successive steps in the following sequence:

1. Applying a special effect basecoat layer (comprising metallic pigments) dispersed in a liquid onto the substrates in one or more successive spray passes
2. Drying or curing of the special effect basecoat layer
3. Applying a clearcoat layer
4. Curing the clearcoat layer.

Basecoats mainly consist of

- Metallic/pearlescent pigments
- Resin medium
- Fast-evaporating solvents
- Flow additives and setting agents.

The main effects in a basecoat/color layer arise from the effect of pigments used in this suspension. Aluminum is subject to various manufacturing processes to produce Al pastes which could be leafing or non-leafing pigments, 'cornflake' or silver dollar pigments. The basic nature of the pigments gives rise to flip-flop effects determining the different gradations of color that arise at different angles of a car.

Some of the salient features of aluminum pigments are:

- High area to weight ratio
- Highly preferred flat, parallel orientation of the flakes in the paint film
- Inherent opacity and spectral response of metallic aluminum.

Industrial grade (leafing or non-leafing) aluminum flakes have the following composition:

- Thickness 0.1–0.2 μm, diameter 1–200 μm
- Metal content: 95–98.8%
- Oxide content: 1–3%
- Lubricant content: 0.2–2%.

Al pigments are generally sold in paste form. Most products contain 65% flake metal and 35% volatile hydrocarbons (solvent naphtha/mineral spirit). Pearlescent pigments offer luster, sparkle, depth and metallic-looking shine, and enable Multiple Color Play.

19.4.3 Basecoat application process

When producing single-tone basecoat/clearcoat two-layer coatings, the single-tone basecoat is conventionally applied by means of electrostatically assisted high-speed rotary application [7]. This is not conventional when producing special effect basecoat/clearcoat two-layer coatings, the special effect basecoat instead generally being applied in two spray passes. In this case, spray application proceeds in the first pass by means of electrostatically assisted high-speed rotary application (approximately 60–70% of the special effect basecoat layer), while in the second pass spray application generally proceeds by pneumatic spraying without electrostatic assistance (approximately 30–40% of the special effect basecoat layer). While the final pneumatic spray application does indeed have the disadvantage of lower application efficiency associated with increased losses due to overspray, it guarantees excellent optical quality of the finished special effect basecoat/clearcoat two-layer coatings with regard to pronounced and uniform development of the special effect, avoidance of clouding and overall appearance. If the subsequent pneumatic spray application is replaced by electrostatically assisted high-speed rotary application, the optical results achieved are generally less good, in particular in the case of special effect basecoats in very light metallic shades or with a strong color flop effect.

19.4.4 Clearcoat technology

Modern automotive original lacquer coatings generally consist of a base lacquer/clear lacquer topcoat, which is applied onto a body which has been electrophoretically primed and coated with surfacer [8]. In such coating processes, the colored and/or effect base lacquer and the clear lacquer are preferably applied wet-on-wet, i.e. the base lacquer and subsequently applied clear lacquer are jointly stoved.

The optical/aesthetic qualities of such base lacquer/clear lacquer two-layer lacquer coatings are substantially influenced by the quality of the clear lacquer layer. Ideally, the texture of the clear lacquer layer is identical on the horizontal and vertical surfaces of a three-dimensional substrate, for example an automotive body, which may be ascertained, for example, by determining the long- and short-wave components of the surface texture of the clear lacquer surface.

This ideal situation is, however, not straightforward to achieve in practice. For example, differences in surface texture or leveling of the outer clear lacquer layer may occur as, once applied and in particular during the heating phase of the stoving process, the clear lacquers have a tendency to run or sag on non-horizontal surfaces due to a temperature-determined reduction in viscosity. There are various ways of counteracting unwanted running phenomena in clear lacquers. For example, additives having a favorable effect on running behavior are added to the stoving clear lacquers. However, this frequently results in reduced gloss of the clear lacquer layer, if the clear lacquer layer is compared with a clear lacquer layer produced from a corresponding, additive-free stoving clear lacquer. Another possibility for counteracting unwanted running phenomena in clear lacquers involves rotating the substrate around an axis after application of the stoving lacquer during the flashing-off and/or stoving operations.

Longer-term retention of the optical/aesthetic qualities of base lacquer/clear lacquer two-coat lacquer coatings, in particular in automotive applications, is substantially determined by the clear lacquer layer's resistance to chemicals and scratching, which is in particular manifested over a relatively long period of service by a greater or lesser resistance to acid rain and washing scratches. This technology achieves mar resistance of the clearcoat by utilizing a two-step curing process of a two-component clearcoat. The clearcoat contains a thermally curable monomer that polymerizes by addition and/or condensation reactions, and a UV-curable olefinic monomer that is free radical polymerizable. The rapid polmerization during the UV cycle minimizes running or sagging of the clearcoat during stoving. The elimination of additives produces a long-lasting lustrous finish.

19.5 Anti-scratch and anti-mar coatings [9]

Ever since the first automobiles were made in the late 1800s, there have been many changes in paint technologies to protect and beautify these man-made transportation devices. Systems from natural products to high-tech polymers have shown impressive results. In the first part of the twentieth century automotive paint technology was based on the same air-dry varnish systems that were used for wooden furniture and horse-drawn carriages.

In 1923, E.I. DuPont De Nemours developed nitrocellulose lacquer systems, which offered many color choices and easier application by use of spray guns. However, lacquer systems required spray application of 3–4 coats of paint to achieve the desired properties. Lacquers also by their very nature have poor resistance to certain chemical solvents. Repeated exposures to gasoline spills could stain and damage lacquer finishes. In fact, in the 1960s some cars had their gas tank filler located under the license plate to avoid spilling gasoline on the lacquer paint. Nitrocellulose lacquers were used on some passenger cars until about 1957, when solution acrylic lacquers were introduced. Acrylic lacquers offered much improved durability and a wider range of bright, pleasing colors – especially metallic finishes.

Enamels formed a very durable film through a chemical reaction after they were sprayed on the vehicle and baked in an oven. The cured paint film was about 2 mils thick (1 mil = 0.001 inch), and it was very resistant to chemicals and solvents. Enamel paints had shorter application times also. Typically, they were applied in 2–3 steps versus 3–4 steps for lacquers. The advent of organic pigments also added many different choices of colors to consumers. However, this alkyd enamel paint system oxidized in sunlight fairly quickly, which caused the colors to begin to show fading and/or dulling in a matter of several weeks. The durability of enamel finishes was improved considerably with the introduction of 'acrylic' enamels in the early 1960s.

To provide further improvements in appearance and durability, a new type of finish, called 'Basecoat/Clearcoat', was developed and introduced in the late 1970s. The topcoat paint system was split into a pigmented enamel basecoat, followed by a clear enamel finish. The key to this technology was the development of a clearcoat material with superior durability in all climates. Initially, the cost of the Basecoat/Clearcoat paint system was prohibitive and it was only used on some high-end automobile finishes. However, refinements in the material technology and processing helped to reduce costs, and by the late 1980s this paint system had become widespread.

As the car industry shifted to lacquer and enamel paint technologies, the protective coating technology improved dramatically. After a few weeks in severe climates, the paint would become somewhat dull again and there was a need to repeat the waxing/polishing process.

To improve performance against all these influences, OEM coating systems moved from colored topcoats to basecoat/clearcoat systems. The clearcoat is the coating layer that forms the last interface to the environment. It carries the biggest part of the technological performance and must be able to resist environmental etch, bird droppings, car wash scratches and other outside influences. The clearcoat in combination with the basecoat forms the automotive topcoat, which gives the vehicle its external appearance. One- and two-component (1K and 2K) clearcoats are applied over solventborne basecoats. Clearcoats may also be tinted to provide a richer, more saturated color. The driving forces for clearcoat development are cost of material and process, appearance, etch and scratch resistance and the environmental footprint.

Since the time when solventborne acrylic-melamine 1K systems were the predominant clearcoats, many technological improvements have been made. Requirements for long-term technological performance led to a portfolio of clearcoats that today fulfill various customer demands. Product specifications are adapted based on customer requirements and the application conditions in the different application facilities, but are based on common chemical approaches and formulating principles.

Both 1K and 2K clearcoats are widely used where plastic components are painted outside the assembly plant. The 1K clearcoats are subdivided into traditional high-solids high-bake solventborne acrylic melamine or silane systems, with the latter offering enhanced etch/mar resistance. The 2K clearcoats include solventborne and super high-solids versions. In either case, rigid or elastomeric versions are available.

In order to protect and preserve the aesthetic qualities of the finish on a vehicle, it is generally known to provide a clear (unpigmented or slightly pigmented) topcoat over a colored (pigmented/metallic) basecoat, so that the basecoat has an attractive aesthetic appearance, including high gloss and DOI (distinctness of image), and remains unaffected even on prolonged exposure to drastic weather changes of environment. It is generally known that alkoxysilane polymers, due to strong silane bonding when cured, provide finishes with excellent resistance to etching from acid rain and other environmental pollutants, along with good scratch resistance. Nowadays, these silane coatings are widely used as clearcoats over pigmented basecoats.

From an original equipment automobile manufacturer's point of view, for achieving smooth workability during the painting process online, i.e. obtaining a film build-up in excess of 40 μm on vertical sides of the vehicle, these silane based lacquers have been reinforced with certain rheological additives that impart pseudo-plasticity to the lacquer when stored in a container. This means that the lacquer when stored in static conditions attains thixotropy (false body). However, when this lacquer is subjected to shear, under the influence of circulation in a paint kitchen, there is a sudden drop in viscosity and it attains the properties of a Newtonian fluid. Furthermore, when this lacquer is used on the painting line, the desired film build-up is obtained in a single-swipe process by modern robotic painting equipment presently used in OEM paint shops.

The superior scratch resistance and environmental etch resistance of silane based clearcoats led to their acceptance as topcoats for eight of the 10 top-selling automobiles since 2000, including the Ford Taunus, Toyota Camry and Honda Civic. This application represents a dramatic increase in volume of the use of hybrid organic–inorganic polymers in the automobile industry.

This enhanced clearcoat, which could be called a 'mar resistance clearcoat', shows enhanced results on various performance fronts on automotive bodies in terms of DOI and wave scan (overall visual appearance). The increased gun tip solids also contribute to low VOCs and improved leveling of the paint film during the application process. Enhanced 'mar resistance clearcoats' also show improved resistance to staining (against bird droppings and insect droppings) and acid resistance (acid rain).

19.6 Special coatings for plastic and other non-metallic components [10]

The automotive industry exploits the entire range of performance characteristics offered by many polymer and plastic families. Elastomeric and cellular materials provide comfort in seating systems, cushion the ride by dampening vibrations from the powertrain and suspension, and absorb and dissipate impact energy. At the other end of the performance spectrum, structural plastics and composites are the lightweight alternatives to metal that provide load-bearing body structures and help the industry meet stringent requirements for lower emissions and higher fuel economy. Plastics also allow cost-reducing consolidation of parts and functions compared to assembled, multipart metal components, and provide desirable features. Major plastics used in automotive applications are polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polyurethane (PU), polyurea, acrylonitrile/butadiene/styrene (ABS), styrene/acrylonitrile (SAN) and TS polyester.

Producers of plastic coatings are doing relatively well in Western Europe at the moment while the longer-term prospects for plastic paints are also looking bright. Demand for plastic coatings has been mostly driven by the automotive industry, which accounts for around half of sales. The desire among European consumers for more color has led to car manufacturers wanting coated plastic components. To comply with the rules, which could necessitate the stripping of paints from plastic parts, OEMs may decide to do without coatings. Also problems with adhesion, stability and other high performance requirements with certain polymer substrates are still posing a technological challenge to plastic coatings formulators. OEMs want coatings which not only adhere well but also have good scratch resistance, weatherfastness and also strong colors. They also have to be applied to a widening range of plastics with different pretreatment needs. At the same time in some applications coatings are expected to be functional and tactile as well as decorative.

19.7 Future developments in automotive coatings

19.7.1 High solids basecoats [11]

A high solids, stable, non-aqueous dispersion, comprising a low T_g copolymer, having a T_g between about –10°C and about 30°C, is particularly adapted for use as a clearcoat automotive finish. The copolymer is the copolymerization product of monomers whose T_g is above about 50°C, polar monomers whose T_g is up to about 15°C, and α, β-ethylenically unsaturated stabilizer copolymers. The stabilizer copolymers are formed from α, β-ethylenically unsaturated monomers and at least one oxirane-containing compound, have a molecular weight of about 2000 to about 25 000, are soluble in aliphatic solvents and have a T_g of about –60°C to about 0°C. These non-aqueous dispersions result in coatings having high percentage solids, ease of application, minimal sagging and good gloss and DOI.

19.7.2 Water based/environmentally friendly paints [12]

Waterborne basecoat/clearcoat paints are used where it is desirable to reduce or eliminate solvents. Clearcoat 100% solids paints are growing in popularity because of their durability and reduced solvent emissions. Next-generation paints could include fluoropolymer modified clearcoats and powder-coated clearcoats. While such finishes could completely eliminate the need for solvents and improve durability even further, these lower energy surfaces will pose greater challenges to adhesive manufacturers.

19.7.3 Powder based clearcoats [13]

Powder clearcoat dispersions (powder slurry clearcoats) are prepared by dispersing a powder clearcoat in an aqueous medium and wet-milling the resulting powder slurry, at least one adduct of ethylene oxide and/or propylene oxide with at least one glycol being added to the powder slurry prior to wet-milling. Powder slurry clearcoats are used for producing clearcoat finishes, especially as part of multicoat color and/or effect finishes.

The market for acrylic powders has emerged in the last two years. Where OEM customers have demanded better performance, GMA acrylic powders are now commercially available for several applications. These are predominantly high-gloss black powders. This chemistry offers powders that have exterior weathering properties comparable to current basecoat/clearcoat systems in a one-coat system. The cost per kilogram of these materials is approximately double that of polyester-urethane powders, which has caused these powders to be specified only where the increased material costs are not an issue.

Clear powders were first used on OEM aluminum wheels during the 1984 model year. Powders were an answer to the wheel manufacturers' dilemma, but there were other advantages. The powders reduced rejected wheels because runs and sags were avoided on complex-shaped wheels. Also, powders could be easily applied more thickly than liquids. This provided much better edge coverage, a major concern in corrosion protection. Metallic-colored powder basecoats soon followed. Powders were able to decorate the wheels with attractive colors while still enhancing their overall corrosion resistance and durability.

19.8 Application and process systems

19.8.1 Three-coat one-bake system (3-WET) [9]

A modern automotive coating is a product of advanced technology affecting production quantities and based on a set of scientific and technical developments. In terms of the paints and equipment used, production technology of these materials is much more complicated than that of conventional paints. Only a large-scale enterprise with its own developed research structure specializing in the development of products for the automotive industry is capable of producing high quality automotive enamels suited to cater to fast-emerging technologies.

Energy conservation in terms of raw materials usage as well as process has been the striving pulse for industrialists over the past few years. Benefits of these efforts are ultimately transferred to customer lines which ultimately yield business potential to sustain constant improvement and growth. The new 3-WET technology is a vibrant example of such development which has brought about a reduction in consumption through reduction in cycle times and corresponding enhancement in productivity. Obviously, this will entail a departure from conventional painting systems. In the conventional painting system, there is a need to have two separate booths for primer and topcoat application and two separate ovens deployed for baking. The three-coat one-bake system (3-WET) involves primer and topcoat application being brought about in a single booth, sequentially followed by baking. This therefore makes the primer booth and the primer oven redundant.

The merits of 3-WET painting could be listed as below:

- Reduction in energy consumption by eliminating the primer oven (the single largest contributor to energy consumption) and eliminating one booth (the primer booth) with considerable energy savings achieved
- Reduction in cycle times – almost two hours of vehicle hold time in a vehicle paint shop is reduced
- Lower capital investment
- Shortening of process length thereby accounting for space savings
- No sanding operations.

Major benefits due to the controlled intercoat merger of primer and basecoats have a direct influence on the visual appearance of the car. The enhanced flexibility of the base resins used for what are now called basecoat 1 and basecoat 2 provide better durability in chipping resistance, thus ensuring longer life of the paint coating. The overall effect is a vehicle produced with advanced technology having a striking appearance and better performance properties.

19.9 Nanomaterials as additives in coatings [14]

19.9.1 Nanoalumina

Predispersed nanoparticles are an ideal way to utilize nanomaterials in coatings since slight agglomeration can cause the loss of nanoeffects. One of the main applications of nanomaterials is to obtain enhanced abrasion and scratch resistance. With the incorporation of nanosized alumina this particular property can be easily achieved. Nanophase technology is one such industry producing commercial nanoalumina. BYK Chemie is another supplier of nanoalumina, which is a 30% dispersion of nanoalumina in tripropylene diacrylate. It is used for UV-curable coating systems.

When a small amount of nanoalumina is incorporated the resistance against mechanical scratching is increased significantly. The increase in haze is due to scratches formed on the coated surface and is measured as an indicator for scratch resistance. If the combination of alumina nanoparticle and polysiloxane based additive is used, the scratch resistance is improved dramatically. Just 1.5% nanoalumina in combination with 0.2% surface-active polysiloxane based additive is sufficient to reach excellent scratch resistance.

19.9.2 Nano TiO_2

Pure rutile (TiO_2) shows photoactivity near the UV region, which is controlled by surface modification. Nanorutile has five times the specific surface area than conventional rutile and hence acts as a powerful UV blocking agent. Unlike an organic UV absorber, nanorutile does not lose its efficiency with time. It is non-toxic, non-migratory and perfectly non-yellowing.

Altair's TiO_2 nanoparticles deliver superior strength and durability compared with traditional rutile when used in coating. Due to their finer size and higher surface area, they can act as crack arresters and enhance toughness, which is important for designings coating for harsh environments.

19.9.3 Nanoparticles of cerium oxide

Cerium oxide is well known for its optical properties and ability to filter UV light. Rhodia has commercially managed the stable cerium oxide nanoparticle sol (10 nm), which is totally transparent when compared with titanium oxide sol of similar particle size, which appears milky.

Titanium dioxide shows photocatalytic activity, generating free radicals. In contrast to this, cerium oxide absorbs UV light without being photoactive and has more localized electrons (4f orbital) than titanium dioxide electrons (3d orbital). Hence the cerium oxygen bond is more ionic than titanium oxygen bonding. Hence the chance of creating free radicals in the case of cerium oxide is less, so cerium oxide does not show any photocatalytic effect.

When cerium oxide nanoparticles are dispersed properly in a coating formulation, they ensure durability of the UV absorption function while improving hardness and strengthening binders that are used in the wood coating industry. Since nanoparticles do not scatter light, the coating remain transparent. This transparency is an important requirement for the wood coating industry.

It is observed that when nano cerium oxide is added 1% by weight to clear wood coating formulation, the hardness increases by almost 60% compared to the standard formulation and the scratch resistance increases by almost 40% compared to the standard formulation. It is also observed that bulk properties of the host matrix such as tensile strength and yield stress are significantly improved in the presence of cerium oxide nanoparticles. The exact mechanism behind this improvement is still unknown. It is thought that probably there must be structural reorganization of the polymer chain around the particles during drying. In a nutshell, the following things are achieved by the use of cerium oxide nanoparticles:

- Improvement in mechanical properties
- UV filter protection
- Improved scratch resistance leading to better durability
- Modification of the hydrophilic properties of the coating leading to improved water resistance.

19.9.4 Nanosilica

Nanosilica is a widely used material. It is prepared by the sol-gel process. The advantages of nanosilica are:

- Improved surface hardness
- Improved dirt pickup resistance
- Increased gloss retention
- Reduced chalking, reduced color difference and reduced gas permeability.

Organic – inorganic nanohybrid polymers with novel properties can be designed by grafting nanosilica with the polymer network by the sol-gel process. This leads to outstanding scratch hardness and wear resistance properties as well as photostability and weatherability.

The following are some examples of nanosilica hybrid polymer:

- For high durability exterior coatings, nanosilica-modified silicone acrylic latexes are preferred. Depending on the extent of nanosilica incorporation, the latex shows significant improvements in chalk resistance, color and gloss retention.
- Siloxane-encapsulated nanosilica provides wear and scratch resistance up to 10 times higher than conventional floor coatings.
- PPG came out with a new and innovative clearcoat known as Ceramiclear for automobiles based on silicate nanoparticles. In this clearcoat, transparency, scratch resistance, mar resistance, UV and acid etch resistance have shown great improvement over the existing clearcoat.

19.9.5 Nano zinc oxide

Commercial-grade nanomaterial zinc oxide is offered by Degussa. Various grades of nanosized zinc oxides are available. Nanosized zinc oxide is an effective UV-A filter. It has distinctly lower photocatalytic activity than titanium oxide. When incorporated in coatings, properties such as high gloss retention and less yellowing are easily achieved.

19.10 Nanocomposites in surface coatings

Paint combines inorganic pigments dispersed in organic components (solvents, interface and interactions exchanged by organic and inorganic components). These hybrids are classified in two categories:

- Class 1 corresponds to all the systems where no covalent or monovalent bonds are present between the organic and inorganic components. In this class, materials with various components exchange only weak interactions such as hydrogen bonding, Van der Waals contact, etc.
- Class 2 corresponds to the systems where materials with at least a fraction of their organic or inorganic components are linked through strong chemical bonds such as covalent or iono-covalent bonds.

Several routes are available for the synthesis of nanocomposites. These are as follows:

- Atom transfer radical polymerization
- Sol-gel process
- Emulsion polymerization
- Interpenetrating network.

Since we are concentrating on materials for the paint industries, the incorporation of inorganic particles and clusters in polymer and intercalation is of particular interest.

19.11 Incorporation of inorganic particles and clusters for hybrid coatings

Physical mixtures of organic polymers and preformed inorganic particles may lead to separation in discrete phases and, in addition, particle agglomeration tends to weaken mechanical and optical properties of the resulting materials. Unmodified inorganic nanoparticles tend to aggregate in the polymer matrix independently of the kind of material and the size. To avoid these drawbacks, the following strategies are being adopted for product development:

- Use of functional polymers
- Surface modification of particles
- Encapsulation of particles in the polymer shell
- *In situ* growth of inorganic particles in the polymer matrix
- Surface modification of the particles with the polymerizable group
- Surface modification of the particles with the initiating group.

Although the above strategies are useful for functional polymers and nanoparticles, modification of nanoparticles with polymerizable and initiating groups is especially useful for reactive coating systems such as high-solids radiation-curable coating systems.

19.12 Self-cleaning paint layers

Different types of coatings such as self-cleaning coatings, lotus effect coatings and dirt-repellent coatings can be designed by imparting super-hydrophobicity to the coating surface. The surface morphology of the coating can be altered by developing a coating with nanoscale roughness, which can help to create a super-hydrophobic surface with water contact angle as high as 160°. An extremely low surface energy prevents bio-adhesion and dirt pickup and thus maintains easy-cleaning properties.

19.13 Abrasion-resistant coatings

The scratch and abrasion resistance property of a coating can be increased by the incorporation of nano zinc oxide or nano titania. Abrasion resistance is increased by 25 times compared to conventional coatings. This finds application for coating rotor blades of gas turbine and jet engines. This increased wear and abrasion resistance helps to reduce maintenance cost.

19.14 Non-chromate corrosion inhibitors

Chromate based corrosion inhibitors, though effective, are banned due to the toxic effects and carcinogenicity of hexavalent chromium. Nanoparticle based organic–inorganic corrosion inhibitors are highly effective corrosion inhibitors. The inorganic functionality bonds with the metal and the organic counterpart interacts with the polymer matrix, giving surface protection in the form of anticorrosion barriers.

19.15 Conclusions

Technology breakthrough is the result of fundamental molecular engineering research and the development of analytical equipment and tools to guide research. According to Robert Matheson of DuPont Performance Coatings, 'The basis of the work is to change the nature of oligomers that are defined as small polymer chains with few structural units and giving them structure by changing their reactivity with each other'.

In product lifecycle assessments, newer technology systems compare favorably with and even exceed existing solvent coating systems. This is based on a total inventory of energy usage and emissions from the time the product is initially produced until it is applied to a vehicle's surface.

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20

Using organic coatings for repainting and maintenance of steel components and structures

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20.1 Introduction

Maintenance painting in philosophy and practice has been changing very rapidly over the past 20–30 years in most Western countries, and I believe that increasing costs, environmental pressures and a realization of true maintenance cost over a structure life cycle are also starting to change practices in most regions around the world.

The true cost of maintenance painting is often much greater than even the sum of paint, preparation, application, labour and access. For offshore maintenance work-boat costs, accommodation and transport all need to be taken into account, and on bridge painting the cost of traffic coning has been shown to be as great as, if not more than, repaint costs. Traditionally there was basically no difference between the new construction and maintenance processes: steel would be erected on site with mill scale present; this would be allowed to weather until it started to detach and then painting could commence. On large plants/structures this would be basically a continuous process which once started never stopped. Coatings used at the time were eminently suitable for this purpose.

Abrasive blast cleaning, and the advent of many of the newer coatings technologies, changed much of this procedure. Steel could be economically fully cleaned in the factory and long-life coating systems applied. Epoxy or silicate zinc-rich coatings, together with high-build epoxies, allowed resistance to handling damage which could never be achieved with oleoresinous or thermoplastic systems. The rapid application in the factory speeded up the construction process, as well as allowing application to be undertaken in a relatively controlled environment, and hence allowing a better quality application to be achieved.

Much of this change has occurred along with a realization that many materials used in paints were harmful to health, e.g. red lead and zinc chromate. Attempts to formulate conventional paints without these materials present have generally been relatively unsuccessful and the same performance parameters have not been achieved.

It is interesting to recall that probably the last major project erected in black steel in the UK was a large integrated steel production complex, erected in the mid 1970s, at a coastal site. After erection and weathering this was then coated with a zinc phosphate alkyd high-build and high-build alkyd finish. Red lead was considered unacceptable. These newer coatings started to show breakdown in the form of pinhead blisters within one year; clearly zinc phosphate based systems in a non-laboratory environment did not give the same performance as traditional red lead based paints.

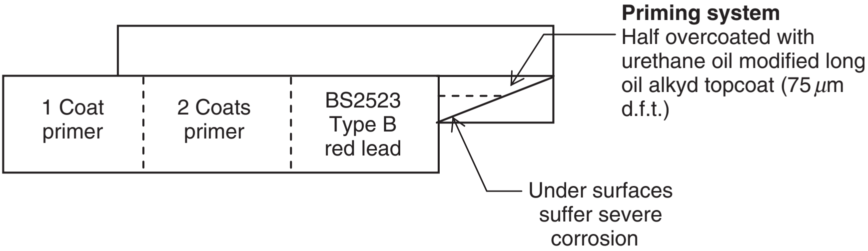
20.2 Conventional systems

In 1978 a major evaluation programme was undertaken to assess the coatings that were specified at that time on hand-prepared rusty steel in order to obtain an overall view of their effectiveness. Rusted girder sections (60 cm) were power wire brushed to St2, fresh water washed and then brushed down, and a range of coatings brush applied using BS2523 Type B red lead in linseed oil as the standard (Fig. 20.1). This was considered to be the best possible preparation that could be hoped for in practice.

Girders were raised around 10 cm above the ground and exposed at a weathering site at International Paints' manufacturing plant in Newcastle in the UK. The finish coat was applied to attempt to reproduce current practice at that time, in that primers are seldom left for prolonged periods untopcoated in a maintenance situation.

An assessment of performance was made after 18 months (Table 20.1), at which time no complete breakdown had occurred. In every case Type B red lead performed better than a single-coat primer and, in some cases, better than two coats. The use of a topcoat considerably improved performance. Breakdown was normally manifested by the onset of dense pinhead blistering.

Undoubtedly one of the reasons for the premature failure on the steel plant mentioned earlier was total film thickness applied in two coats. The



20.1 Test girder section.

Table 20.1 Performance assessment after 18 months' exposure (systems listed in order of performance)

Primer		D.F.T. per coat	Performance
(1)	Short oil alkyd/vinyl resin high zinc phosphate pigmentation	30 microns	Good, 2 coats
(2)	Tung oil phenolic zinc chromate	50 microns	Good, 2 coats
(3)	Tung oil phenolic zinc chromate/zinc phosphate	50 microns	Good, 2 coats
(4)	Urethane alkyd zinc phosphate	75 microns	Good, 2 coats Better than (1) for 1 coat
(5)	Urethane alkyd zinc phosphate/zinc chromate	75 microns	Good, 2 coats Better than (1) for 1 coat
(6)	Long oil alkyd/linseed oil red lead	50 microns	Fair, 2 coats
(7)	Epoxy ester zinc phosphate	75 microns	Fair, 2 coats
(8)	Epoxy ester red lead	50 microns	Fair, 2 coats
(9)	Phenolic modified alkyd zinc chromate	50 microns	Fair, 2 coats
(10)	Chlorinated rubber red lead (linseed oil plasticizer no chlor paraffin)	50 microns	Poor
(11)	Short oil alkyd zinc phosphate/zinc chromate	50 microns	Poor
(12)	Short oil alkyd zinc phosphate	50 microns	Poor
(13)	Alkyd zinc chromate	40 microns	Poor
(14)	Epoxy ester zinc chromate	40 microns	Poor
(15)	'Beat Rust' proprietary material		Very poor
(16)	'D Rust' pre-treatment		Very poor

products used were thixotropic alkyds formulated to give high build by brush application and also good through-dry due to a urethane oil modification. However, volume solids of these materials is only around 50%, and although the recommended 75 microns d.f.t. could be achieved with care, it is not easy to obtain this consistently, i.e. applying 150 microns wet film. Experience has shown that typically 100–125 microns wet film thickness can be applied consistently (which is why future work was driven along the 80% volume solids route).

Although many of the results from the series were as expected, there were some significant findings:

- Zinc phosphate primers could perform well, better than many modified red lead systems, where red lead level and other properties had been compromised for cost and improved drying characteristics.
- Tung oil phenolic based systems appeared good in wetting the surface, but not necessarily in giving good protection in thin films.
- Results obtained were too good compared with those found in practice.
- ‘H’ girders were best for testing – flat panels can give misleading results.
- Short oil alkyd zinc phosphate on correct solvent blends can give surprisingly good results.
- Reproduction of practical field performance was best achieved by using a surface treatment of a hard scrape and light wire brush. Although high standards could be specified for hard or power tool cleaning, these are unlikely to be consistently achieved in practice.

20.3 Developments in conventional coatings

Due to the somewhat surprising results obtained with quick drying short oil alkyd based systems, further testing on other short oil alkyds with various anti-corrosive pigments was carried out, confirming the results obtained above. An investigation was carried out to find the optimum resin, PVC and zinc phosphate level (20%, 40%, 60%).

Best results were obtained using a TMP short oil alkyd, based on a slow evaporating aromatic solvent with 60% of pigment zinc phosphate and a PVC of 40%. A further advantage of this type of resin at the time was that it gave the only route to use two-pack materials over hand-prepared steel, as it could be overcoated by epoxies, polyurethanes and chlorinated rubbers.

It is interesting to note that improvement in performance was consistently found by increasing the zinc phosphate level, e.g. in both chlorinated rubber and urethane alkyd based systems. Increasing the level from 20% of the pigment in the standard product to 40% and then 60% consistently improved performance. On testing over blasted steel, little difference could be seen between the levels of zinc phosphate (and in fact calcium hydrogen phosphate, a lower cost material, gave equal performance).

Results obtained here were later borne out by trials on 25 metre high steel trestles in a steel plant and were generally utilized in formulations supplied for maintenance painting.

20.4 'High-performance' coatings

Although the term was not used at the time, the coatings described above are 'surface tolerant' paints, i.e. they could be applied over non-ideal substrates in terms of both hand-prepared rusty steel and old coatings.

The approach to using epoxies, for example, on hand-prepared steel was to use a suitable alkyd as the primer. However, this could lead to difficulties:

- Over-application of epoxy topcoats can cause adhesion problems.
- Over-application of primer can cause splitting and/or wrinkling problems.
- When used on pipes subject to heat purging at 100ºC embrittlement causes splitting of the epoxy.
- In a maintenance situation if one coat of primer is left for any period it starts to break down.

Work was then undertaken on a high-solids epoxy system suitable for hand-prepared steel, a major departure from normal thinking which was that epoxies had to be applied to blasted steel with a profile (note that it has always been recommended that the steel surface is not polished when using power tool cleaning for preparation; the recommendation now would be to use SSPC SP11).

The prototype system was based on liquid epoxy resin, with flexibilizing crosslinking resin and aluminium flake. A range of curing agents were evaluated, including various low viscosity polyamides, which might be expected to give the best results, cycloaliphatic amines based on IPD, and DDM based aromatic amines; surprisingly, the best results were obtained using the DDM based aromatic amine. Finally, addition of rust complexing additives gave a further improvement in performance in terms of reducing blistering from the scribe on accelerated testing on rusty steel. Field testing in 1978–79 at various sites around the UK confirmed the good results, and comparisons against Type B red lead showed this to be the only material to give equal performance in a single coat (in many ways this is not surprising, Type B red lead having similar characteristics in terms of volume solids and viscosity, ignoring secondary reactions). This material gave excellent adhesion to hand-prepared rusty steel, could be made suitable for use in a wide range of climatic situations by varying the level of salicylic acid in the curing agent, and gave very good anti-corrosive performance. There were difficulties with overcoating with low PVC thin film finishes such as chlorinated rubbers and vinyls, but overall results were excellent. There was obvious concern over the use of the DDM based curing agents but, despite continuous investigation, no suitable alternatives were found which would give equal performance. A suitable alternative curing agent was finally obtained around 1988 and in many regions this original surface-tolerant paint was changed from 1989–90, although it continued to be sold in some countries until the late 1990s.

20.5 Alternative approaches

Given that the requirements for application to hand-prepared steel appeared to be

- good wetting and penetration of the substrate, giving good adhesion,
- low internal stress to prevent adhesion loss,
- high solids to maximize the barrier effect and reduce solvent attack on the substrate,

other approaches were investigated, primarily the use of 'grease' paints, i.e. calcium, barium or lead soaps of oxidized petrolatum. Using MIO pigmentation, good results could be obtained, but the epoxy mentioned above consistently gave better performance, although these materials gave equivalent performance to modified red lead paints. The approach was finally abandoned because of problems in hot areas and unacceptable levels of dirt pickup, although products of this type have continued to be used, for example, on the internals of bridge base girder sections.

20.6 Complete surface tolerance

Most of the discussion to date has centred around the use of coatings applied directly to prepared rusty steel. In fact, when a coating system has broken down to ISO 4628 Re4, this is generally considered to be the point at which refurbishment must take place and breakdown is only 8% of the total area. Thus in maintenance painting by far the greatest area which is painted is not rusty steel but old coatings of various degrees of soundness and adhesion. Further to this, in many cases the actual composition of the underlying existing coatings is often unknown; simple site tests, such as solvent swabbing, can give an indication of what may be there but this only applies to a very specific area, not necessarily the complete site, and detailed chemical analysis of multiple samples is clearly not practical.

When maintenance is undertaken with oleoresinous paints there are not many difficulties. Except when multiple thick coatings are built up there are limited internal stresses, and because mineral spirits are the normal solvent there is very little solvent attack on the substrate coatings. Much of our thinking regarding the tolerance of surface-tolerant paints to 'any' aged coating was gained from recoating oil production platforms from 1982 to 1984. The original construction specification used on these consisted of zinc primer, high-build epoxy build coat and a finish of chlorinated rubber to alleviate possible difficulties with aged overcoating. However, chlorinated rubbers were deemed to pick up too much dirt and oil contamination, and thus the request was to change this back to epoxy to obtain better resistance. In these conditions where there is not a large diurnal temperature change, it is possible (surprisingly) to apply epoxy over this substrate. There is softening of the chlorinated rubber but it recovers and the system appears relatively sound (thermoplasticity). Cracking will only occur with rapid temperature fluctuations. It is this scenario which allows generalized 'epoxy mastics' to be used as surface tolerants on any aged coating in the marine industry, but when the same materials are used on bridges, for example, cracking can occur.

However, difficulty was encountered in the offshore situation described above in that cracking started to occur when overcoating the chlorinated rubber. Investigation revealed that the chlorinated rubber had been maintained with alkyd (presumably because it was easier to obtain special colours in alkyd than in chlorinated rubber, especially when rapid response maintenance was required). Application of the epoxy with strong solvents and internal stresses in this situation, with a differential in coating properties in the substrate already present, then caused cracking.

This highlighted a situation which exists widely in maintenance painting in that what appears to be a sound substrate of known paint type can be very variable. In most instances no records are kept when parts of a site are given a rapid cosmetic repaint before the arrival of an important visitor such as the chairman of the company, for example. A test method was thus evolved which consisted of paint systems of 250 microns dry film thickness of chlorinated rubber followed by alkyd, this being judged as a worst-case scenario. The recommended dry film thickness and double dry film thickness of experimental surface-tolerant epoxy could then be applied to this. When no cracking occurred the experimental coating could be deemed adequately surface tolerant for 'any' substrate. The coating itself required considerable flexibilization, not with external plasticizers which can leach out, causing embrittlement over a prolonged period, but with flexible polymers which contain epoxide, e.g. polyglycol epoxide groups, allowing reaction into the epoxy matrix. The difficulty with this approach is that this major flexibilization does decrease corrosion resistance significantly, making this type of product unsuitable for application directly to steel in corrosive environments, or for application to heavily pitted surfaces. In these situations the recommendation is to use an aluminium epoxy, of the type described previously, direct to steel and then to overcoat the entire surface with the flexibilized epoxy material. In practice two coats are always necessary, as it has been found that:

- Best performance on hand-prepared rusty steel is obtained by brush application.
- A minimum dry film thickness of 200 microns is needed to give good corrosion resistance; this can easily be achieved in two coats but *not* in a single coat.

These materials give corrosion resistance by adhesion and barrier properties.

The use of the flexibilized epoxy also has some other limitations: using longer-chain flexible higher-molecular-weight epoxy species reduces overall reactivity, especially affecting low temperature cure and also increasing walk-on and resistance to damage times; and using an epoxy as a finish coat gives the well-known problems of yellowing and chalking. It is therefore necessary to apply a durable finish such as polyurethane; fortunately the epoxy formulation allows easy overcoating after any time period. It is worth noting, however, that in the 15 years of sales of this type of material there have been no recorded problems of it flaking or cracking when applied over unknown old coatings. The criteria worked to have been that if the substrate is sound enough on examination with a penknife to allow application of a typical alkyd primer, then this type of product can be applied. Surface-tolerant paints will not stick down unsound substrates.

It is worth summarizing the properties that are expected in practice from a 'surface tolerant paint':

- Application to rusting surfaces.
- Application to old coatings.
- Application to damp surfaces.
- Application to contaminated surfaces – oil, salts, etc.?
- Application to millscale.*
- Application under adverse weather conditions – temperature, humidity, etc.
- Thin films give total protection.*
- Can be used as an alternative to preparing substrate to correct standard and will give equal performance.*
- Will give better performance than standard products when applied over Sa2½ steel.*

*Some of these expectations are correct, others are quite erroneous.

20.7 Urethane surface tolerance

Recognition of the problems inherent in the flexibilized epoxy approach then led to developments to investigate whether these could be alleviated.

This is clearly not possible utilizing epoxy technology and thus flexibilized aliphatic urethane technology was used, obtaining all the same parameters of high solids, flexibility and total substrate tolerance, along with good durability, colour retention and low temperature cure. Some improvement in corrosion resistance was also obtained by this route, but not sufficient to allow direct application to corroded steel in aggressive environments. As with the epoxy system above, this material has been marketed worldwide for around 12 years, again with no recorded problems regarding cracking, flaking or other detrimental effects on substrates.

Both of the substrate-tolerant materials described above meet some key parameters required to achieve tolerance, i.e. flexibility, elongation characteristics and coefficient of expansion. This gives the ability to apply them over all aged coatings.

20.8 Epoxy 'mastics'

Epoxy 'mastics' now appears to be the generic term used for maintenance epoxies in general and can cover a multitude of performance parameters. In general they are not formulated via the route described above, but rather they consist of crosslinked liquid epoxy together with hydrocarbon resin or other external plasticizer to attempt to gain some degree of flexibility. When subjected to thermal cycling tests on thermoplastic substrates, cracking can occur, and this has been observed in practice on bridges in both northern Europe and the USA and Canada, which has led these products now to be treated with some reservations in this type of overcoating situation. Generally these products are applied to sweep blasted or hydroblasted steel, and on old coatings which are thermoset types that have been abraded.

However, this type of coating does have a number of advantages and taking, for example, the material sold by International Paints in this area, the following properties can be obtained:

- Excellent water immersion characteristics
- Excellent corrosion resistance on blasted steel
- Suitable for white oil immersion, etc.

The flexibilized substrate-tolerant materials above are not suitable for any of the above areas and the products designed for rusty steel, although showing advantages in performance in that situation, do not give the same difference when used on blasted steel.

Table 20.2 illustrates the difference between the truly surface-tolerant flexibilized coatings, which can basically be applied to any aged coating, and the commonly used epoxy mastics.

Table 20.2 Comparison between 'epoxy mastics' and 'substrate tolerant' coatings

Coating	Mandrel bend test, 14 days' cure (low diameter, more flexible)	Temperature cycling over thermoplastic/alkyd (number of cycles before cracking)	Overcoatable with PU (5 = excellent, 0 = no adhesion)
Epoxy mastic – I	13 mm	9	¾
Epoxy mastic – A	13 mm	9	1
Epoxy mastic – B	13 mm	13	½
Flexibilized epoxy	5 mm	>20	4
Flexibilized urethane	5 mm	>20	5

20.9 Current development

In both Western Europe and North America most chemical plants operate to high standards of prevention of environmental pollution. However, we have found that as we have started to undertake maintenance painting on plants in Eastern Europe there can be much more severe substrate contamination, especially with sulphates from sulphur dioxide and hydrogen sulphide. This has led to further investigation and evaluation of materials, this time on hand-prepared contaminated rusty steel (from site) and then, as well as normal testing, also subjecting the material to a sulphur dioxide cyclic test (Kesternich Test). Materials have now been formulated which give good performance both in accelerated testing as above and on site in these aggressive contaminated conditions.

20.10 Moisture-cured urethanes (MCUs)

This type of technology has been used for anti-corrosive paint systems for around 20 years, but has been relatively limited in use until the last few years, when MCUs have been started to be used on the extensive US Bridge Painting Program. From a technology viewpoint this chemistry is very interesting in that it is relatively easy to formulate for different film flexibilities and cure rates, even at low ambient temperatures. Limitations are solids content, which can limit easily applied film thickness (typical volume solids 50–60%), and cost, but probably most importantly, difficulties in manufacturing due to the inherent water sensitivity of moisture curing systems.

Most currently used systems are based on either MDI based prepolymers or higher molecular weight TDI based prepolymers. In this instance the priming coat again relies on being of low viscosity to give good penetration into any corrosion on the substrate, but only a limited (30–40 microns) thickness is applied. Generally two subsequent coats are needed to give a reasonable barrier thickness. The primer used in this situation is normally pigmented mainly with aluminium; however, it has been found from recent laboratory testing that surprisingly good results have been obtained on hand-prepared rusty steel, and hydroblasted rusty steel, using a primer pigmented with zinc dust and micaceous iron oxide, and alternative pigmentation can also give good results. Application was to hand-prepared weathered rusty steel and exposure was for four years at an industrial site in Germany. It can be clearly seen that where the full system is present, significantly better adhesion is obtained from the moisture-cured urethane system, and that the epoxy largely hides the corrosion and having poor adhesion is likely to delaminate at some point.

An active programme is now underway following a re-evaluation of our laboratory results with moisture-cured urethanes and field evaluations where they have been shown to have significantly less detrimental effect on old coatings than the ‘epoxy mastics’ described earlier, despite their higher solvent content. This is almost certainly due to the ability to ‘build in’ stable flexibility into urethane systems, whereas in many instances epoxies tend to become more brittle with age due to migration of low molecular weight plasticizing species.

This technology gives potentially a single-pack high performance solvent-tolerant system, which is especially useful in low temperature, high humidity environments. It is interesting to note that, in general, moisture-cured urethanes appear to outperform epoxies on a thickness for thickness basis, 70–80% of epoxy dry film thickness giving equal performance when MCUs are used.

20.11 Rust converters

This type of material is often promoted heavily in the literature and appears to be the solution to many of the problems of painting rusty steel:

- minimizes effort required in surface preparation;
- improves performance;
- ‘chemically converts’ an inherently unstable substrate into a stable one.

There are basically two types of these materials, one based on tannic acid as the active component, which can sometimes act simply as an active chemical and sometimes in conjunction with a film-forming resin (e.g. acid-stable PVDC resins), and the other on phosphoric acid chemistry.

Experiments have shown that the claim of tannic acid reacting with rust is correct; however, it does not stabilize voluminous corrosion products or scale but rather tightly bound corrosion adjacent to the steel surface. To give longer-term protection, both variants need to be overcoated with at least some type of barrier coating system. Comparison of this on the same substrate as for the rust converter shows little advantage to using the rust converter.

The other approach of using phosphoric acid type materials can give very good substrates for painting, but is more suitable for dipping treatment of small articles rather than using on large areas in the field. Given the correct exposure time and temperature, uniformly grey surfaces of phosphate can be produced by this process that are ideal for painting and give excellent performance. The practicality of achieving this reaction in the field, and the environmental and health and safety issues associated with the used of acid, limit this approach to small areas and articles.

20.12 Conclusions

From all of the above review, it can be seen that the basic requirements for successful surface-tolerant coatings are:

- Long term coating flexibility – no embrittlement on ageing
- Adhesion
- High solids
- High barrier effect.

However, it must be realized that even when an excellently formulated and developed coating is applied to a rusty surface, this surface is not only potentially extremely variable in character but it is also thermodynamically unstable, with the corrosion process already underway. Given this scenario, we can slow down this process by using the correct coatings, but we cannot stop it. It is thus unlikely that without thorough blast cleaning (or preferably ultra high pressure hydroblasting) a suitable surface, free of contamination, will be achieved. Thus it is unlikely that, even with all care and precautions taken, maintenance painting will give the same coating lifetime as that obtained from new construction systems. With hand or power tool cleaning only, the expected time before repaint is likely to be only 30–50% of the time for a suitable high quality new construction system in the same environment, and significantly less than these times (10–20%) if incorrect coatings are used.

This is found to be especially the case in severe offshore/marine environments where correctly applied high quality coatings on clean grit-blasted steel can be expected to last 12–15 years or more, whereas experience has shown that maintenance coatings applied onto power tool cleaned, and possibly contaminated, surfaces often need further repair within 3–5 years. This difference tends to be less obvious in milder environments where there is less electrolyte, much less surface contamination, and considerably less stress on the film due to continuous wetting and drying out. Here maintenance systems can easily last in excess of 10 years, even when applied to power tool cleaned steel.

The old adage that the performance and lifetime of a coating system is directly related to the degree of surface preparation holds as well today as ever, and the ideal of a coating directly over rust with long life has still not been achieved, and questionably never will be.