Analysis of Paints and Related Materials:

Current Techniques for Solving Coatings Problems

William C. Golton, editor

ASTM

STP 1119

STP 1119

Analysis of Paints and Related Materials: Current Techniques for Solving Coatings Problems

William C. Golton, editor

ASTM Publication Code Number (PCN)
04-011190-14

ASTM
1916 Race Street
Philadelphia, PA 19103

Library of Congress Cataloging-in-Publication Data

Analysis of paints and related materials: current techniques for solving coatings problems.
p. cm.—(ASTM special technical publication; 1119)
Includes bibliographical references and index.
ISBN 0-8031-1465-6
1. Paint—Analysis. I. Series.
TP936.5.A527 1992
667'.6—dc20 92-22563
CIP

Photocopy Rights

Peer Review Policy

Each paper published in this volume was evaluated by three peer reviewers. The authors addressed all of the reviewers' comments to the satisfaction of both the technical editor(s) and the ASTM Committee on Publications.

The quality of the papers in this publication reflects not only the obvious efforts of the authors and the technical editor(s), but also the work of these peer reviewers. The ASTM Committee on Publications acknowledges with appreciation their dedication and contribution to time and effort on behalf of ASTM.

Printed in Baltimore, MD
August, 1992

Foreword

This publication, *Analysis of Paints and Related Materials: Current Techniques for Solving Coatings Problems*, contains papers presented at the symposium of the same name held in Pittsburgh, Pennsylvania on 13–14 May 1990. The symposium was sponsored by ASTM Committee D-1 on Paint and Related Materials and its Subcommittee D01.21 on Chemical Analysis of Paints and Paint Materials. The symposium chairman was William C. Golton, E. I. duPont de Nemours & Company, Inc., Philadelphia. He also served as editor of this publication.

Contents

Overview

The purpose of the two-day symposium was to present and discuss the latest techniques and instruments used to analyze and characterize paints, coatings, and related materials. The symposium was sponsored by ASTM standards-writing Committee D-1 on Paint and Related Coatings and Materials and its Subcommittee D01.21 on Chemical Analysis of Paints and Paint Materials.

This book is divided into four sections that reflect the order of papers given at the symposium. Section I is *Analysis and Characterization of Whole Paint.* Two papers were presented in this category: (1) "Modern Analytical Techniques for Coating and Coating Materials," by Ulrich Schernau, Bernhard Hueser, and Karin Weber; and (2) "Mass Spectrometric Techniques for Coatings Characterization," by William J. Simonsick, Jr.

Section II is *Analysis and Characterization of Paint Components.* Four papers were presented in this category: (1) "HPLC Analysis for Epoxy Coatings Resins," by David P. Sheih and Donald E. Benton; (2) "Application of Size Exclusion Chromatography to Polymers and Coatings," by Cheng-Yih Kuo and Theodore Provder; (3) "X-Ray Techniques for Coatings Analysis," by A. Monroe Snider, Jr.; and (4) "Practical Applications of Gas Chromatography in the Paint and Coatings Industry," by Francis X. Young.

Section III is *Cure Characterization, Durability, and Coating Problems.* Three papers were presented in this category: (1) "Applications of FTIR to Paint Analysis," by Jack H. Hartshorn; (2) "Chemical Characterization of Cross-Linked Polyurethane Films," by L. G. J. van der Ven, G. D. B. Van Houwelingen, and R. R. Lamping; and (3) "Principles and Applications of Photoelectron and Ion Spectroscopy for the Analysis of Polymer Surfaces," by Joseph A. Gardella, Jr.

Section IV is *Paint Failure and Defects.* Two papers were presented in this category: (1) "FTIR Techniques for the Analysis of Coating Problems: Solid Sampling Accessories," by Anne M. Millon and James M. Julian; and (2) "Failure Analysis of Applied Coatings," by Kenneth B. Tator and Dwight G. Weldon.

Analysis and Characterization of Whole Paint

Ulrich Schernau,[1] Bernhard Hueser,[1] and Karin Weber[1]

Modern Analytical Techniques for Coating and Coating Materials

---

REFERENCE: Schernau, U., Hueser, B., and Weber, K., "**Modern Analytical Techniques for Coating and Coating Materials,**" *Analysis of Paints and Related Materials: Current Techniques for Solving Coatings Problems, ASTM STP 1119,* American Society for Testing and Materials, Philadelphia, 1992, pp. 3–21.

ABSTRACT: The past decade has been characterized by an evolution from electronic-regulated to computer-controlled analytical equipment. This holds especially true for spectroscopic instruments, e.g. FT-IR spectrometers and FT-NMR spectrometers, where the application of Fourier transform techniques requires computer support. But chromatographic instruments are nowadays also equipped with dedicated computers or PCs for controlling the instrument and for data acquisition and evaluation.

The development has led to an improved performance of the instruments in terms of enhanced information, sensitivity, and reliability. These modern analytical instruments can be used favorably for the analysis of coatings and coating materials, making them a valuable tool for the analyst working in this field. In this paper the most important methods will be described and illustrated with examples from daily work.

Since coating materials very often represent complex mixtures, in some cases the combination of different instrumental methods is necessary to obtain the required information. Examples that will be dealt with are pyrolysis-GC/MS and the coupling of chromatographic and spectroscopic methods, e.g. GPC/FT-IR or GPC/FT-NMR.

In many cases a work-up procedure as a preparatory step prior to the instrumental method is advisable in order to achieve sufficient information. Since many of the coating materials contain saponifiable groups, saponification is still the most prominent method. A general scheme for carrying out such a saponification will be outlined. In addition, we would also like to demonstrate a recently developed method using trimethylsulfonium hydroxide as the reagent. This method, which can be easily applied in the same way as the well-known GC derivatization procedures, yields more reliable results for fatty acids and polyols than the conventional method.

KEY WORDS: coatings, review of analytical methods, infrared spectroscopy, nuclear magnetic resonance spectroscopy gas, liquid chromatography

Paints represent complex multicomponent systems. In most cases the individual components, i.e. the binder, the pigment, and the solvent, are also of complex composition. Therefore, the thorough and complete analysis of a paint requires a great deal of experience and the use of a whole set of modern analytical techniques.

The most prominent instrumental methods which have found widespread use in the different analytical laboratories can also be favorably utilized for the analysis of paint and related materials. In our paper we would like to briefly discuss some important spectroscopic methods—infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy, and chromatographic methods—gas chromatography and liquid chromatography. These methods meet to a high degree the requirements for a successful analytical technique, namely efficiency, i.e. the gaining of substantial information about the sample composition within a reasonable period, and simple handling, including sample preparation and measurement.

[1] BASF Lacke and Farben AG, 4400 Munster, Germany.

The past decade has been characterized by a rapid development of computer-controlled analytical equipment, especially in the spectroscopic field. For modern Fourier transform (FT) IR and NMR spectrometers, the computer is an integral part of the equipment and a prerequisite for operating them. Furthermore, it has distinctly improved the performance of the instruments in terms of efficiency and handling. In the chromatography area, computers are mainly used for facilitating the operation of the instrument and for data acquisition and evaluation, thus providing the means for an automation of the respective methods.

Often, analytical problems can be better solved by combining specialized instrumental methods. Some of these coupled methods, which yield more detailed information about the sample, will be outlined; two methods—pyrolysis-gas chromatography/mass spectroscopy and offline coupling liquid chromatography/FT-IR spectroscopy—will be dealt with more thoroughly.

Despite the fact that the powerful instrumental methods mentioned are available to us, we regard chemical degradation techniques as inevitable for solving specific analytical problems. Therefore we also want to discuss some aspects of chemical degradation.

The methods we are going to discuss are mainly suitable for the analysis of binders and resins and in part also for solvents. But they can also be applied to the elucidation of coating defects and contaminants and for the determination of substances released during the curing process.

Spectroscopic Methods

Electromagnetic radiation of different wavelength is used to investigate different aspects of molecular structures. Among the different spectroscopic methods, IR spectroscopy and NMR spectroscopy play a dominant role in the analysis of coating materials; both are efficient methods for the characterization of binders and resins, and both require minimal sample preparation.

In our opinion Raman spectroscopy will probably gain more interest. In the form of near infrared Fourier transform (NIR FT) Raman spectroscopy, a method is now available where the strongly interfering fluorescence of conventional Raman spectroscopy using visible laser excitation is largely suppressed. NIR-FT Raman spectroscopy can be performed with the help of a FT-IR spectrometer equipped with a FT Raman accessory [*1*]. In this way, the advantages of FT techniques outlined below can also be utilized for Raman spectroscopy, which has the additional advantage that it can be applied to waterborne samples.

In the following, modern FT techniques for IR and NMR spectroscopy will be discussed which extend both the range of application and the gain of information of these spectroscopic methods to coatings and coating materials.

Fourier Transform Infrared (FT-IR) Spectroscopy

Fourier transform infrared spectrometers have replaced conventional grating instruments in many laboratories. These instruments show significant advantages over dispersive ones. The so-called multiplex advantage, i.e. the fact that the data are simultaneously measured for the complete frequency range, leads to a significantly improved signal-to-noise ratio of the spectra. As a result, it is possible to use techniques which are known to yield rather poor spectra or to consume extended recording times with dispersive spectrometers. Examples are diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), attenuated total reflectance spectroscopy (ATR), spectroscopy on micropellets, microspectroscopy, and photoacoustic spectroscopy (PAS). In addition, the built-in computer necessary to operate the FT-IR spectrometer allows useful spectral manipulation, e.g. baseline correction, deconvolution, or subtraction of spectra, which help to improve the spectral information. Building up spectral libraries and library searches are also possible. A detailed monograph about the theory of FT-IR spectroscopy, the various measuring methods and their application to different analytical problems, has been published by Griffiths and de Haseth [2].

We would like to briefly outline the application of some of these newer techniques to the analysis of coating materials.

Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)—DRIFTS is characterized by simple sample preparation and a high-detection sensitivity. It is applicable to solid samples either by mixing them with potassium bromide (KBr) powder or transferring the dissolved sample onto KBr powder. Instead of KBr, other suitable matrix materials can be used, such as potassium chloride (KCl) or sulfur.

We see mainly two areas where DRIFTS shows an advantage over a measurement in transmission. One is the field of opaque samples, e.g. pigments containing aluminum flakes. This is demonstrated in Fig. 1. The transmission spectrum from a KBr pellet reveals only little information, whereas the diffuse reflectance spectrum displays pronounced absorption bands which can be easily assigned.

Another domain of DRIFTS is the characterization of fractions from liquid chromatography; some aspects of this method will be given below when combined instrumental techniques are discussed.

Attenuated Total Reflectance (ATR) FT-IR Spectroscopy—ATR spectroscopy is a surface technique employing optical plates with a high refractive index (KRS-5 or Ge) designed to give multiple internal reflectance. The material to be analyzed is placed in contact with the internal reflectance plate. To establish an intimate contact of the sample with the optical plate, a sufficient pressure has to be applied.

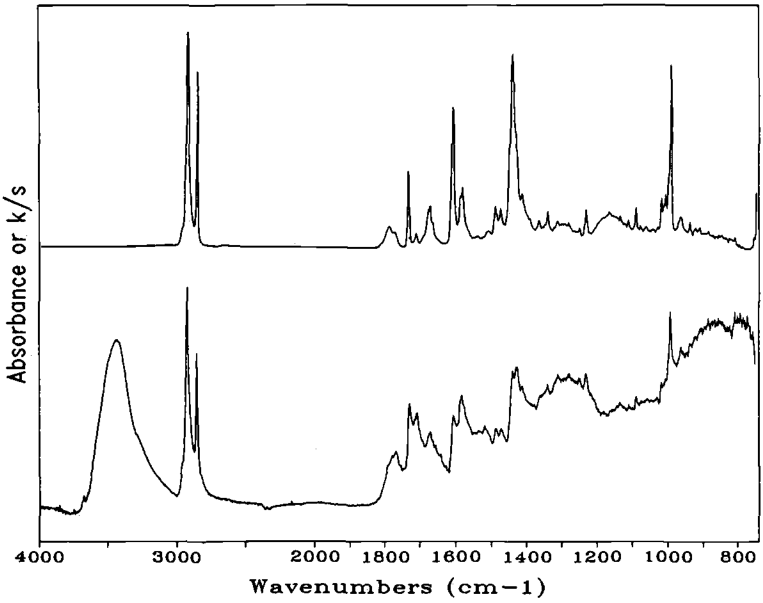


FIG. 1—*Infrared spectra of a mixture of an Indanthron pigment and aluminum flakes. Top: diffuse reflectance spectrum; bottom: KBr pellet.*

The incident infrared radiation is almost completely reflected internally, i.e. within the ATR crystal. A small portion, however, passes the boundary between the crystal and the sample and is reflected from there into the crystal. Due to absorption processes, the intensity of this portion of radiation is attenuated. The resultant infrared spectrum resembles a transmission spectrum with one restriction: since the depth of penetration is proportional to the wavelength, the absorption bands become more intense when going from shorter to longer wavelengths. Typical depths of penetration vary from about 0.1 to about 10 μm depending on the refractive indices of the crystal and the sample and the reflection angle. ATR spectroscopy can be favorably used for the characterization of the surface of a coating, e.g. with respect to degradation or curing. An example for a two-component polyurethane clear coat cured under different conditions is given in Fig. 2.

Infrared Microspectroscopy (Infrared Microscope)—Since the early 1980s the growing interest in equipment for infrared microspectroscopy has become obvious. The high sensitivity of Fourier transform infrared spectrometers made the coupling with an all-reflecting microscope useful. In addition, there was an increasing number of analytical problems which called for such a microanalytical method. The theoretical aspects of infrared microspectroscopy, and a considerable number of applications in different fields, are dealt with in a recently published handbook [*3*].

Infrared microspectroscopy is especially well suited for the analysis of surface imperfections in the form of small inclusions, as demonstrated in the following example. The photomicrograph in Fig. 3 shows an inclusion of about 50 μm in diameter in a repair base coat. A cross section of the inclusion is prepared with the help of a scalpel. As "sample holder," 100-μm apertures mounted on a wire grid are employed. The infrared spectrum shown in Fig. 4 clearly demonstrates that the inclusion is mainly made up of a yellow pigment of the Flavanthron type, indicating a seeding problem of this pigment.

The characterization of the individual layers in a multilayered coating is relatively simple when done with infrared microspectroscopy. Figure 5 shows a photomicrograph of a cross

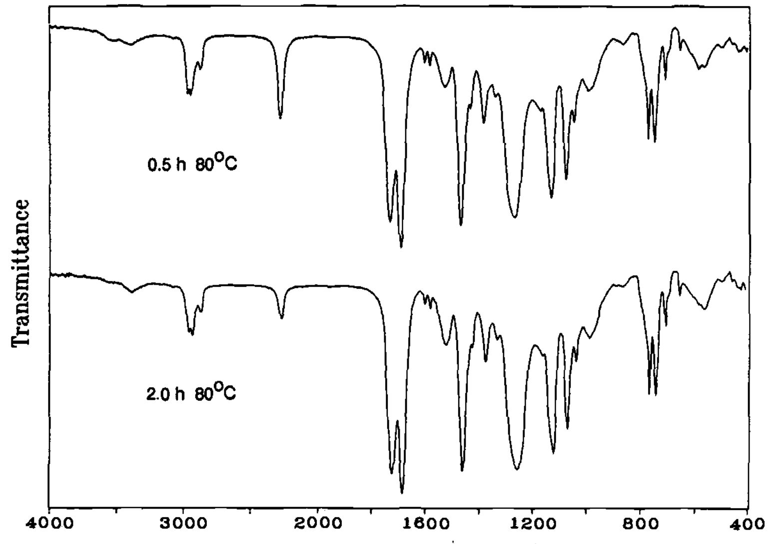


FIG. 2—*ATR spectra of a two-component polyurethane coat cured under different conditions: KRS-5 crystal, 45°.*

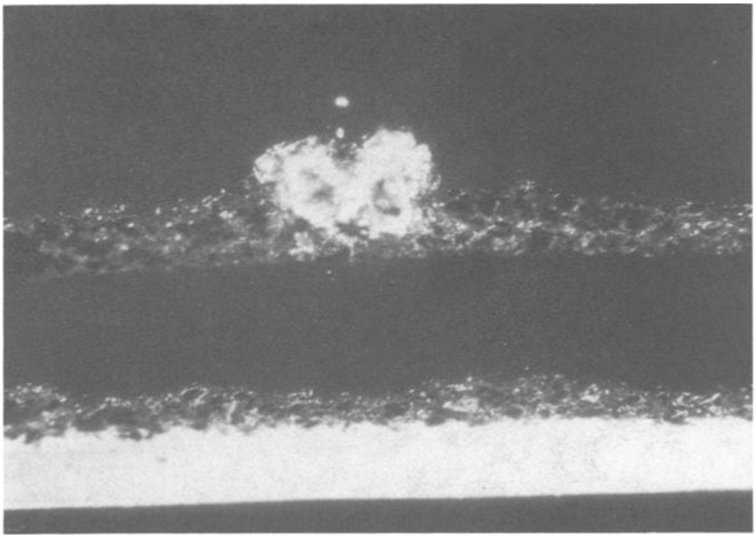


FIG. 3—*Photomicrograph of an inclusion in a repair base coat.*

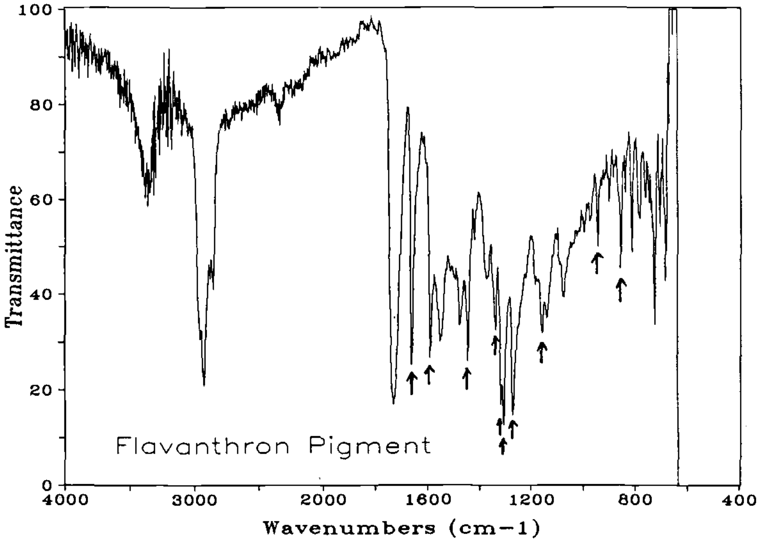


FIG. 4—*Spectrum of the inclusion in a base coat recorded with the help of the infrared microscope; sampling area is about 30 by 30 μm.*

section of a three-layered coating consisting of a cathodic electrodeposition coat, a primer surfacer, and a top coat. In Fig. 6, the corresponding infrared spectra are presented.

In addition to the methods described, another technique should be mentioned that appears extremely suitable for the analysis of coatings—photoacoustic FT-IR spectroscopy. Photoacoustic spectroscopy (PAS) is a nondestructive surface technique with the ability to perform surface depth profiling. The principle of PAS and its application to the character-

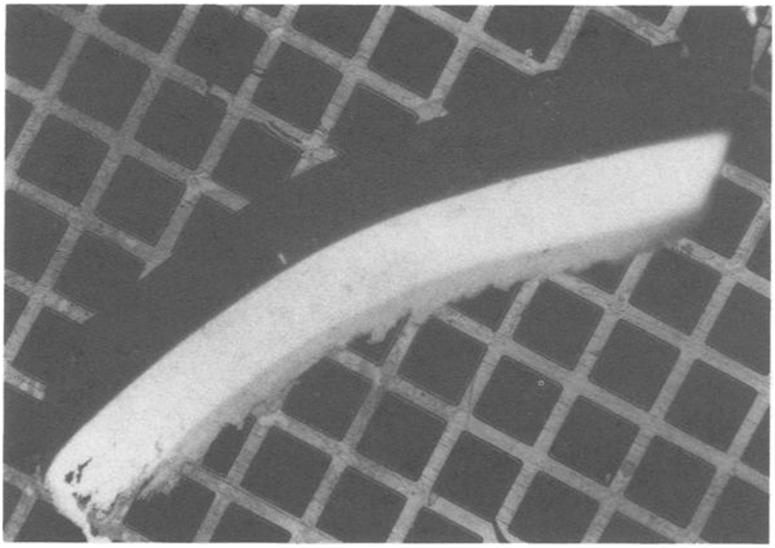


FIG. 5—*Photomicrograph of a cross section of a three-layered coating. Bottom: E-coat; medium primer surfacer; top: top coat.*

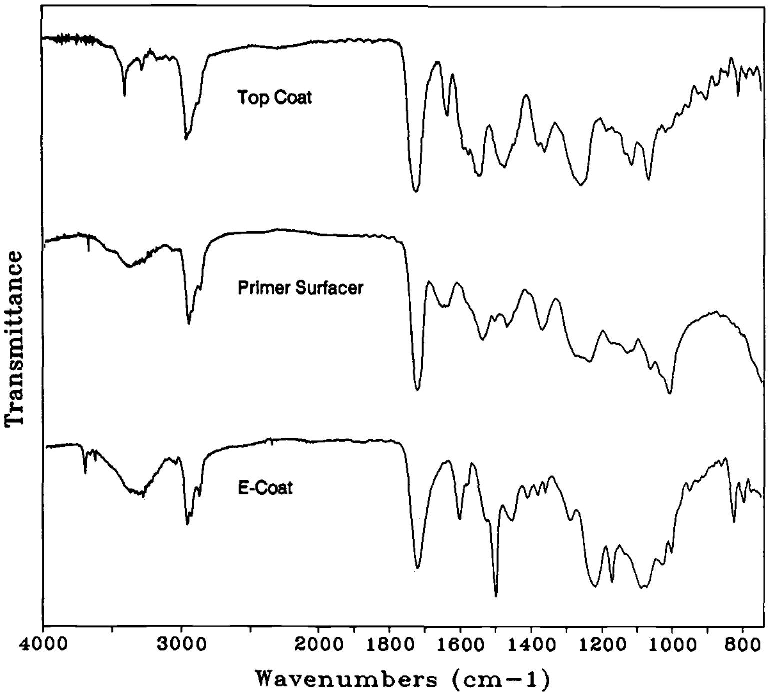


FIG. 6—*Microscope infrared spectra of the individual layers of a three-layered coating.*

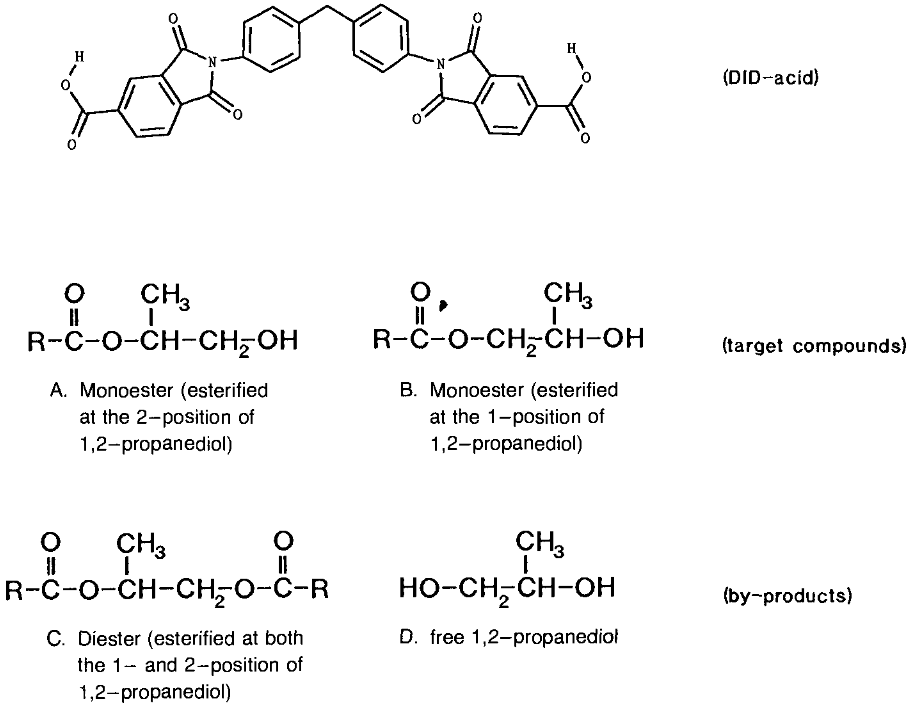
ization of coatings with respect to curing, crosslinking, and weathering has been recently described by Urban [*4*].

Fourier Transform Nuclear Magnetic Resonance (FT-NMR) Spectroscopy

In terms of efficiency and handling, NMR spectroscopy has an outstanding position for the analysis of organic materials. This technique yields both qualitative and quantitative results and requires only little sample preparation. During the past decade, computer-controlled pulse FT-NMR spectrometers equipped with superconducting magnets have become commercially available. As a result, high-resolution 1H- and 13C-NMR spectroscopy became routine methods as did the more sophisticated 2D-NMR techniques, which yield detailed information about spin-spin coupling. Thus, it is possible to deduce even complicated structures and, by measuring relaxation times, to achieve information about the dynamics of organic compounds. The high field strength of the superconducting magnets (> 4.7 T) improved both resolution and sensitivity of NMR spectroscopy.

NMR spectroscopy is a very helpful tool for supporting organic synthesis work, e.g. by tracing different reaction pathways. As an example, we would like to present the qualitative and quantitative analysis of the reaction products of the esterification of diimido dicarboxylic acid (DID acid) with 1,2-propanediol. The diacid, the target compounds, and the by-products are shown in Fig. 7.

The 1H-NMR and the 13C-NMR spectrum (Fig. 8) reveal that all products (A, B, C, D) were present in the reaction mixture. This could be proved with the help of a 2D-NMR



A. Monoester (esterified at the 2-position of 1,2-propanediol)

B. Monoester (esterified at the 1-position of 1,2-propanediol)

C. Diester (esterified at both the 1- and 2-position of 1,2-propanediol)

D. free 1,2-propanediol

FIG. 7—*Reaction products of DID acid and 1.2 propanediol.*

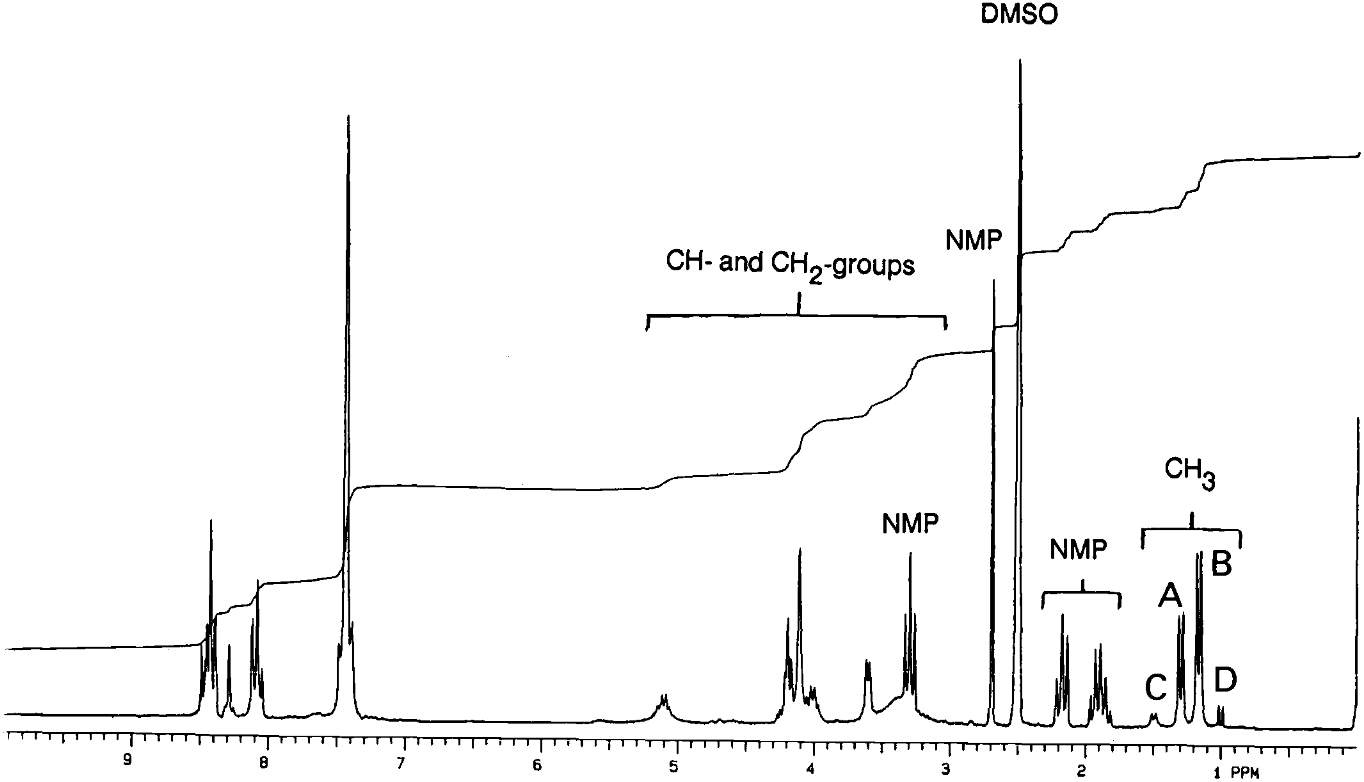


FIG. 8—*^{1}H-NMR and ^{13}C-NMR spectrum of the reaction products of DID acid and 1.2 propanediol. NMP = N-methyl pyrrolidon; DMSO = dimethyl sulfoxide.*

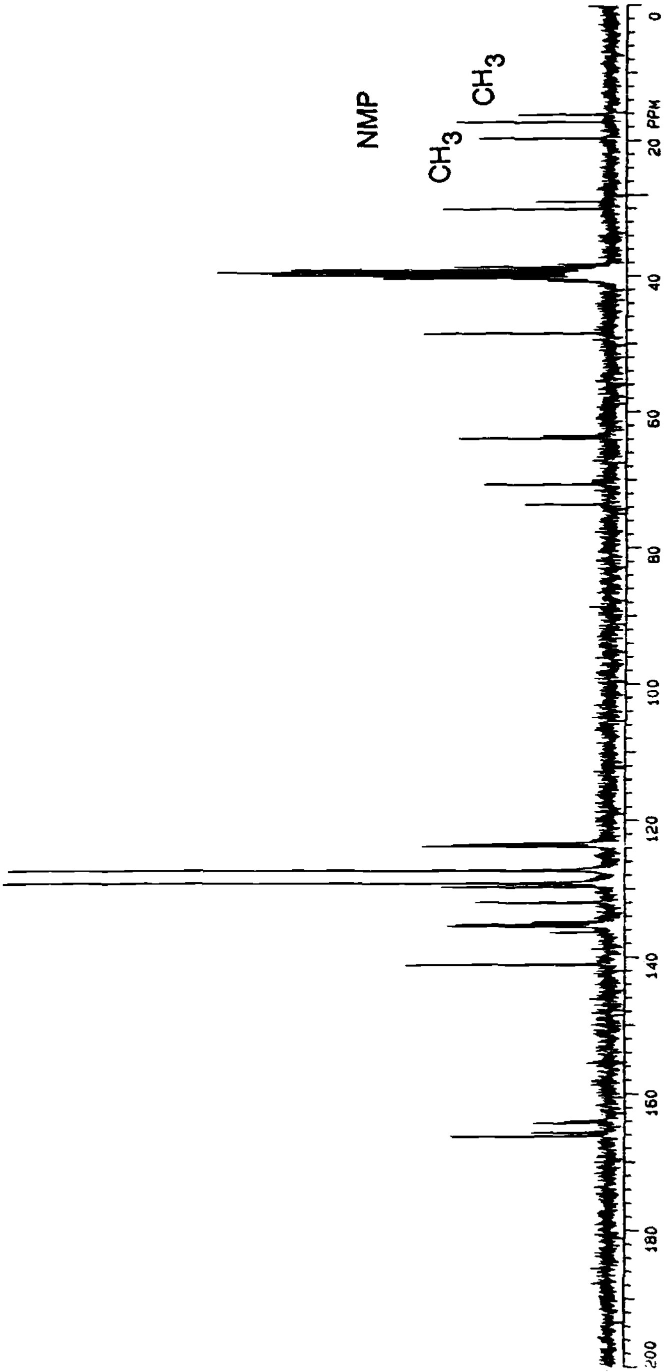


FIG. 8—*(Continued).*

experiment which allowed the methyl group of propanediol incorporated in the different compounds to be unequivocally assigned. Thus, the respective compounds, namely the monoesters (A, B), the diester (C), and free propanediol (D), could be quantified. The homonuclear correlation spectrum (H, H-COSY) and the spectral range of the 1H-NMR spectrum used for quantitative evaluation are shown in Fig. 9. The following concentrations were found

$$A = 34\% \quad B = 55\% \quad C = 6\% \quad D = 5\%$$

This means that the monoesters A and B (target compounds) represent the major products and that esterification in the 1-position of propanediol is preferred in comparison to the 2-position.

Chromatographic Methods

Chromatography is the most widely used analytical technique. Among the different methods which employ different stationary and mobile phases, gas chromatography (GC) and liquid chromatography (LC) play the most prominent role for the analysis of paints and related materials.

Gas Chromatography

Gas chromatographic separations are particularly well suited for the investigation of complex (volatile) mixtures. Modern column technology offers an excellent separation efficiency. The groundwork for this separation efficiency was done by Golay [*5*] more than 30 years ago with the invention of capillary columns (open tubular metal columns coated with a thin layer of a liquid, stationary phase). Since handling and availability of these first columns were poor, capillary gas chromatography found only limited application. The situation gradually improved when glass capillary columns became commercially available in the 1970s. Difficulty in handling these breakable columns was one of the reasons which prevented a real breakthrough of capillary chromatography at that time. This was changed with the introduction of fused silica columns in the late 1970s [*6*]. Handling of these flexible columns is now easy, and they exhibit a high durability, especially when coated with immobilized stationary phases.

The widespread application of gas chromatography to the analysis of organic compounds is also related to the fact that—in the form of the hydrogen flame ionization detector—a universal and very sensitive detector is available.

Though modern capillary columns have a high separation efficiency, it is not always feasible to separate a complex mixture into the individual compounds within one single-column run. In order to accomplish the determination of the compounds under study, though, two principal approaches have been chosen: (1) enhancement of separation, and (2) specific detection.

One obvious way to enhance separation is to run the analysis on columns of different polarity, i.e. different selectivity for different classes of compounds. In most cases separation of compounds that are not separated on the first column can be achieved by the second one. This technique can also be carried out simultaneously by mounting two (or even three) columns into one injector and equipping each of the columns with a separate detector.

A more sophisticated enhancement of separation is achieved by the so-called column-switching technique [*7*]. Two columns of different selectivity are coupled in a way that allows preseparated fractions from the first column to be swept onto the second column for further separation.

Specific detectors such as nitrogen/phosphorous, halogen, or sulfur-sensitive detectors are used for the investigation of the respective compounds. The main application of gas chromatography for the analysis of paints is the broad field of organic solvents. Typical examples are the determination of solvents in complete paints and in the atmosphere at the workplace.

Gas chromatography can also be favorably applied to the analysis of individual resin components, e.g. polyols, fatty acids, dicarboxylic acids either as raw materials or after chemical degradation of the respective resins. In the form of pyrolysis GC, which will be dealt with in more detail in a subsequent section, gas chromatography is also applicable to the analysis of complete resins or binders.

Liquid Chromatography

Liquid chromatography (LC) is the collective name for a whole set of different techniques, e.g. high-performance liquid chromatography (HPLC), ion chromatography, ion-exchange chromatography, or size-exclusion chromatography (SEC). For the analysis of coating materials, reversed phase HPLC and SEC are the most important techniques.

HPLC is mainly used in areas where GC is not suitable, i.e. for substances that are polar, nonvolatile, or thermally sensitive. When compared to GC, there is no universal, sensitive detector for the HPLC. The most widely used UV detector is restricted to the detection of compounds with UV-absorbing properties; the refractive index detector cannot be used in connection with gradient elution. Therefore, the application of HPLC to the analysis of coating materials is limited to some selected areas where UV-detection is possible, e.g. UV absorbers, melamine resins, epoxy resins, stabilizers, and plasticizers.

Universal detection techniques will broaden the field of application. A low-priced approach is the so-called mass detector, the principal design of which is described by Charlesworth [*8*]. The technique employs a light-scattering technique for monitoring fine analyte particles. These particles are generated by nebulizing the effluent from the chromatographic column into a preheated carrier gas stream. The solvent of the droplets formed evaporates during the passage through a temperature-controlled tube, leaving very fine particles of the analyte, which then pass for detection through a laser beam. In the recent years, this type of detector has become commercially available.

In size-exclusion chromatography (SEC) the molecules of the sample are sorted according to their size. This technique is mainly used for the determination of the molecular weight and the molecular weight distribution of polymers. The application of SEC to the characterization of resins used for coatings has been thoroughly dealt with by Kuo and Provder [*9*].

Since the SEC columns are usually calibrated with narrowly distributed polystyrene standards, the molecular weight data obtained represent polystyrene equivalent values, i.e. these are only relative values. The determination of absolute molecular weights requires more complicated procedures, e.g. calibration with specific polymers of known molecular weight or multiple detection using a concentration detector and a second detector whose signal is proportional to the size of the molecules (light scattering detector, viscosimeter).

Combined Instrumental Techniques

In some cases, the linkage of specialized instrumental methods is necessary to obtain the required information about the sample composition.

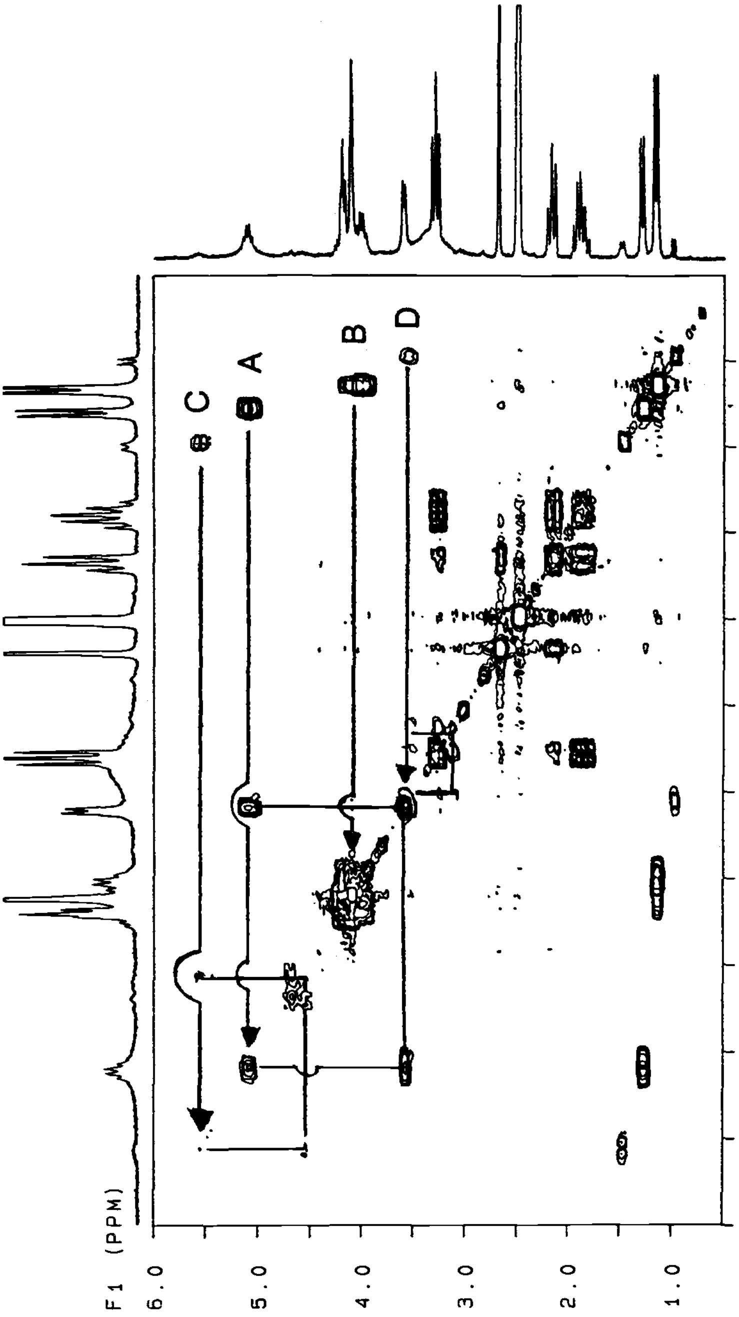


FIG. 9—*COSY spectrum and section of the* ^1H*-NMR spectrum of the reaction products of DID acid and 1.2 propanediol.*

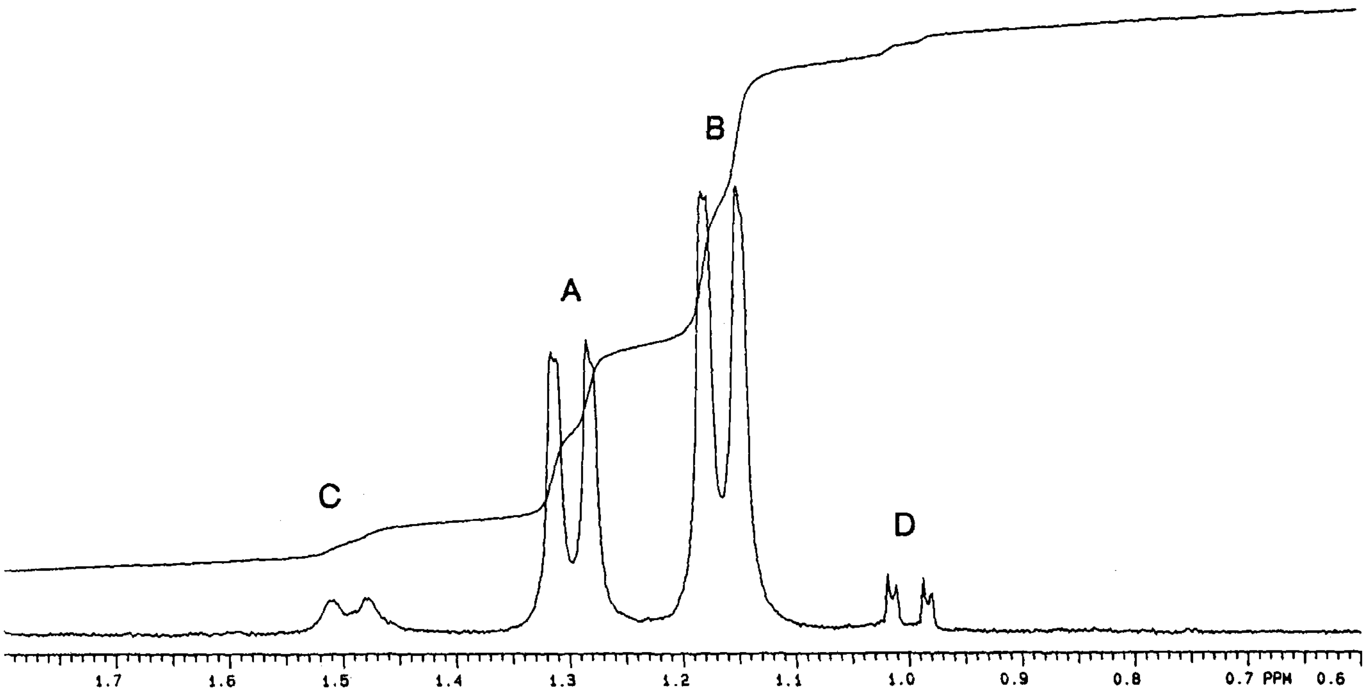


FIG. 9—*(Continued)*.

Typically, a separation step in the form of a chromatographic method is coupled with a spectroscopic identification step. As far as the ease of operation, i.e. handling is concerned, online couplings are advantageous.

The development of low-priced mass spectrometers (ion trap or quadrupole) allows them to be used as sensitive and selective gas chromatographic detectors. Also, modern Fourier transform infrared spectrometers provide the necessary sensitivity for an online coupling with capillary gas chromatography. This type of coupling is realized with the help of the light-pipe technique. More sensitive methods use a matrix isolation or a tracer GC/FT-IR interface.

In liquid chromatography such a coupling is, however, not always easily feasible. The mobile phases used, in both reversed-phase liquid chromatography and in size-exclusion chromatography, frequently interfere with the spectroscopic analysis. Therefore, the removal of the liquid phase is advisable. This can be realized by a quasi-online coupling (as used, for example, in LC/thermospray MS and other LC/MS interfaces) or by an offline coupling.

In the following we want to demonstrate the application of two of these combined methods—pyrolysis GC/MS (online coupling) and LC/FT-IR (offline coupling)—to the analysis of coating materials.

Pyrolysis GC/MS

The use of pyrolysis GC/MS for the analysis of a variety of resins and other binder components has been described in detail in the literature, e.g. by Ohtani and Tsuge [*10*] and by Denig [*11*]. Useful information is obtained for resins such as polyacrylates, polyesters, polyurethanes, and phenolic resins. We would like to discuss in more detail some aspects of the pyrolysis GC/MS of hydroxy and carboxy functional polyacrylates, which play an important role as binders in two-pack polyurethane coatings. To our knowledge there was only limited information in the literature concerning the positive identification of carboxy and hydroxy functional monomers.

Some time ago we reported a method which allows the unequivocal determination of virtually all monomers (including carboxy and hydroxy functional) of a polyacrylate with one single pyrolysis-GC/MS run [*12*]. This method is based on the silylation of the sample prior to pyrolysis.

Silylation of polyacrylates represents a polymer-analog reaction between the carboxy groups and hydroxy groups of the polyacrylate and the silylation reagent, where the corresponding trimethylsilyl esters or trimethylsilyl ethers are formed.

The silyl ester and silyl ether bonds formed have such a high thermal stability that they are not split during pyrolysis. Retropolymerization of the silylated polyacrylates takes place in the same way as for the unsilylated one. Therefore, the same fragments are generated, with the exception that the hydroxy and carboxy groups are silylated. The determination of the fragments (mainly reformed acrylic and methacrylic monomers) is accomplished by gas chromatographic separation and subsequent mass spectral identification. The latter is especially useful when complex mixtures of resins with different chemical composition are pyrolyzed, resulting in a variety of different fragments.

The pyrograms in Fig. 10 clearly depict that without silylation only the monomers without a carboxy or hydroxy group can be determined, whereas silylation also allows the positive identification of acrylic and methacrylic acid, hydroxyethyl methacrylate, hydroxypropyl methacrylate, and hydroxybutyl acrylate.

Liquid Chromatography/FT-IR Spectroscopy

As pointed out above, offline coupling of liquid chromatography with infrared spectros-

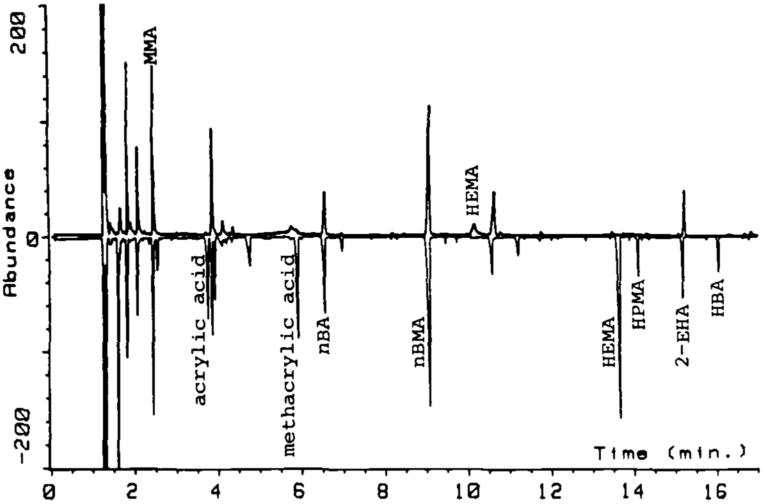


FIG. 10—*GC/MS pyrograms (TIC) of a polyacrylate obtained after silylation of the polyacrylate (bottom) and without silylation (top).*

copy offers the advantage that undisturbed spectra with the complete spectral information are obtained which can be interpreted in a meaningful way. The infrared technique of choice for such a coupling is, in our opinion, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). DRIFTS ideally combines the necessary sensitivity with ease of operation. The method is sensitive enough to give excellent spectra even for fractions from analytical separations, where the sample amounts are in the μg range. The sample handling is straightforward. The fractions are collected in small vessels and the solvent evaporated at room or slightly elevated temperatures. Subsequently, the residue is redissolved in about 100 μL tetrahydrofuran and transferred onto the KBr powder in the sampling cup with the help of a syringe.

In the following, an example is given for the offline coupling of size-exclusion chromatography with DRIFTS. Figure 11 shows the gel chromatogram of the binder of an organosol. The infrared spectra of three selected fractions are shown in Fig. 12.

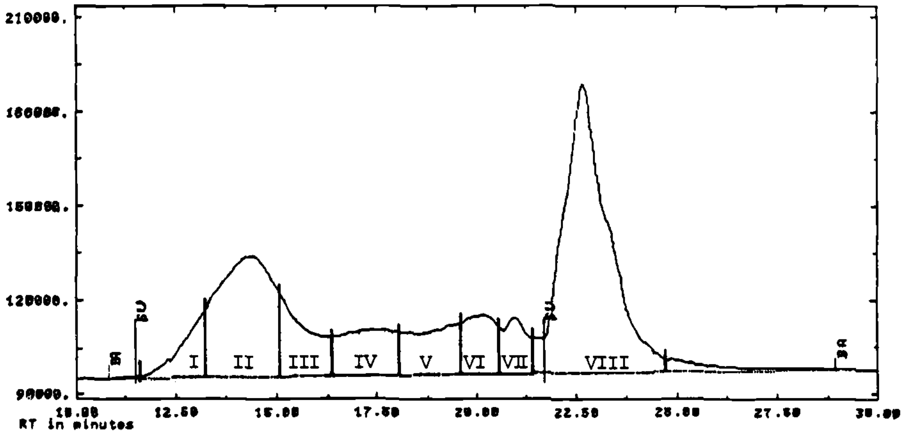


FIG. 11—*Gel chromatogram of an organosol; the lines represent the limits of the fractions collected.*

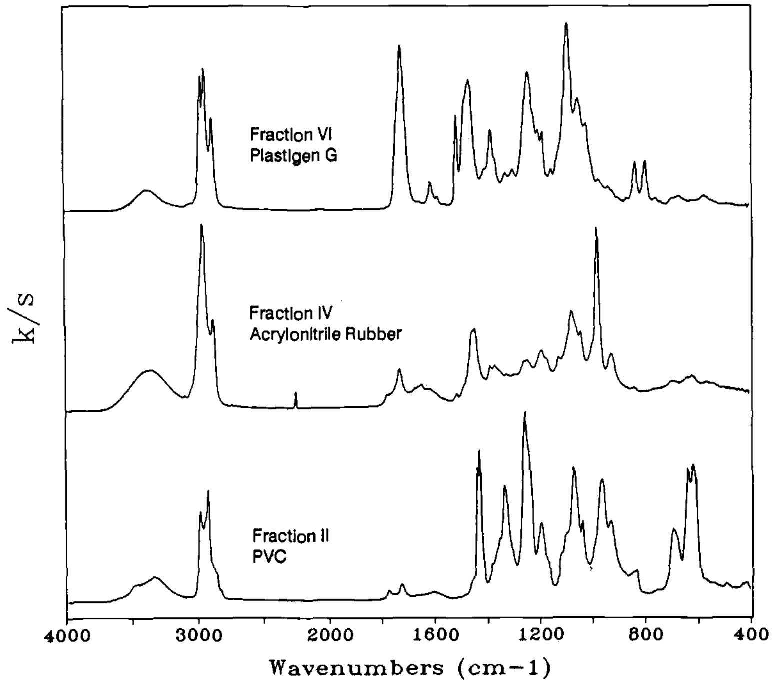


FIG. 12—*Diffuse reflectance spectra of three selected fractions from an analytical SEC run.*

Chemical Degradation Techniques

In order to meet the customers' requirements for a coating in terms of mechanical properties and durability, binder formulations can be quite complex. A mixture of different resins such as alkyd resins, polyesters, polyurethanes, polyacrylates, melamine resins, phenolic resins, etc. has to be used. In such cases, the determination of the individual building blocks of alkyd resins, polyesters, and polyurethanes, even qualitatively, can be difficult. Spectroscopic identification is not always feasible due to the fact that the concentration of some species can be rather low and/or the spectra are not very characteristic. Since the building blocks are incorporated in a polymer chain, chromatographic analysis of the intact polymer is not suitable for their identification.

A frequently used procedure employs the degradation of the polymers by chemical methods followed by chromatographic determination of the fragments. The methods applied, e.g. saponification with ethanolic potassium hydroxide, alkali fusion, aminolysis with hydrazin, and transesterification with sodium methoxide, have been comprehensively reviewed by Haken [*13*].

Alkaline Saponification

For polyesters and alkyd resins, we have for many years used a modification of the method devised by Kappelmeier [*14*] for the analysis of *o*-phthalic acid alkyd resins. Saponification with ethanolic potassium hydroxide yields the potassium salts of the fatty and dicarboxylic acids and the free polyols. If there are resins present which cannot be saponified in part or at all, an unsaponifiable portion will also occur.

Figure 13 shows, in a schematic form, the working-up procedure by which pure fractions of fatty and dicarboxylic acids can be isolated. Polyols are worked up in a separate step, including purification with the help of cation and anion exchange (see schematic diagram in Fig. 14). This separate working-up step for the polyols is necessary for optimum recovery.

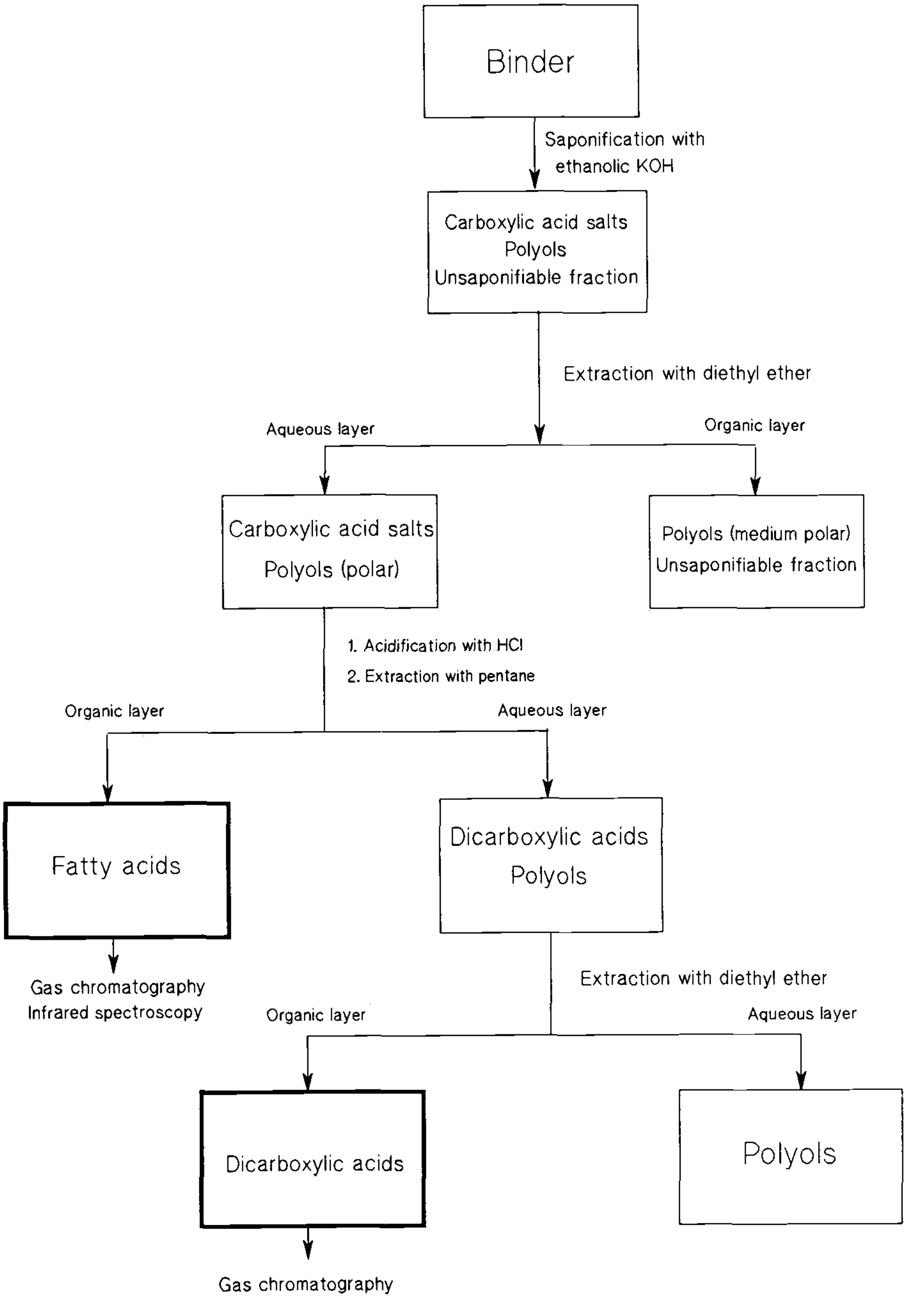


FIG. 13—*Working-up procedure for fatty and dicarboxylic acids.*

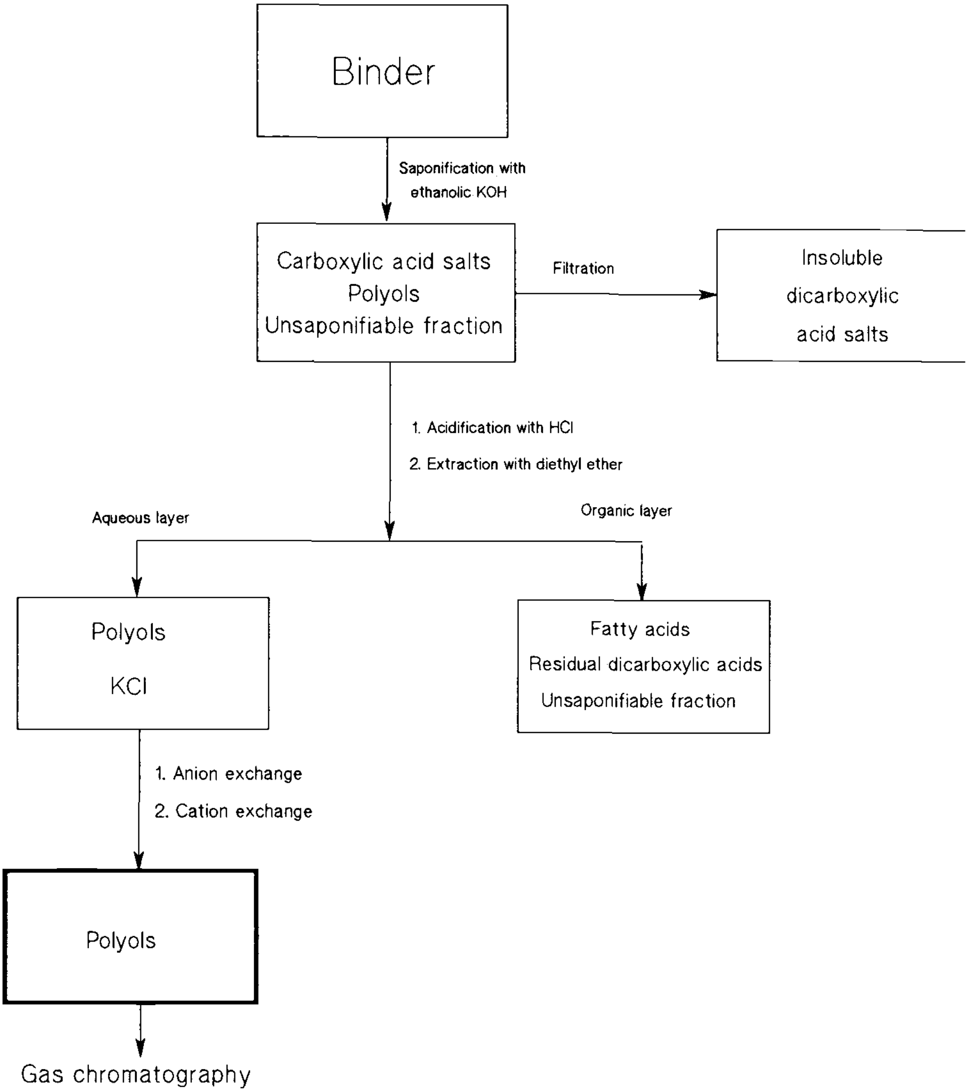


FIG. 14—*Working-up procedure for polyols.*

The fractions are characterized qualitatively and quantitatively by gas chromatography of the methylated acids or the silylated polyols, respectively.

The methods briefly outlined suffer from the fact that not all components are completely recovered. Unsaturated fatty acids may form reaction products (crosslinking, degradation) which are either not susceptible to conventional gas chromatography or are not detected under the conditions employed. Such products will be formed even if the saponification and the concentration step is carried out in an inert atmosphere. The recovery of some low-boiling polyols, such as ethylene glycol and propylene glycol, is also not quantitative, probably due to losses during cation exchange and the concentration step.

Catalyzed Transesterification with Methanol

Butte [*15*] described the transesterification of triglycerides with methanol catalyzed by trimethylsulfonium hydroxide (TMSH).

We have tested this reagent for chemical degradation of polyesters and alkyd resins. The method is based on the principle that TMSH catalyzes the transesterification of fatty and dicarboxylic acids incorporated in the resins to the corresponding methyl esters even at lower temperatures.

Without further isolation or purification steps, the methyl esters are determined by gas chromatography; the excess of TMSH is pyrolyzed to dimethyl sulfide and methanol in the hot injector of the gas chromatograph. The TMSH method was applied to the analysis of some alkyd resins. Our results show that with this method distinctly higher amounts for unsaturated fatty acids are obtained than with conventional methods. This holds especially true for linoleic and conjugated octadecadienoic acid.

The gas chromatographic determination of the polyols is conducted in a straightforward way from the reaction mixture obtained after adding methanol/TMSH. To this end, methanol is carefully evaporated and the polyols are silylated with the help of N-methyl-N-trimethylsilyl trifluoracetamide (MSTFA). The results obtained for several polyesters indicate that the recovery of polyols is also better than with conventional methods, especially for lower boiling ones.

References

[*1*] Schrader, B., Simon, A., and Sawatzki, J., BRUKER FT-IR, Application Note 29, 1989.
[*2*] Griffiths, P. R. and de Haseth, J. A., *Fourier Transform Infrared Spectrometry,* John Wiley and Sons, New York, 1986.
[*3*] Messerschmidt, R. G. and Harthcock, M. A., *Infrared Microspectroscopy,* Marcel Dekker, Inc., New York, 1988.
[*4*] Urban, M. W., *Progress in Organic Coatings,* Vol. 16, 1989, p. 321.
[*5*] Golay, M. J. E., *Analytical Chemistry,* Vol. 29, 1957, p. 928.
[*6*] Dandeneau, R. and Zerrenner, E., *Journal of High Resolution Gas Chromatography and Chromatography Communications,* Vol. 2, 1979, p. 351.
[*7*] Deans, D. R., *Chromatographia,* Vol. 1, 1968, p. 18.
[*8*] Charlesworth, J. H., *Analytical Chemistry,* Vol. 50, 1978, p. 1414.
[*9*] Kuo, C. Y. and Provder, T., *Journal of Coating Technology,* Vol. 53, 1981, p. 69.
[*10*] Ohtani, H. and Tsuge, S., *International Polymer Science and Technology,* Vol. 15, 1988, p. T 48.
[*11*] Denig, R. in *Analytiker Taschenbuch,* Springer Verlag Berlin, Heidelberg, New York, 1983.
[*12*] Schernau, U. and Freitag, M., XIX FATIPEC Congress, Aachen 1988, Vol. I, p. 419.
[*13*] Haken, J. K., *Progress in Organic Coatings,* Vol. 14, 1986, p. 247.
[*14*] Kappelmeier, C. P. A., *Chemical Analysis of Resin-Based Coating Materials,* Interscience Publishers, Inc., New York, 1959, p. 134.
[*15*] Butte, W., *Journal of Chromatography,* Vol. 261, 1983, p. 142.

William J. Simonsick, Jr.[1]

Mass Spectrometric Techniques for Coatings Characterization

REFERENCE: Simonsick, W. J., Jr., "**Mass Spectrometric Techniques for Coatings Characterization,**" *Analysis of Paints and Related Materials: Current Techniques for Solving Coatings Problems, ASTM STP 1119*, American Society for Testing and Materials, Philadelphia, 1992, pp. 22–38.

ABSTRACT: Low detection limits, molecular weight and structural information, and complex mixture analysis capabilities are attributes which make mass spectrometry a powerful tool for paint analysis. This presentation will describe how mass spectrometry has been used to characterize binder systems, stabilization packages, and solvent formulations. These components of coatings contain a variety of chemical moieties encompassing a range of molecular weights from low-weight solvents to high-weight polymers and therefore offer quite a challenge to the analytical chemist.

Solvent formulations are easily identified and quantified by a capillary gas chromatograph coupled to a mass spectrometer (GC/MS). The paint is loaded into a heated injector. The solvent components are volatilized and carried onto a cooled GC column. The column is temperature programmed, and the individual solvent constituents are separated by a high-efficiency capillary column. As the compounds elute, they are ionized by an electron beam. The ions are mass filtered, and a reproducible mass spectrum is recorded. Identification is based upon library comparison.

Stabilization packages (antioxidants, UV stabilizers) can also be analyzed in a similar fashion. These packages are added to paints to prolong the usable lifetime of the coating. Unfortunately, stabilizers are much less volatile than solvents and therefore more difficult to analyze by GC/MS. Aluminum-clad columns have extended the molecular weight range amenable to GC/MS. However, many stabilizers are not volatile enough for GC/MS analysis. Circumventing the volatility constraints imposed by GC, stabilizers can be introduced directly into the mass spectrometer. Chemical ionization MS can be used to selectively ionize the stabilizer in the presence of a complex binder matrix.

Pyrolysis (Py) or thermal degradation is the most common method for analyzing binder systems by mass spectrometry. The polymers are thermally degraded into lower-molecular-weight fragments which can be loaded onto a cooled GC column, chromatographed, detected, and identified by MS. Typically, low-molecular-weight fragments or monomers are identified. The analyst tries to elucidate the original binder structure from the low-weight thermal fragments. The GC prohibits the analysis of higher weight fragments. Alternatively, the pyrolyzates can be introduced directly into the ion source, ionized, and subsequently identified (Py-MS). Unfortunately, the mass spectra are often too complicated for easy interpretation. Other ionization strategies affording simpler spectra must be used. Py-GC/MS and direct Py-MS methods are reproducible and therefore the spectra can be archived for later library comparison in quality control/assurance or in competitive product analysis.

A shortcoming of pyrolytic methods is that the molecular weight integrity of the sample is lost. Copolymers may often not be distinguished from blends. In recent years the advent of desorption/ionization techniques have allowed the analysis of intact molecules exceeding 10 000 Daltons. This work has been primarily focused in the biochemical arena; however, there has been success on synthetic polymers. Furthermore, as the solvent content of paints is lowered to comply with federal regulations, lower-molecular-weight, more reactive oligomers must be used. Examples of desorption/ionization techniques for the molecular weight and

---

[1] E. I. du Pont de Nemours & Co., Automotive Products, Marshall R&D Laboratory, Philadelphia, PA 19146.

structural characterization of polyester oligomers, targeted reaction products, and melamine crosslinkers will be shown.

KEY WORDS: gas chromatography, mass spectrometry, pyrolysis, potassium ionization of desorbed species, binders, stabilizers, crosslinkers, functionalized monomers

The chemistry of automotive coatings has undergone considerable changes over the past half century, culminating in the commercialization of long-lasting glamorous finishes. The technology of creating such coatings has evolved from more of an art to a complex science. In order to characterize and thereby understand new coating technologies, sophisticated analytical methods are necessary. Mass spectrometry is a powerful analytical technique which can be used to characterize many of the chemicals used in coatings. Coatings are typically composed of a binder system dissolved in an appropriate solvent formulation. In addition, stabilization packages (antioxidants, photostabilizers) are added to lengthen the usable lifetime of the coating. Each of the above constituents contain a variety of chemical functionalities encompassing a wide range of molecular weights. Solvents are usually mixtures of low-molecular-weight materials of high volatility which are removed from the binder during the curing or drying process. Many of the commercial stabilizers have molecular weights in the range of 300 to 2000 Daltons (Da) and are, therefore, not volatilized during the curing process. Binders are traditionally high-molecular-weight polymers (>50 000 Da). Functionalized monomers allow the anchoring of stabilizer moieties to the polymer backbone. However, the use of low-molecular-weight reactive oligomers (<5000 Da), crosslinkers, and functionalized monomers have recently gained popularity. Higher solids and therefore reduced air emissions are the benefits of employing reactive low-molecular-weight oligomers with crosslinkers.

Mass spectrometry, because of its sensitivity and specificity, plays a key role in the characterization of paint formulations. Low detection limits, rapid analysis times, and universal detection based upon mass are attributes which make mass spectrometry an essential component of the modern analytical coatings laboratory. However, a requirement of traditional mass spectrometry is that the analyte of interest must be in the vapor phase prior to mass spectrometric analysis. To comply with this prerequisite, several sample introduction schemes have been devised. Therefore, depending on the coating constituent of interest, different strategies for sample introduction can be employed.

Recently, advances in instrument design and alternative ionization schemes have lessened the strict volatility requirements of mass spectrometry. These new approaches allow the collection of intact molecular weight information up to about 10 000 Da. These recent approaches will be discussed for the characterization of compounds in the molecular weight range of 300 to 1800 Da.

In this review the introduction methods used most frequently in our laboratory will be emphasized. For example, gas-chromatography mass-spectrometry (GC/MS) is our preferred method for solvent analysis. Stabilizer packages can be analyzed by GC/MS or by direct introduction into the mass spectrometer. High-molecular-weight binder systems because of their low volatility must be degraded prior to conventional mass spectrometric analysis. We use a resistively heated pyrolyzer to thermally degrade the binders. Finally, soft ionization methods, which afford molecular weight information, are used to characterized low-molecular-weight oligomers, crosslinkers, and functionalized monomers.

Mass Spectrometry

A brief description of the essential components of a commercial mass spectrometer will first be described. For a more detailed discussion of the operational aspects of mass spectrometry, several excellent texts are available [*1–3*]. Only single stage mass spectrometry will be discussed in this review. However, tandem mass spectrometry [*4*] will be playing an ever increasing role in the characterization of organic compounds, but is beyond the scope of this review. Furthermore, LC/MS techniques have become available and utilized for polymeric materials analysis [*5*]. These approaches will not be discussed in this review; however, a text has recently been published [*6*].

Figure 1 is a block diagram of a typical GC/MS system. Depending on the volatility of the compounds under investigation, the analyst has a choice of introduction methods at his disposal. Vapor phase sample components can be introduced into the mass spectrometer through a thermally controlled probe, a gas chromatograph, or by a pyrolyzer. The mass spectrometer consists of four major components: the ion source, the mass analyzer, the ion detection system, and the data system. Ions are produced in the ion source, separated by the mass analyzer, and detected and digitized by the detection system. The data system relates the digitized ion current with the ion's mass-to-charge ratio (*m/z*), stores the mass-intensity pairs, and can be used to compare acquired mass spectra to databases of archived spectra.

The method of producing ions is an important concern, depending on the information needed. The most common method of ion production is by electron impact. Under electron impact mass spectrometry (EIMS) gaseous molecules enter the ion source and are bombarded by a 70-eV electron beam. The beam interacts with the sample molecules, producing an ensemble of molecular and fragment ions. The ion cloud is collimated and focused using electric lenses. Since the ionization potential of most organic molecules is in the range of 7 to 13 eV, the resulting ions possess excess internal energy. To dissipate this excess energy, several bonds within the molecule are broken, giving rise to fragment ions and radicals. The molecular and fragment ions are mass analyzed, and the resulting distribution of different *m/z* ions is the mass spectrum. EIMS, owing to the fragmentation, provides information regarding the structure of the molecule. However, due to the numerous fragment ions produced under EIMS conditions, the spectra are often complex. Therefore, it is difficult to extract an individual component's spectrum from overlapping spectra and prohibits the easy interpretation of mixtures. Some form of separation, usually chromatographic or thermal, usually precedes the EIMS analysis.

To minimize fragmentation, therefore simplifying the spectra, alternative soft ionization schemes have been devised. Chemical ionization mass spectrometry (CIMS) is the most popular [*7,8*]. Under CIMS conditions, a high pressure of gas (~1 torr) is bombarded with high-energy electrons (70 to 500 eV). The gas is ionized and undergoes extensive collisions and reactions with nonionized gas, forming a collection of ions which react with organic

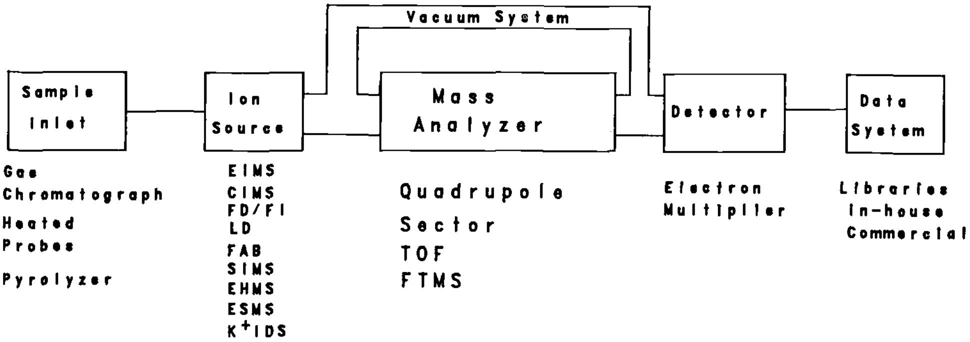


FIG. 1—*The basic components of a commercial mass spectrometer.*

molecules. The internal energy transfer is much lower; hence, the organic molecule does not fragment. The resulting mass spectrum is simpler than EIMS; however, much of the structural information afforded by EIMS is lost.

A limitation of EIMS and CIMS is that the sample molecule must be in the gas phase for ionization to occur. Recently, several desorption/ionization techniques have been developed to minimize this shortcoming. Field desorption (FD) and field ionization (FI) were the first of these techniques to appear in the literature [*9,10*] and have recently been reviewed [*11*]. Laser desorption [*12–14*], ^{252}CF plasma desorption (PD) [*15*], secondary ion mass spectrometry (SIMS) [*16,17*], and fast atom bombardment (FAB) [*18,19*] are techniques which afford molecular weight data on relatively nonvolatile compounds. Because mass spectrometers separate ions based on their m/z, the analysis of multiple-charged ions extends the usable mass range of mass spectrometers. Electrospray (ES) [*20,21*] and electrohydrodynamic ionization (EH) [*22*] are soft ionization schemes which take advantage of increasing the number of charges on a macromolecule. Molecular weights in excess of 17 000 Da for polyethylene glycol oligomers have been probed. Molecular weights of compounds over 100 000 Da have been accurately measured. Several of the techniques which furnish molecular weight data have been reviewed in light of polymer analysis [*23–26*].

In our laboratory we use a technique based upon rapid heating to the desorbed intact compounds [*27*]. Ions are produced by potassium attachment and the internal energy transfer is low; therefore, molecular ions with little or no fragmentation are observed [*28*]. The technique, pioneered by Allison and workers, is potassium ionization of desorbed species termed K^+IDS [*29,30*]. Implementation of K^+IDS in our laboratory required no modification of existing commercial equipment, no capital investment, and is performed on quadrupole mass spectrometers [*31*].

The experimental procedure to perform K^+IDS is briefly described below; however, a detailed explanation appears in Ref 31. Commercially available Finnigan direct-exposure probe filaments are coated with a 10% wt/wt slurry of $Al_2O_3{:}2KNO_3{:}2SiO_2$ in acetone. The coated filaments are dried and conditioned by heating to approximately 500°C under vacuum. Samples ($\sim$0.1 mg) are deposited on a stainless steel ribbon which is adjacent to the conditioned filament. The filament and sample are inserted into the electron impact ionization source of the mass spectrometer. The application of a high current to the filament causes resistive heating with subsequent K^+ emission. The sample, which is in close proximity to the filament, is radiatively heated. The mass spectrometer is scanned according to the sample under study.

The ions which are formed via any of the above processes exit the source and are separated by the mass analyzer. Gas phase negative and positive ions can be analyzed. The separation is based upon their m/z. Electric and/or magnetic fields are applied to the ion trajectory to facilitate separation. Quadrupoles, rugged and inexpensive mass analyzers, use a combination of dc and R_F electric fields. The analyzers operate under a prescribed scan law which is a function of the magnetic or electric fields and determine which ions of a certain m/z exit the analyzer and impinge upon the detector. The analyzer settings are scanned to allow different masses to pass through at different times.

The time-of-flight (TOF) analyzers function by accelerating ions through a specific voltage drop. All ions are given the same initial kinetic energy. The lighter ions move faster than the larger ions. The ion flight time is electronically related to the m/z of the ion. Ion cyclotron resonance or Fourier transform mass spectrometers separate ions based upon their circular path in a magnetic field. A concise overview of the mass analyzers mentioned above is available [*32*].

As the ions exit the mass analyzer, they impinge upon a detector. The most common type of detector and the one used in our laboratory is the electron multiplier. The ion current for each *m/z* is stored, and the mass-intensity pairs are recorded on the data system for later processing.

Solvent Analysis

The identification and quantification of the solvent composition of a paint formulation is important for quality control/assurance (QC/QA) and in competitive intelligence studies. Furthermore, the appropriate solvent combination allows for dissolution of the binder and affords proper film formation. We use GC/EIMS as our method of choice for solvent identification. The GC performs the separation while the mass spectrometer provides detection, structural information, and subsequent identification.

Whole paint formulations can be loaded into a heated injector. The more volatile solvent components are vaporized and loaded onto a cooled capillary GC column. The column is temperature programmed, and the solvent components are separated and elute into the ion source of the mass spectrometer. The low volume of flow through a capillary column permits a direct coupling to the mass spectrometer [*33*].

As the solvent components eluted, they are ionized by a 70-eV beam, mass separated, and detected. Figure 2 is a portion of the total ion chromatogram (TIC) of a solvent blend. Once a peak is detected, the averaged mass spectrum is background subtracted and then compared to our in-house library of spectra. Figure 2 shows the mass spectrum of Peak 5, the mass spectrum of the closest match in our library, and the difference between the two. Our data system outputs a numerical measure the similarity of two spectra. A similarity index of 0 indicates no peaks in common, whereas an index of 1000 indicates identical mass peaks and ion intensities. We chose a similarity index of greater than 800 for confidence in our identification. For example, Peak 5 yielded a 951/1000 when compared to our library spectrum of methyl isobutyl ketone (MIBK). Therefore, we conclude that Peak 5 is MIBK.

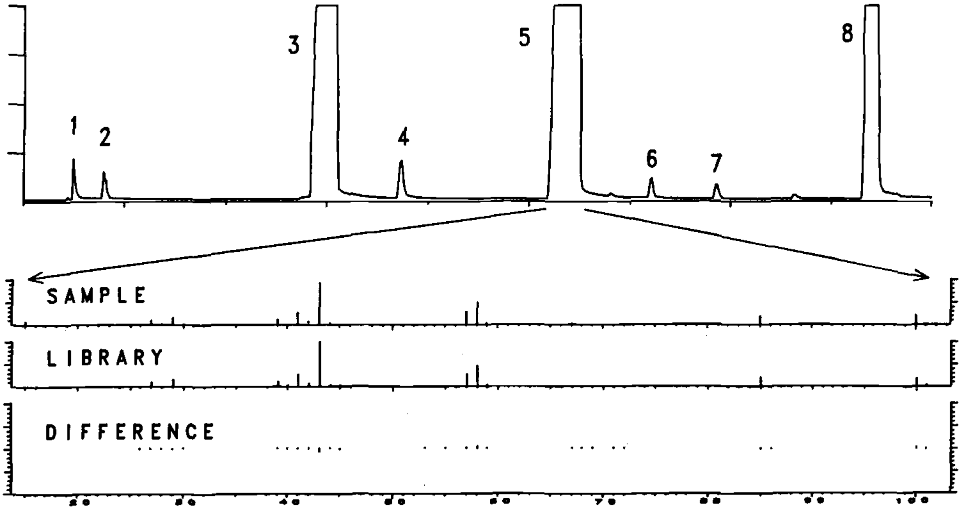


FIG. 2—*Total ion chromatogram (TIC) of a solvent formulation. Peaks were identified by comparison to an in-house library of EIMS spectra. The numerical measure of spectra similarity is also reported. Peak 1—water (965); Peak 2—acetone (935); Peak 3—2-propanol, 1-methoxy (899); Peak 4—t-butanol (804); Peak 5—methyl isobutyl ketone (951); Peak 6—toluene (971); Peak 7—sec-butylacetate (940); Peak 8—*n*-butylacetate (935). Conditions: GC—20°C/5 min to 300°C at 10°C/min; MS—70-eV ionization; scanned from 10 to 400 Da/0.5 s.*

The most probable compounds based upon comparison to our in-house library of mass spectra are reported. The numerical measure of the similarity is also output. If no similarity of greater than 800/1000 is found, our system is programmed to automatically search additional libraries. Solvent analysis and quantitation by GC/MS is a routine method in our laboratory. The complete process from injection to peak detection, identification, and quantitation takes less than an hour. In addition to furnishing the solvent composition, we can detect residual monomers, which provides insight into the binder system.

Stabilization Packages

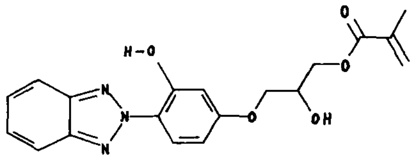
The useful lifetime of polymeric materials is prolonged by the addition of stabilizers. Identification of these components in paints are important for durability studies, QA/QC, and competitive intelligence studies. Most stabilizers are relatively nonvolatile, so they do not vaporize during the curing process or rapidly exude from the coating over time. Some stabilizers can be analyzed by GC/MS in a fashion similar to solvent analysis; however, owing to their low volatility, they are generally difficult to analyze by GC. Aluminum-clad coated fused silica columns are commercially available and have extended the molecular weight range amenable to gas chromatography [*34*]. Unfortunately, many stabilizers are too high in molecular weight and therefore not amenable to GC analysis.

To circumvent the volatility constraints imposed by GC, the stabilizer can be introduced via a heated probe into the mass spectrometer. However, unless the stabilizer has been isolated from the binder, the traditional EIMS analysis is complicated by the binder pyrolysis fragments. The extraction of an individual component spectrum from overlapping spectra is not a simple task. Rudewicz and Munson used selective chemical ionization mass spectrometry to quantitatively analyze for additives in polypropylene [*35*]. The researchers used an ammonia methane reagent gas mixture, which produced reactive ions that preferentially reacted with the stabilizers and not with the more abundant binder matrix. This is an excellent approach; however, depending on the chemical functionality of the binder system, it may not be possible to choose a chemical ionization reagent gas that preferentially ionizes the stabilizer.

We have used K^+IDS to identify commercial stabilizers in complex binder systems. The approach requires minimal sample preparation. For example, we identified Tinuvin™ 292 as the hindered amine light stabilizer in an acrylic formulation. Tinuvin 292 has a molecular weight of 508 Da; therefore, it yields a $[M]K^+$ of 547 Da, which is a particularly uncommon ion. In our present studies, we have not observed any acrylic formulations yielding a 547-Da ion. The quantitative aspects of this approach have not been investigated.

The use of polymerizable stabilizers, ultraviolet absorbers, and antioxidants in particular have advantages over conventional stabilizers. Thin-film coatings benefit from polymer-bound nonleachable stabilizers for protection against the harmful effects of increased temperature during curing. Furthermore, once these polymerizable stabilizers are incorporated into the polymer backbone, long-lasting UV stability, oxidative stability, and gloss retention are the recognized payoffs [*36,37*]. However, the successful synthesis of such materials can be difficult and produce a host of undesirable byproducts.

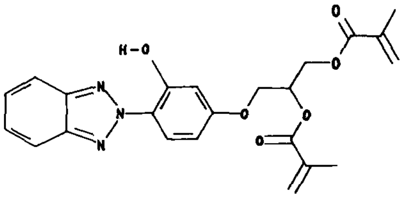
We have found that K^+IDS with mass spectrometric detection provides a quick check on the success of a targeted synthesis and can be used to identify undesirable side products [*38*]. For example, the structure of a methacrylate-type UV stabilizer is given (I) (Fig. 3). The molecular weight of this material is 369 Da; therefore, the potassiated (m/z = 39 Da) ion, $[M]K^+$, should appear at m/z = 408 Da. This is the base peak seen in Fig. 4. However, we also observe a significant ion at m/z = 476 Da. The addition of 68 Da in molecular weight results from either of the two dimethacrylates (II,III) (Fig. 3). Residual methacrylic



MOLECULAR WEIGHT - 369 g/mol

$[M]K^+$ - 408 Da

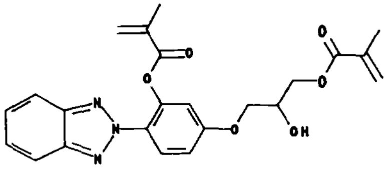
(I)



MOLECULAR WEIGHT - 437 g/mol

$[M]K^+$ - 476 Da

(I I)



MOLECULAR WEIGHT - 437 g/mol

$[M]K^+$ - 476 Da

(I I I)

FIG. 3—*Structures of the targeted functionalized UV-absorbing monomer (I) and undesirable by-products (II,III).*

acid [molecular weight (mol. wt.) = 86 Da], which is used in the synthesis, could react with the labile protons of the targeted product (mol. wt. = 369 Da) coupled with water (mol. wt. = 18 Da) evolution to produce either of these compounds (II,III) ([369 Da + 86 Da − 18 Da]K^+ = 476 Da). It is important to identify and quantify the dimethacrylates because small amounts can rapidly build molecular weight and gel reactions.

Binder Systems

The most important component in a paint is the binder, which affects the appearance and long-term durability. Pyrolysis or thermal decomposition is the most common method of introducing polymers into the mass spectrometer. Polymers are usually too large to vaporize

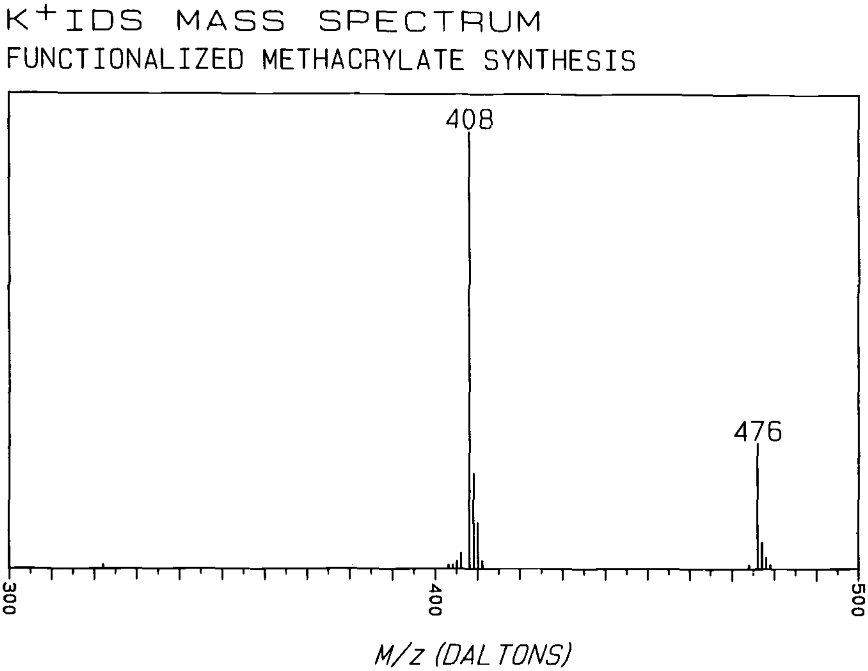


FIG. 4—*K^+IDS mass spectrum of the reaction mixture targeted at the synthesis of a functionalized monomer (I).*

for traditional mass spectrometric analysis. Therefore, the polymer must be degraded into smaller pieces or thermal fragments prior to mass spectrometric investigation. The analyst identifies the thermal decomposition products, termed pyrolyzates, and attempts to elucidate the structure of the original material. The researcher has the choice of several types of pyrolyzers such as specialty microfurnaces, resistively heated filament type, lasers, and Curie point systems. Kristemaker and Haverkamp have discussed the pyrolysis systems suitable for coupling with mass spectrometers [*39*]. We use a resistively heated filament pyrolyzer because of the capability to perform experiments at several different heating rates and final temperatures. Pyrolysis mass spectrometric methods have several advantages and provide complementery information to the more traditional infrared spectroscopy and ^{13}C-NMR methods. Small sample sizes (submilligram) are required, and a minimum of sample pretreatment is necessary. In fact, we analyze cured paint films without any sample pretreatment. Targeted compounds can also be rapidly screened. Moreover, the pyrograms of synthetic polymers are reproducible [*40*] and therefore can be archived for subsequence library searching. Such approaches are useful in QA/QC experiments [*41*]. The Federal Bureau of Investigation has created libraries of automotive paints, and the data have been successfully used in forensic matters [*42*]. Several reviews have appeared on the topic of pyrolysis techniques coupled to various detectors. In fact, a bibliographical listing of about 500 references addressing a wide variety of applications has recently been published [*43*].

One can introduce the pyrolyzates directly into the mass spectrometer (Py-MS) or through a GC prior to mass spectrometric analysis (Py-GC/MS). The GC separates the pyrolyzates and allows EIMS detection; therefore, automated identification by library comparison is possible. Several reports have demonstrated the utility of interfacing a pyrolyzer to a high-resolution capillary GC column [*44,45*]. Identification of pyrolyzates is based upon the retention times of authentic standards. However, diverse operational practices make standardization of such a technique difficult. Furthermore, a single matching of retention times may suffice for simple homopolymers, but the data are not reliable for more complex samples. Py-GC/MS has proven to be an extremely powerful method for determining polymer composition [*46*].

Figure 5 is the pyrogram of an acrylic coating. The material was cured and highly crosslinked and therefore difficult to solubilize for ^{13}C-NMR analysis. A small sample (<1 mg) was loaded into our pyrolyzer and a temperature setting of 800°C applied for 10 s. The acrylic binder was thermally degraded to its monomeric constituents. The volatile monomers were loaded onto a cooled GC column, separated, and detected by EIMS. The components identified by library comparison were methylmethacrylate (MMA), ethylacrylate (EA), and styrene (STY). We also detected a significant amount of isobutanol, which we attribute to unreacted isobutylated melamines, the crosslinker. In addition to the identification of the monomers used in polymers and serving as a fingerprint to distinguish various coatings, we have used Py-GC/MS to separate and identify additives contained in the paint (cured or wet). Unfortunately, only additives which are volatile enough for GC analysis can be successfully characterized by Py-GC/MS. This bottleneck is the major limitation of Py-GC/MS. Only nonreactive, thermally stable, volatile components can be studied by Py-GC/MS. Higher molecular weight fragments which contain more informative pieces of the original polymer cannot be analyzed by Py-GC/MS. The barrier being the GC.

Direct introduction into the mass spectrometer obviates the volatility requirement of GC [*47*]. However, as mentioned previously, the numerous pyrolyzates which are ionized by EIMS produce a complicated array of peaks and therefore make simple spectral interpretation nearly impossible. To simplify the mass spectra in Py-MS, alternative ionization strategies yielding molecular weight data and fewer fragment ions are employed. CIMS [*48–50*] and FI [*51*] have been among the most successful. Furthermore, the analysis times

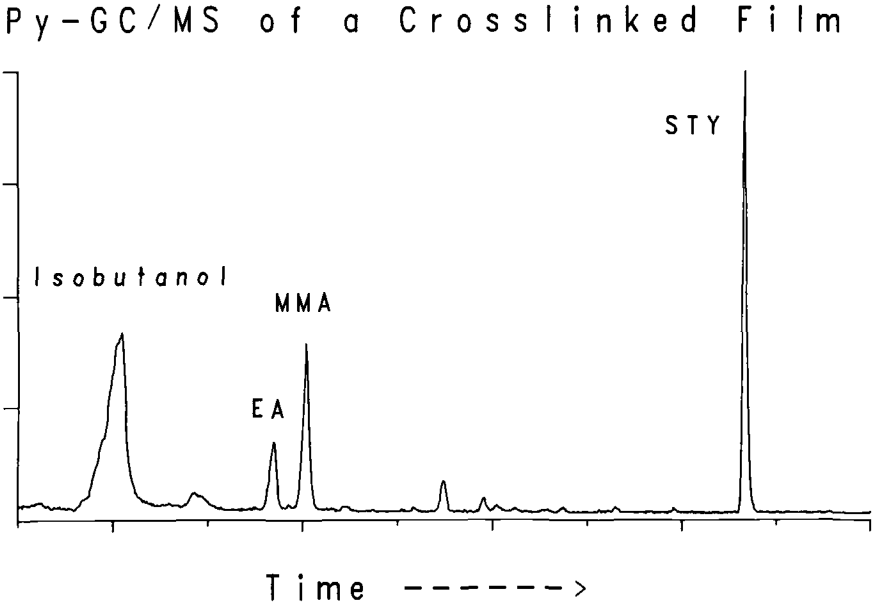


FIG. 5—*Portion of a pyrogram of a cured crosslinked acrylic film. Conditions: Pyrolysis—800°C for 10 s; GC—20°C/2 min to 300°C at 10°C/min; MS—70 eV-ionization scanned from 10 to 400 Da/0.5 s.*

are also significantly reduced when compared to Py-GC/MS. We have recently begun using K^+IDS to examine the pyrolyzates introduced directly into the mass spectrometer. The mass spectra afforded by K^+IDS are much simpler than EIMS and even CIMS. K^+IDS produces only one ion for each pyrolyzate of a given molecular weight. K^+IDS affords data similar to FI; one obtains molecular weight information. We do not have capability to perform FI experiments, but have been using K^+IDS, a technique which is compatible with our quadrupole mass filtering system. The following discussion illustrates the utility of K^+IDS for the analysis of pyrolyzates. Keep in mind that similar information can be obtained using several of the soft ionization schemes already discussed.

Figure 6 is a portion of a pyrogram of a simple acrylic terpolymer dissolved in toluene. The sample was not completely dried as evident by the toluene component. We identified the constituents by Py-GC/MS as previously described. However, only the monomers of MMA, *n*-butylmethacrylate (BMA), and butylacrylate (BA) were detected. The molecular weight integrity of the sample was lost. We were unable to distinguish terpolymers from a blend of homopolymers. Furthermore, the analysis time was about an hour.

Figure 7 is the K^+IDS mass spectrum of the pyrolyzates introduced directly into the ion source. The spectrum is rich in information. The ions seen at m/z = 139 Da, 167 Da, and 181 Da are the cationized monomers. MMA has a molecular weight of 100 Da ($[M]K^+$ = 139 Da), BA weighs 128 Da ($[M]K^+$ = 167 Da), and BMA weighs 142 Da ($[M]K^+$ = 181 Da). Prior to analysis, the sample was dried to remove the toluene solvent. Common solvents such as toluene ($[M]K^+$ = 131 Da), tetrahydrofuran ($[M]K^+$ = 111 Da), and *N*-methyl-2-pyrrolidone ($[M]K^+$ = 138 Da) are also amenable to K^+IDS analysis. Pyrolysis followed by K^+ ionization is a quick method to screen for acrylic monomeric constituents. A shortcoming of this methodology is the inability to distinguish isomeric compounds.

The base peak at 395 Da is due to a potassiated $[BA]_2[MMA]$ fragment. Unfortunately, no information concerning the specific monomer sequence of the pyrolyzates is furnished.

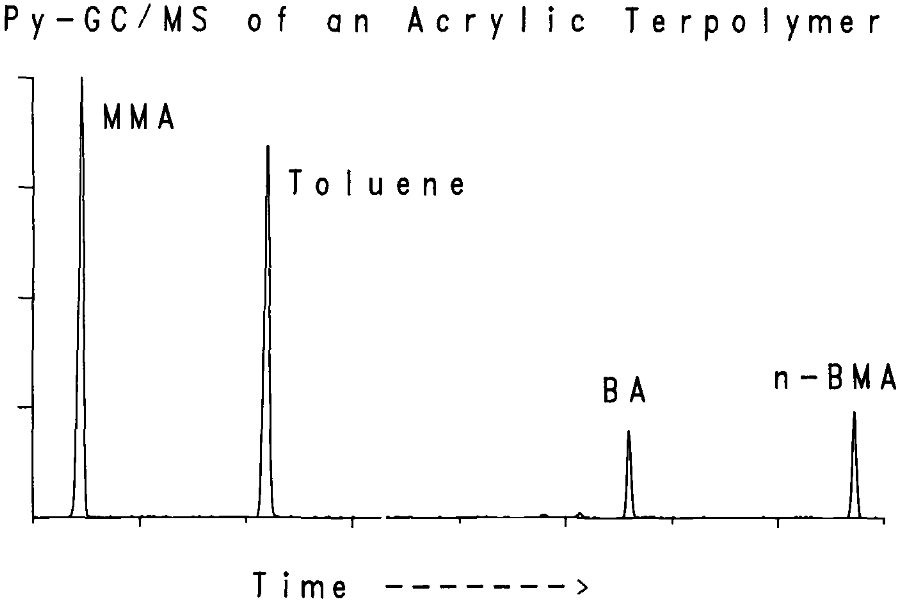


FIG. 6—*Portion of a pyrogram of an acrylic terpolymer. Conditions: Pyrolysis—600°C for 10 s; GC—20°C/2 min to 300°C at 10°C/min; MS—70-eV ionization scanned from 10 to 400 Da/0.5 s.*

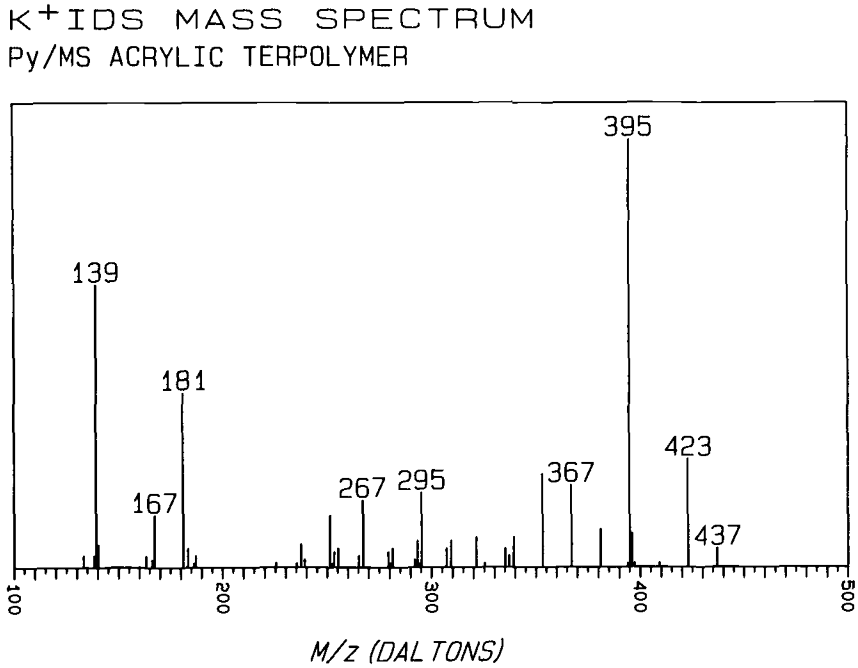


FIG. 7—*K$^+$IDS mass spectrum of the pyrolyzates of a terpolymer. Conditions: MS scanned 100 to 1000 Da/s.*

However, we can propose structures for several of the cationized thermal fragments seen in Fig. 7. Table 1 summarizes our assignments. One can conclude that the polymer is not a mixture of blended homopolymers, but rather a terpolymer because of the numerous thermal fragments which contain various combinations of the starting monomers. In support of our conclusions, we analyzed acrylic blends and found no evidence for the reassociating of thermal fragments to give higher mass ions. We find the analysis of pyrolyzates by K$^+$IDS complementary to Py-GC/MS and other spectroscopic methods. Furthermore, the total time for the analysis including sample preparation is only 10 min.

Reactive Oligomers and Crosslinkers

The Environmental Protection Agency regulates the amount of solvents which can be discharged into the atmosphere. There is a continuing trend to reduce solvent emissions. Unfortunately, high-molecular-weight polymers require a substantial amount of solvent for solubilization. The most successful approach to lowering solvent emissions has been high-solids enamels [52]. This is accomplished by the use of low-molecular-weight polymers possessing functional groups for crosslinking. Crosslinking is necessary for satisfactory film properties and durability. Low-molecular-weight polyesters (1000 to 2000 Da) or hydroxyl-functionalized acrylics (5000 to 10 000 Da) can be crosslinked with low-molecular-weight, melamine-formaldehyde resins [52].

Py-GC/MS and Py-MS can be used to characterize these materials; however, the weight integrity of the sample is lost. Moreover, the molecular weight of these materials is an important descriptor that can be useful for structural confirmation or elucidation. The advent of the desorption/ionization methods afford molecular weight information. K$^+$IDS is the desorption/ionization method we employ for the characterization of reactive oligomers and

TABLE 1—*Proposed structures for the ions seen in Fig. 7.*

Potassiated Ion, Da	Monomeric Units
139	MMA
167	BA
181	BMA
267	[MMA][BA]
295	$[BA]_2$
309	[BA][BMA]
339	$[MMA]_3$
367	$[MMA]_2BA$
395	$[BA]_2[MMA]$
423	$[BA]_3$ or $[MMA][BMA]_2$
437	$[BA]_2BMA$

crosslinkers. The molecular weight information is extremely useful for characterizing mixtures possessing compounds in the molecular weight range of 300 to 1800 Da. We emphasize once again that many of the ionization strategies discussed earlier provide similar information; however, we found K^+IDS was the simplest and least expensive to implement in our laboratory.

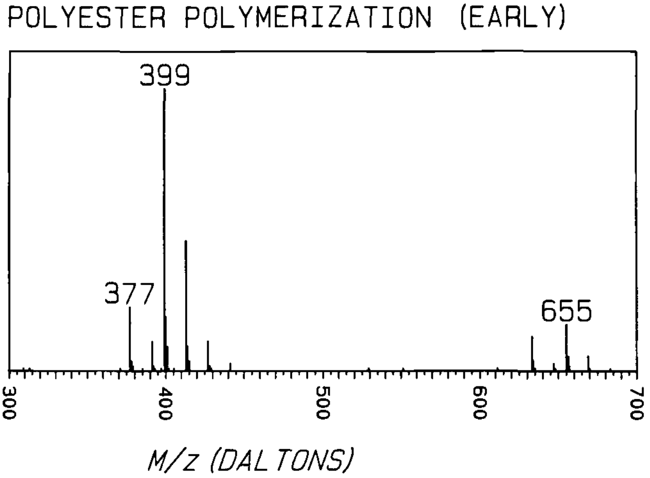
Because of the commercial success of polyesters crosslinked with low-molecular-weight, melamine-formaldehyde resins, we choose to explain how the molecular weight data furnished by K^+IDS is valuable for characterizing these components of high-solids coatings. K^+IDS can also be used to provide molecular weight data on polyisocyanates, polysilanes, epoxide oligomers [*31*], and reactive oligomers synthesized by group-transfer-polymerization methods [*53*].

Polyesters are the reaction products of polyfunctional acids and alcohols. Many of today's commercial polyester resins are prepared from mixtures of diacids and diols. This mixture of ingredients imparts a desirable balance of physical properties to the finished polyester resin. For example, dipropylene glycol imparts flexibility and toughness to a resin, whereas neopentyl glycol provides corrosion resistance. The molecular weights of these starting materials are different. Therefore, a mass spectrometric technique which furnishes molecular weight information is an excellent tool for sequencing oligomer chains and monitoring the progression of a polyester polymerization [*54*].

The simplicity of the K^+IDS spectra, affording only molecular weight information, is sufficient to assign molecular formula to the ions seen in the K^+IDS mass spectra of polyester syntheses. For example, Fig. 8 shows a portion of the K^+IDS mass spectrum taken different times during a mixed polyester synthesis. The resin was prepared with a mixture of neopentyl glycol (NG), hexanediol (HD) azelaic acid (AA), and isophthalic acid (IA). As expected, the relative abundance of the higher order oligomers increase with polymerization time.

Based upon molecular weight we propose structures for the ions seen in Fig. 8. The base peak at $m/z = 399$ Da is the potassiated NG-AA-NG. NG has a molecular weight of 104 Da, whereas AA weighs 188 Da. The reaction of two molecules of NG with each of the two carboxylate groups of AA coupled with the evolution of two water molecules (2×18 Da) produces the NG-AA-NG moiety which has a molecular weight of 360 Da. Cationization by potassium adds 39 Da, hence the 399 Da ion. With a knowledge of the molecular weights of the starting ingredients, the assignment of structures to the potassiated ions is possible. Table 2 summarizes our proposed structures for the major ions seen in the K^+IDS mass spectrum of the mixed polyester.

We realize that the NG, AA, HD, IA is an ideal system for differentiation by molecular weights. However, our methodology will work until different combinations of monomers yield the same molecular weight. The ability to examine the incorporation of any monomer


POLYESTER POLYMERIZATION (EARLY)

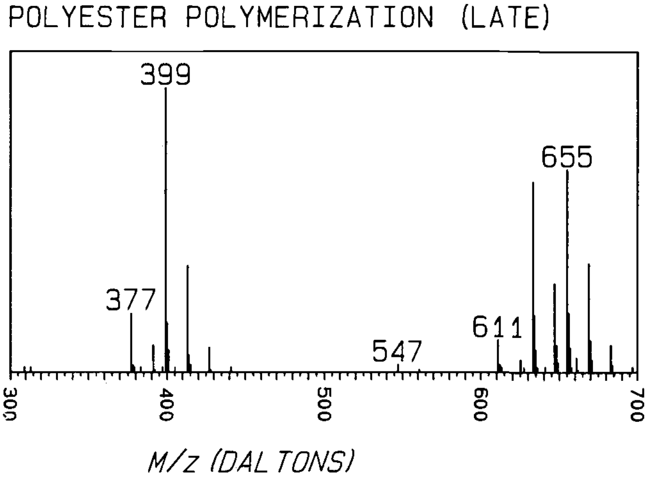

POLYESTER POLYMERIZATION (LATE)

FIG. 8—*K^+IDS mass spectrum of a mixed polyester taken at different times during the polymerization Conditions: MS—scanned 100 to 1000 Dals.*

TABLE 2—*Proposed structures for the ions seen in Fig. 8.*

Potassiated Ion, Da	Proposed Structure
377	[NG-IA-NG]K^+
391	[HD-IA-NG]K^+
399	[NG-AA-NG]K^+
413	[HD-AA-NG]K^+
427	[HD-AA-HD]K^+
611	[NG-IA-NG-IA-NG]K^+
633	[HD-IA-NG-AA-NG]K^+
647	[HD-IA-HD-AA-NG]K^+
655	[NG-AA-NG-AA-NG]K^+
669	[HD-AA-NG-AA-NG]K^+
683	[HD-AA-HD-AA-NG]K^+

or reactive functionality into the oligomers can be measured as long as the molecular formula of the component is different than the other constituents. This allows the synthetic chemist to identify the products formed in each step of a multistep synthesis targeted at a highly functionalized macromonomer. Furthermore, K^+IDS has provided quantitative information in a polyester synthesis as the raw material loading of monomers was easily checked [*54*].

In order to form a durable coating, low-molecular-weight oligomers must be crosslinked. Melamine-formaldehyde resins provide the crosslinking functionality for hydroxyl-containing resins. K^+IDS analysis of melamine-formaldehyde resins furnishes molecular weight information from which specific structures can be proposed. For example, Fig. 9 is the K^+IDS mass spectrum of a partially isobutylated melamine-formaldehyde resin. The base peak at m/z = 423 Da results from the potassiated tributylated compound (IV) (Fig. 10). Each methylene butoxy unit adds 86 Da to the compound. Therefore, the ions seen at m/z 509 Da and 337 Da correspond to the tetra- and difunctional compounds. The ions seen above 600 Da are attributed to dimers, one of which is shown in structure (V) (Fig. 10). K^+IDS provides a quick check on the functionality of the melamine, and these data assist in the understanding of the effect of crosslinking on final properties. We have a tool to probe the available crosslinker sites. The data are reproducible and can be used to check the control along each step of the synthesis. Methyl melamine-formaldehyde resins have also been analyzed in a similar fashion [*31*].

The above analyses have shown that by using soft-ionization methods one is able to characterize the compounds involved in forming a durable highly cross-linked film. We chose to use K^+IDS to provide these data; however, numerous other soft ionization schemes furnish the same data.

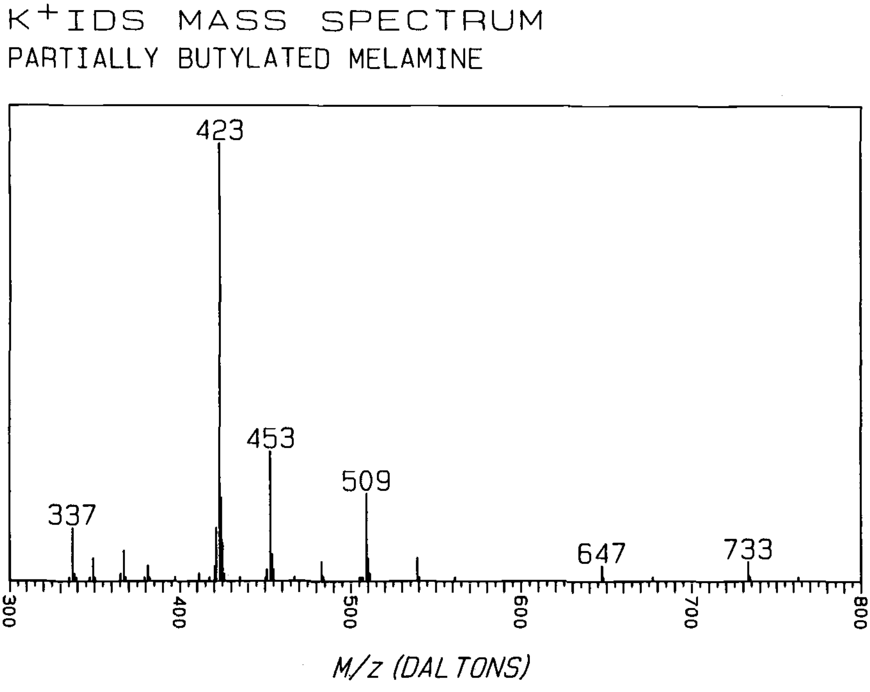
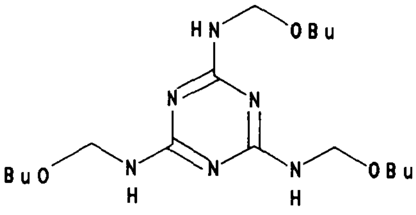


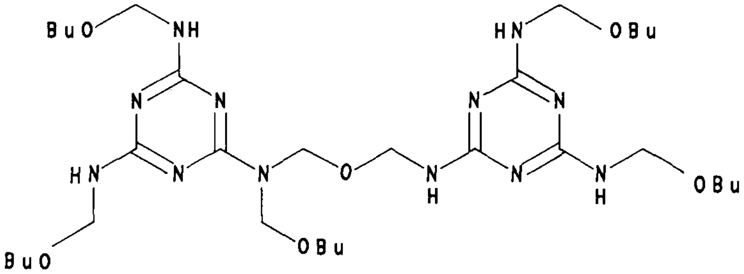
FIG. 9—*K^+IDS mass spectrum of a partially butylated melamine-formaldehyde resin. Conditions: MS scanned 100 to 1000 Da/s.*



Mol. Wt. = 384 g/mol

$[M]K^+$ = 423 Da

(IV)



Mol. Wt. = 694 g/mol

$[M]K^+$ = 733 Da

(V)

FIG. 10—*Representative structures of monomeric (IV) and dimeric (V) isobutylated melamine-formaldehyde resin.*

Conclusions

Mass spectrometry is a versatile invaluable tool for characterizing the major components in coatings. Depending on the component of interest, different methods for sample introduction into the mass spectrometer are used. GC/MS is the preferred method to analyze the more volatile solvent components. Less volatile compounds not amenable to GC may be introduced directly into the ion source. Once in the source, the analyst can choose to selectively analyze for a targeted class of compounds. The synthesis of low-volatility functionalized monomers can be evaluated by soft ionization techniques.

High-molecular-weight polymers are thermally degraded and the thermal fragments identified by mass spectrometry. The analyst has the option to choose how the fragments can be characterized. Py-GC/MS is useful for determining the monomeric constituents of polymers. Binder analysis by Py-GC/MS requires minimal investigator intervention; however, much of the structural integrity can be lost by the pyrolysis, the GC column, and the electron ionization process. The Py-MS experiment offers a quicker method of characterization, and there is no volatility constraint. The Py-MS spectra are reproducible, but extremely complex.

Novel ionization approaches which induce less fragmentation and preserve more of the molecular architecture are useful for elucidation of the original polymer. Structures can be assigned based upon molecular weight.

The data provided by mass spectrometry are most useful when combined with other spectroscopic techniques. We always use at least two independent methods for binder characterization. In many instances the data are complementary; for example, soft ionization single stage mass spectrometry cannot discern isomers. However, ^{13}C-NMR can distinguish many isomers.

As low-molecular-weight materials are used in a continuing effort to reduce air emissions, mass spectrometric techniques which furnish molecular weight data will play a more important role in characterization. The ability to elucidate all chemical structures contained in high-solids formulations is important because small quantities of impurities in the reactive materials manifest themselves in unacceptable product properties. Mass spectrometry provides structural data on the compounds formed during each step of a multistep synthesis of a macromonomeric crosslinker or functionalized monomer. Finally, most of the data afforded by mass spectrometry can be acquired in under an hour.

Acknowledgments

Doris Young is acknowledged for the clerical assistance and patience during the preparation of this manuscript. Many of the experiments described in this report were performed by T. P. Volpe and Maryann Silva. The Automotive Products Sector of duPont de Nemours is acknowledged for their support and permission to publish this work.

References

[*1*] Roboz, J., *Introduction to Mass Spectrometry*, Plenum Press, New York, 1968.

[*2*] Watson, J., *Introduction to Mass Spectrometry*, Raven Press, New York, 1976.

[*3*] McLafferty, *Interpretation of Mass Spectra*, 3rd ed., University Science Books, Mill Valley, CA, 1980.

[*4*] Busch, K. L., Glish, G. L., and McLuckey, S. A., *Mass Spectrometry/Mass Spectrometry: Techniques and Applications of Tandem Mass Spectrometry*, VCH Publishing, Inc., New York, 1988.

[*5*] Cutie, S. S., Kallos, G. J., and Smith, P. B., *Journal of Chromatography*, Vol. 408, 1987, pp. 349–355.

[*6*] Yergey, A. L., Edmonds, C. G., Lewis, I. A. S., Vestal, M. L., *Liquid Chromatography/Mass Spectrometry Techniques and Applications*, Plenum Press, New York, 1990.

[*7*] Munson, M. S. B. and Field, F. H., *Journal of the American Chemical Society*, Vol. 88, 1966, pp. 2621–2630.

[*8*] Harrison, A. G., *Chemical Ionization Mass Spectrometry*, CRC Press, Boca Raton, FL, 1983.

[*9*] Beckey, H. D., *Field Ionization Mass Spectrometry*, Pergamon Press, Oxford, 1971.

[*10*] Prokai, L., *Field Desorption Mass Spectrometry*, Marcel Dekker, Inc., New York, 1989.

[*11*] Lattimer, R. P. and Schulten, H. R., *Analytical Chemistry*, Vol. 61, 1989, pp. 1201A–1215A.

[*12*] Cotter, R. J., Honovich, J. P., Olthoff, J. K., and Lattimer, R. P., *Macromolecules*, Vol. 19, 1986, pp. 2996–3001.

[*13*] Nuwaysir, L. M. and Wilkins, C. L., *Analytical Chemistry*, Vol. 60, 1988, pp. 279–282.

[*14*] Ijames, C. F. and Wilkins, C. L., *Journal of the American Chemical Society*, Vol. 110, 1988, pp. 2687–2688.

[*15*] Macfarlane, R. D. and Torgerson, D. F., *Science*, Vol. 191, 1976, pp. 920–925.

[*16*] Benninghoven, A., Rudenauer, F. G., and Werner, H. W., *Secondary Ion Mass Spectrometry: Basic Concepts, Instrumental Aspects, Applications and Trends*, John Wiley & Sons, New York, 1987.

[*17*] Bletsos, I. V., Hercules, D. M., van Leyen, D., and Benninghoven, A., *Macromolecules*, Vol. 20, 1987, pp. 407–413.

[*18*] Montaudo, G., Scamporrino, E., and Vitalini, D., *Polymer*, Vol. 30, 1989, pp. 297–303.

[*19*] Kyranos, J. N., Vouros, P., and Zukas, W. X., *Macromolecules*, Vol. 22, 1989, pp. 1189–1195.

[20] Dole, M., Mack, L. L., Hines, R. L., Mobley, R. C., Ferguson, L. D., and Alice, M. B., *Journal of Chemistry and Physics*, Vol. 49, 1968, pp. 2240–2249.

[21] Wong, S. F., Meng, C. K., and Fenn, J. B., *Journal of Physics and Chemistry*, Vol. 92, 1988, pp. 546–556.

[22] Lai, S. T. F., Chan, K. W., and Cook, K. D., *Macromolecules*, Vol. 13, 1980, pp. 953–956.

[23] Schulten, H. R. and Lattimer, R. P., *Mass Spectrometry Reviews*, Vol. 3, 1984, pp. 231–315.

[24] Lattimer, R. P., Harris, R. E., and Schulten, H. R., *Rubber Chemical Technology*, Vol. 58, 1985, pp. 577–621.

[25] Kyranos, J. N. and Vouros, P., *Journal of Applied Polymer Science: Applied Polymer Symposium*, Vol. 43, 1989, pp. 211–240.

[26] Israel, S. C., *Flame-Retardant Polymeric Materials*, Vol. 3, 1982, pp. 201–232.

[27] Beuhler, R. J., Flanigan, E., Green, L. J., and Friedman, L., *Journal of the American Chemistry Society*, Vol. 96, 1974, pp. 3390–3399.

[28] Rollgen, F. W. and Schulten, H. R., *Organic Mass Spectrometry*, Vol. 10, 1975, pp. 660–668.

[29] Bombick, D., Pinkston, J. D., and Allison, J., *Analytical Chemistry*, Vol. 56, 1984, pp. 396–402.

[30] Bombick, D. and Allison, J., *Analytical Chemistry*, Vol. 59, 1987, pp. 458–466.

[31] Simonsick, W. J., Jr., *Journal of Applied Polymer Science: Applied Polymer Symposium*, Vol. 43, 1989, pp. 257–274.

[32] Holland, J. F., Enke, C. G., Allison, J., Stults, J. T., Pinkston, J. D., Newcome, B., and Watson, J. T., *Analytical Chemistry*, Vol. 55, 1983, pp. 997A–1012A.

[33] Jensen, T., Kaminsky, R., McVeety, B., Wozniak, T., and Hites, R. A., *Analytical Chemistry*, Vol. 54, 1982, pp. 2388–2390.

[34] Dawes, P. and Cumbers, M., *American Laboratory*, Vol. 21, 1989, pp. 102–111.

[35] Rudewicz, P. and Munson, M. S. B., *Analytical Chemistry*, Vol. 58, 1986, pp. 358–361.

[36] Dickstein, W. and Vogl, O., *Journal of Macromolecular Science Chemistry*, Vol. A22, 1985, pp. 387–402.

[37] Debergalis, M. and O'Fee, R. P., U. S. Patent 4,495,325, E. I. Du Pont de Nemours & Co., Inc., Wilmington, DE, 1985.

[38] Simonsick, W. J., Jr., Berge, C. T., Vogl, O., and Sustic, A. in *Pacific Polymer Reprints*, Anderson, B. C., Ed., Vol. 1, 1989, pp. 271–272.

[39] Haverkamp, J. and Kristemaker, P. G., *International Journal of Mass Spectrometry Ion Processes*, Vol. 45, 1982, pp. 275–292.

[40] Whitehouse, M. J., Boon, J. J., Bracewell, J. M., Gutteridge, G. S., Pidduck, A. J., and Puckey, D. J., *Journal of Analytical and Applied Pyrolysis*, Vol. 8, 1985, pp. 515–532.

[41] Meuzelaar, H. L. C., Windig, W., Huff, S. M., Richards, J. M., *Analytica Chimica Acta*, Vol. 190, 1986, pp. 119–132.

[42] McMinn, D. G., Carlson, T. L., Munson, T. O., *Journal of Forensic Science*, Vol. 30, 1985, pp. 1064–1073.

[43] Wampler, T. P., *Journal of Analytical and Applied Pyrolysis*, Vol. 16, 1989, pp. 291–322.

[44] Raynor, M. W., Waring, R. M., and Davies, I. L., *Journal of Chromatographic Science*, Vol. 25, 1987, pp. 104–111.

[45] Liebman, S. A. and Levy, E. J., Eds., *Pyrolysis and GC in Polymer Analysis*, Marcel Dekker, Inc., New York, 1985.

[46] Irwin, M. J., *Analytical Pyrolysis*, New York, Marcel Dekker, Inc., New York, 1982.

[47] Montaudo, G., *British Polymer Journal*, Vol. 18, 1986, pp. 231–235.

[48] Shimizu, Y. and Munson, M. S. B., *Journal of Polymer Science: Polymer Chemistry Edition*, Vol. 17, 1979, pp. 1991–2001.

[49] Adams, R. E., *Analytical Chemistry*, Vol. 55, 1983, pp. 414–416.

[50] Israel, S. C., Yang, W. C., and Bechard, M. J., *Macromolecular Science Chemistry*, Vol. A22, 1985, pp. 779–801.

[51] Saito, J., Waki, H., Teramae, N., Tanaka, S., *Progress in Organic Coatings*, Vol. 15, pp. 311–335.

[52] Armour, A. G., Wu, D. T., Antonelli, J. A., and Lowell, J. H., presented at the 186th American Chemical Society Meeting, Symposium of the History of Coatings, 14 Sept. 1989, Paper 38.

[53] Fulginiti, M. and Simonsick, W. J., Jr. in *Proceedings*, 37th American Society for Mass Spectrometry, Conference on Mass Spectrometry and Allied Topics, 1989, pp. 291–292.

[54] Grady, M. C. and Simonsick, W. J., Jr. in *Proceedings*, 36th American Society for Mass Spectrometry, Conference on Mass Spectrometry and Allied Topics, 1988, pp. 468–469.

Analysis and Characterization of Paint Components

David P. Sheih[1] *and Donald E. Benton*[1]

HPLC Analysis for Epoxy Coatings Resins

REFERENCE: Sheih, D. P. and Benton, D. E., "**HPLC Analysis for Epoxy Coatings Resins,**" *Analysis of Paints and Related Materials: Current Techniques for Solving Coatings Problems, ASTM STP 1119*, American Society for Testing and Materials, Philadelphia, 1992, pp. 41–56.

ABSTRACT: A review of the recent progress in development of HPLC techniques for the analysis of epoxy resins is presented in this paper. Three categories of epoxy resins, i.e., liquid, solid, and novolac epoxy resins, are included in the discussion. For analyzing oligomers and other components of these resins, HPLC has been recognized as the best choice based on speed, reliability, and accuracy of analysis. Successful resolutions of major components in the epoxy resins have been reported based on using reversed phase HPLC, UV detection, and acetonitrile/water or tetrahydrofuran/water solvent mixes and gradient elution techniques. Different components of the epoxy resins can be responsible for the success or failure in the performance of a coating formulation. Examples are given of some component identifications and their possible relationships to epoxy coatings properties, such as adhesion, viscosity, and flexibility.

KEY WORDS: epoxy, liquid epoxy resin, solid epoxy resin, analysis, HPLC, high performance liquid chromatography, chemical properties, coatings, adhesion, performance characteristics

Introduction

High performance liquid chromatography (HPLC) is a powerful and sometimes indispensable technique for analysis of a variety of epoxy products, particularly for those used in the preparation of coatings. A great number of papers and reviews of chromatographic analyses, e.g., gel permeation chromatography (GPC), size exclusion chromatography (SEC), or HPLC, for epoxy resins have been published [*1–29*]. However, most of the publications are devoted to the epoxy resins used in either aerospace resins or composite prepregs. Very little analysis information is publicly available for those epoxy resins used in the coatings industry. In this paper, we will focus our discussion on the current status of the HPLC technology employed in characterization of epoxy coating resins.

Epoxy resins are widely used for protective coatings mainly due to the fine balance of properties, such as good adhesion, impact resistance, flexibility, chemical and solvent resistance, etc. Due to the unique and excellent combination of the properties, about one half of the epoxy resin production (total 400 million lb in 1990) in the United States is used in protective coating applications.

The majority of the epoxy resins used in coatings are primarily based upon the polymeric products of bisphenol A and epichlorohydrin [*10,30,31*]. However, a variety of epoxy resins made from different raw materials and/or processes to meet the diversified requirements for coating applications are also readily available in today's marketplace. Consequently, good analytical techniques have become increasingly important to the users as well as to the manufacturers of epoxy resins.

---

[1] Dow Chemical Co., Freeport, TX 77541.

Since the early seventies, HPLC has been the fastest growing analytical technique due to various advances in columns and column packings, pumps, detectors, and automated control and data handling facilities [*32–41*]. These advances in the HPLC technology have made not only improvements in peak resolution and accuracy, but have also resulted in savings on analysis times. Other methods for analyzing the reactive groups of an epoxy resin, e.g., oxirane, hydroxyl, chlorohydrin, alpha-glycol, etc., are also essential [*31,32,42*], but provide only limited information and often lack accuracy or reproducibility. HPLC, on the other hand, with proper setups can provide valuable insights via fingerprinting components, impurities, and oligomers in the epoxy resins or in paint formulations. The effects of impurities and the oligomer distribution are well recognized to be very important to the properties of cured epoxy resins and also to the rate of the curing reaction [*3,43–47*]. With the advantages of high resolution, reproducibility, and short analysis times, HPLC is widely used in the epoxy resin industry for manufacturing quality control as well as for research purposes.

In this paper, a review of the recent progress in the development of HPLC techniques for the analysis of epoxy resins will be discussed. All common epoxy resins used in the coating industry, i.e., liquid, solid, and novolac epoxy resins, are included in the discussion. In some cases, analytical data of resin impurities or components will be related to their coating properties or performances.

Experimental

HPLC

HPLC has become one of the most important analytical tools available to chemical analysts. A wide range of components can be separated by HPLC techniques, and, depending upon the type of detector used, a large number of chemical species can be detected and quantitated. This discussion will address the equipment and techniques required to analyze epoxy resins by HPLC.

The basic HPLC equipment needed consists of the following:

1. Solvent or solvent mixture.
2. Solvent delivery system—pumps and controller.
3. Sample injection system—manual or automatic.
4. A column suitable to separate the species of interest.
5. A column heater—temperature controller.
6. A detection system.
7. A data recording and/or integration system.

Components may be separated by either normal phase HPLC (polar column material and relatively nonpolar solvents) or reversed phase HPLC (nonpolar column material and relatively polar solvents). Both types of separations have been used to analyze epoxy resins. However, reversed phase has proven to be the better method and the most widely used. The most common column material used for epoxy resins is the octadecyl silane (ODS), C_{18}, columns that can be obtained from a wide variety of manufacturers. The columns packed with spherical packing materials give the best resolution and peak symmetry. Other columns, C_8 and nitrile (CN), have been used for epoxies, but the C_{18} columns are the most preferred.

The two most commonly used solvent systems for epoxy resins are acetonitrile (ACN)/water and tetrahydrofuran (THF)/water. These are usually employed using gradient elution techniques. ACN/water systems are good for low molecular weight epoxies, but are limited by the solubility of higher molecular weight resins in ACN. This can be overcome by using

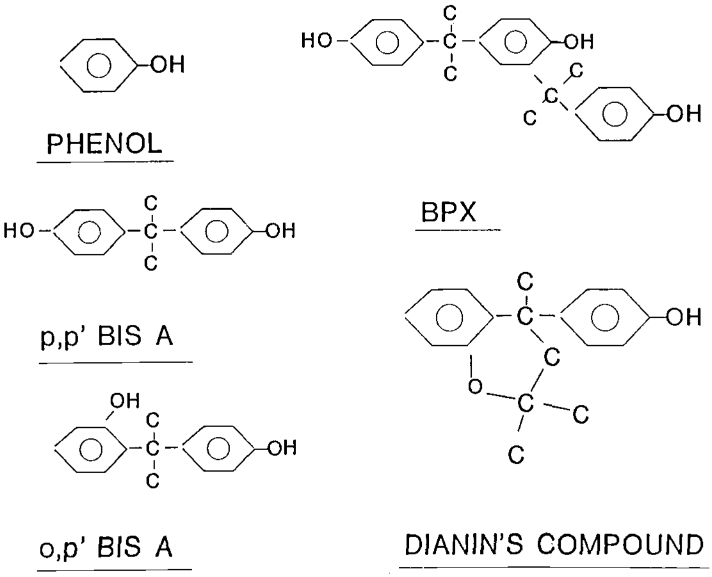


FIG. 1—*Known components in Bisphenol A.*

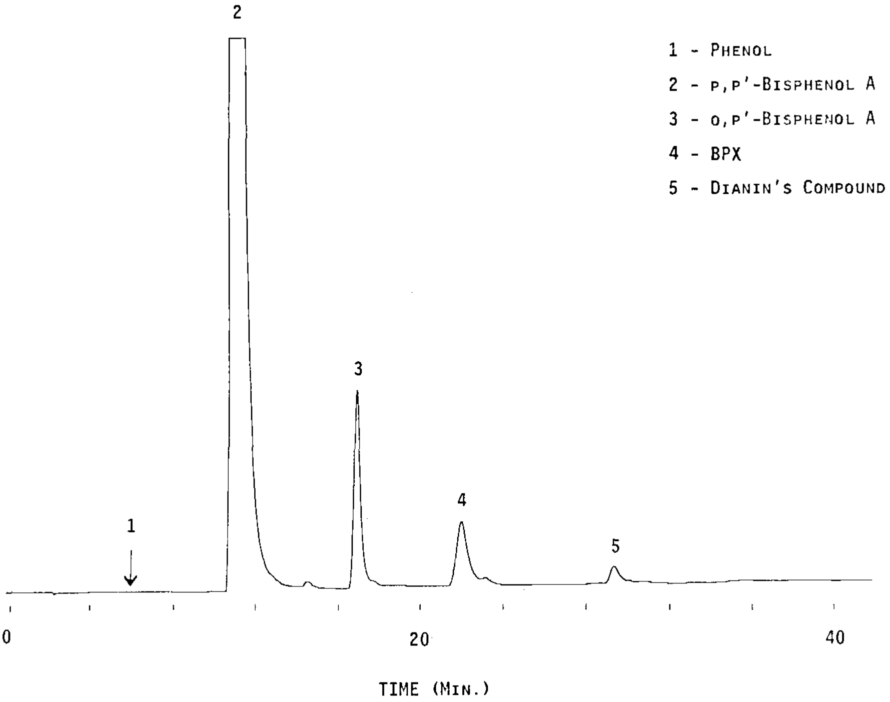


FIG. 2—*HPLC analysis of Bisphenol A.*

a THF/water eluant and THF as the resin solvent. The best of both systems can be achieved by using an ACN/THF/water ternary gradient technique. This technique was used to produce the chromatograms of solid epoxy resins used in this work.

The most commonly used detector for epoxy resins is the ultra violet (UV) detector. The most sensitive wavelengths for bisphenol A based epoxies are 230 and 280 nm, although good results with less sensitivity can be obtained at 254 nm also. Multiwavelength detectors can also be used, and diode array detectors can present a wealth of information about these resins to the analysts.

Modern data handling systems offer an almost unlimited number of choices for data collection, storage, calculation, and recalculation. Modern fluid handling equipment, controllers, and auto injectors to complete the HPLC system can also be chosen to fit the needs and budgets of most of the analytical or quality control laboratories.

The following ranges of conditions apply to the analysis of epoxy resins by HPLC. However, in order to obtain good resolution of all components of interest, analysis procedures must be modified in many cases to obtain the desired separations and/or speed of analysis.

Columns: Reversed phase C_8 or C_{18}

Solvents:
A. Binary gradients:
   ACN/water—40 to 100% ACN
   THF/water—30 to 100% THF
B. Ternary gradients:
   ACN/THF/water—40 to 100% organic

Flow rate: 1 to 2 mL/min

Detection: 230, 254, 280-nm UV detector

Sample concentration: 1 to 2% resin in ACN or THF

Injection size: 5 to 100 μL

T-Peel Test

All adhesion data were measured by T-peel test {ASTM Test Method for Peel Resistance of Adhesives (T-Peel Test) [D 1876-72 (1983)]} using an Instron. The T-peel test trips were prepared by first cutting the cured panels into 5-mm-wide strips. Next, a strip of thermoplastic adhesive was placed between two panel strips with the coatings facing the adhesive. Each unit was then heat bonded under a pressure of 150 psig (11.34 bar) at a temperature of 205°C for 30 s. The panels were then tested for dry adhesion using the Instron for a T-peel test. Wet adhesion was measured in the same manner after the specimen was soaked on 90°C water for four days.

Discussion

As mentioned before, there are a great number of epoxy resin families commercially available in the marketplace. However, in the epoxy coating industry, the bisphenol A based epoxy resin family is commonly used in protective coating formulations. Novolac epoxy family is also commonly used to enhance certain coating properties but to a much less extent.

Aliphatic epoxy resins, the third epoxy family, are very popular among the coating formulators because of their excellent flexibility, low viscosity, and good weatherability. However, HPLC analysis of the aliphatic epoxy resins were rarely reported, perhaps because of a lack of a UV chromophore on the aliphatic backbone for detection by the commonly used UV detectors. In this paper, we will therefore center our discussions on HPLC analysis of epoxy families derived from bisphenol A and novolacs with only a brief discussion on aliphatic epoxy resins.

Bisphenol A Based Epoxy Resins

Bisphenol A is prepared from phenol and acetone and is one of the two most important raw materials (epichlorohydrin is the other) in the production of epoxy resins. It is quite common that commercial bisphenol A often contains some by-product (see examples shown in Fig. 1). Those by-products and their epoxidized derivatives could also exist in the final epoxy resin products.

HPLC analysis has been known for a long time to be a very powerful tool in monitoring the by-products in both bisphenol A and the epoxy resins. Gas chromatography (GC) is frequently used for analyzing bisphenol A, but the HPLC method has shown its advantages in simplicity, ease of operation, and most importantly as a reliable and nondestructive analysis for higher molecular weight species without encountering the risk of thermal decomposition of the molecules as normally occur in GC methods. A HPLC chromatogram of bisphenol A containing some by-products is shown in Fig. 2.

Liquid epoxy resins (LER) are normally prepared by reacting bisphenol A with epichlorohydrin using a catalyst, such as caustic, in a typical condensation reaction (Fig. 3). Due to the impurities from bisphenol A in conjunction with some side reactions in the LER process, a variety of components are present in the LER. Not all but most of the components have been identified, mostly via HPLC/MS technique. For example, several known com-

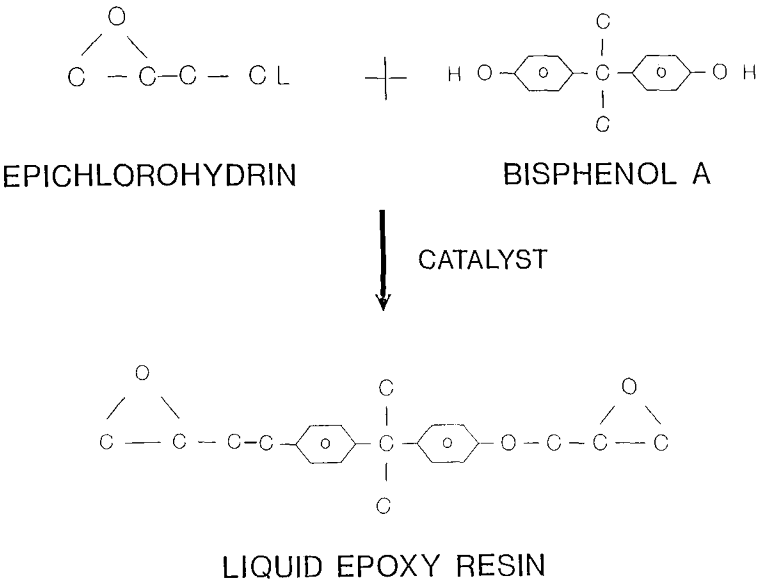


FIG. 3—*Preparation of liquid epoxy resin.*

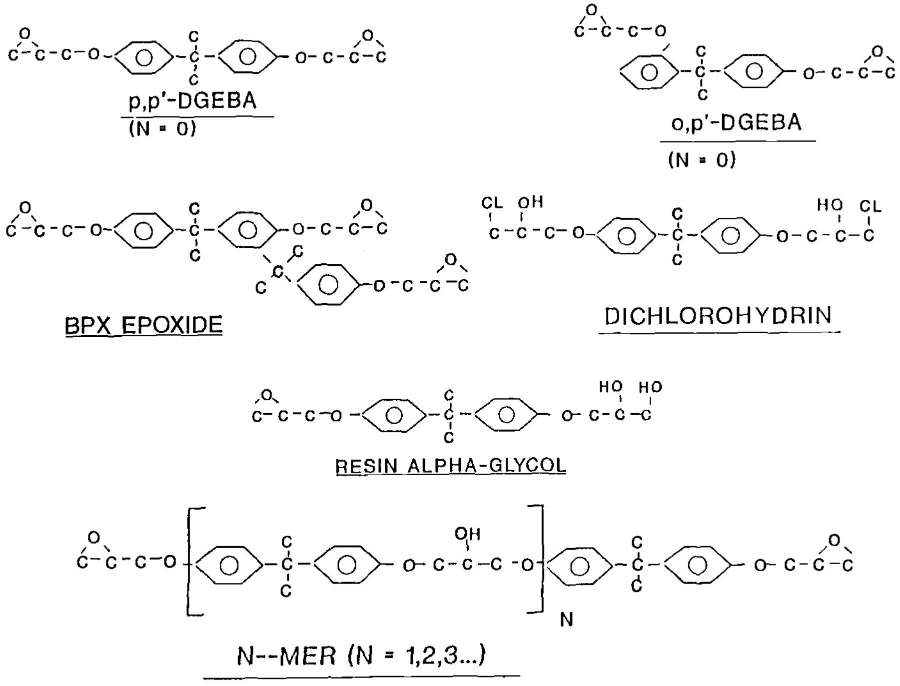


FIG. 4—*Known components in LER.*

ponents detected by HPLC are shown in Fig. 4. In the latter part of this section, we will discuss and show some examples of the effects of these components on the properties and performance of the LER.

Generally speaking, many paint formulators prefer to use higher weight average molecular weight (Mw) epoxy resins in their formulations. The main reason for this is because of the superior properties of the advanced solid epoxy resins. To prepare the advanced resin, bisphenol A is reacted with either epichlorohydrin (via the "taffy" process) or a LER (via the "fusion" process) (Fig. 5) with a base or weak acid as the catalyst. The finished products generally consist of a wide range of high Mw oligomers and are in a solid state at ambient temperatures. Their glass transition temperatures (Tg's) are dependent on Mw, which consequently are predetermined by the charge ratio of bisphenol A in the advancement reaction. For analysis, GPC is the most commonly used method for measuring Mw of the advanced epoxy resins (see Fig. 6 for a typical GPC chromatogram).

Unlike the LER, most of the advanced solid epoxy resins (SER), e.g., D.E.R.[2] 664 and D.E.R.[2] 667, would not be completely soluble in an acetonitrile/water system, which is the most commonly used by the HPLC analysts for characterization of LER. Therefore, we cannot use the conventional HPLC system to analyze solid epoxy resins. A third solvent with higher solvency power, such as THF, is required to dissolve the high Mw oligomers and still ensure the excellent resolution of the chromatographic peaks for each component. Figure 7 demonstrates the typical HPLC chromatogram of solid epoxy resins with the ternary solvent system. The chromatogram on the top of Fig. 7 is of a solid resin produced via "fusion" process in which only even N-numbered oligomers are present. However, the

---

[2] Trademark of Dow Chemical Co.

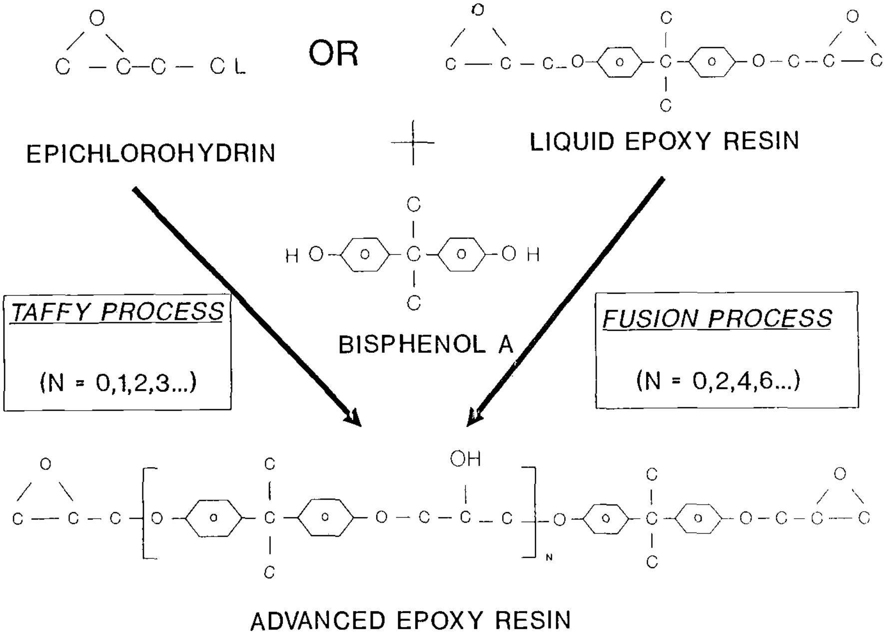
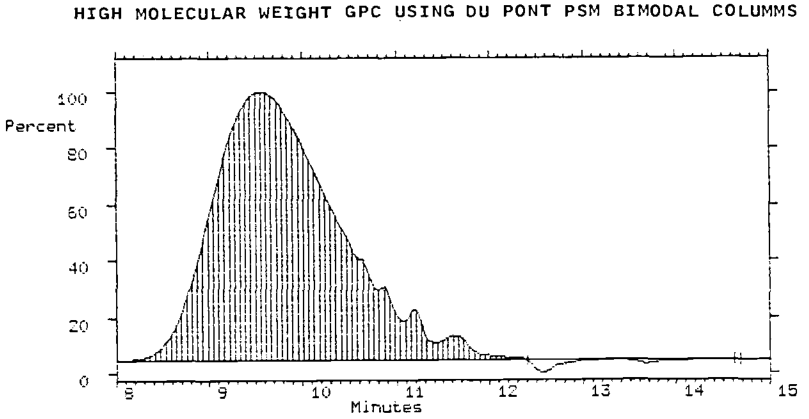


FIG. 5—*Chemistry of resin advancement.*

product made from "taffy" process, shown on the bottom, consists of both even and odd N-numbered oligomers.

Figure 8 is a demonstration of the capability of what HPLC can do to differentiate the Mw of solid epoxy resins and to exhibit the growth of N-mers while Mw is increased. As the Mw increases, such as from D.E.R. 661 (Mw = 1500 to 2000) to D.E.R. 664 (Mw = 4000 to 6000), the HPLC scan shows the appearance of higher oligomers (N = 14 and N =



NUMBER AVERAGE	2036	WEIGHT AVERAGE	7619
Z AVERAGE	15907	DISPERSITY	3.74

FIG. 6—*GPC analysis of solid epoxy resin.*

16) and as Mw continues to increase, as to D.E.R.[2] 667 (Mw = 10 000 to 12 000), oligomers of N = 18 and N = 20 and higher begin to show up in the chromatograms. Oligomers up to N = 32 have been observed in some high molecular weight samples. At the same time, areas of lower molecular weight oligomers, i.e., N = 0 and N = 2, etc., become smaller as these species are consumed in the advancement reactions.

Figures 7 and 8 have clearly demonstrated that the HPLC method is a powerful tool for not only having the capability of identifying the components but also to differentiate the processes employed to produce solid epoxy resins. The main oligomers can be identified as well as oligomers that form from side reactions and from impurities present (further details of this are discussed in the section entitled "Applications"). Liquid chromotography methods should lead to better understanding of resin processes and products and also to help to produce better quality resin products for the market.

In some other cases, a certain type of nonepoxy advanced bisphenol A resins are used either as coreactants for further advancement or as crosslinkers for epoxy cure [*47*]. Generally, the resins are classified as phenolic resins which are capped with bisphenol A at the both ends of the polymer molecules, forming terminal phenolic groups. HPLC, again, is a useful analytical tool for characterizing this type of resin (see Fig. 9).

Novolac Epoxy Resins

Novolac epoxy resins are not as widely used as bisphenol A based epoxy resins in coating formulations. However, novolac epoxy resin is frequently employed as an additive in coating formulations to enhance Tg, solvent and chemical resistance, cross-linking density, etc., for

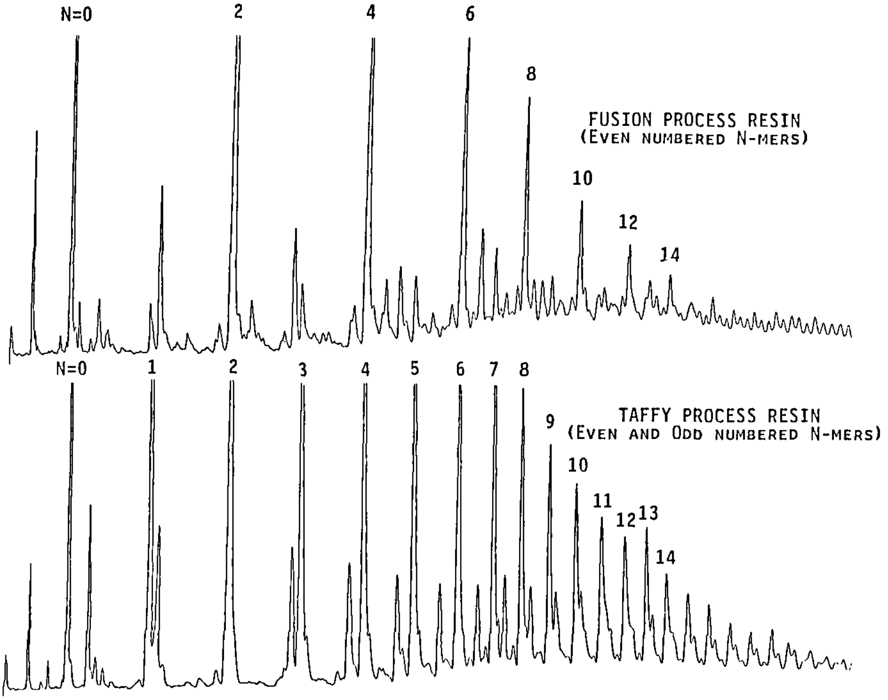


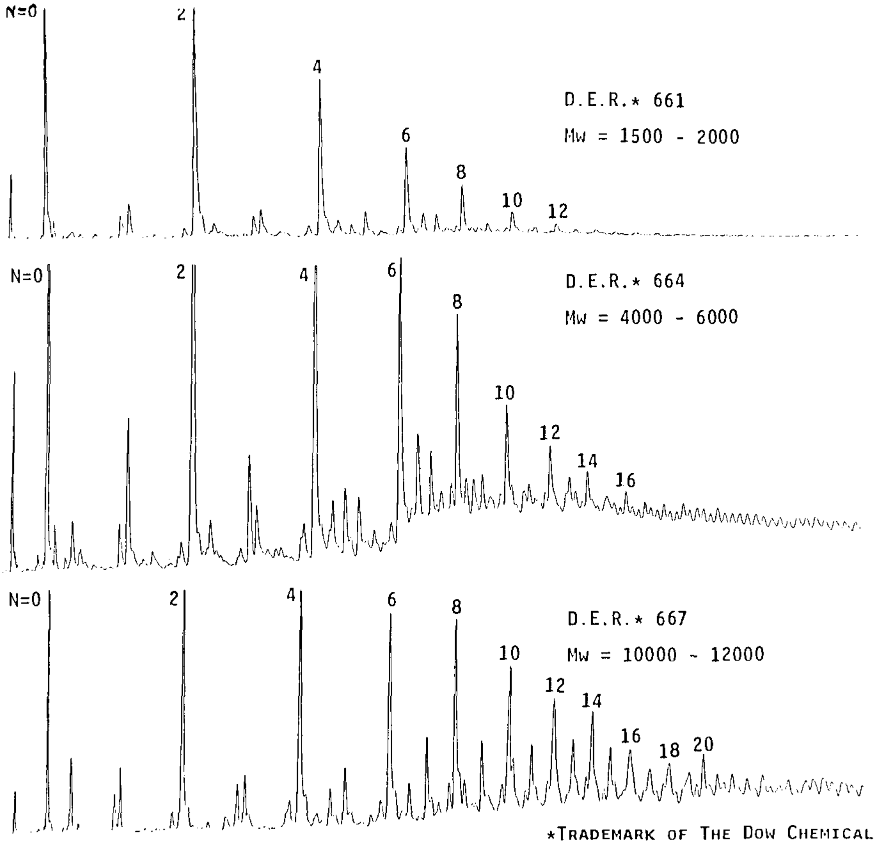
FIG. 7—*HPLC of solid epoxy resins made by fusion and taffy processes.*

improvement of coating performance. Since novolac epoxy resin also contains the UV-sensitive (aromatic) chromophore on the molecular backbone, HPLC again is a powerful tool for analyzing the resin and process as well (see Fig. 10 for isomers identification). With a good data processing capability, HPLC should be able to detect and identify novolac resin quantitatively from other epoxy resins in paint formulations. This capability provides the paint formulators and the paint users a handle to control the quality of their products.

Not surprisingly, HPLC is also often used by the novolac manufacturers to monitor the quality of the novolac precursor, the phenolic precursor of the epoxy resin. A HPLC chromatogram of a low Mw novolac precursor, two to three functional species, is shown in Fig. 11 with a good separation of the isomers.

Aliphatic Epoxy Resins

Aliphatic epoxy resins are widely used by the coating formulators to reduce the viscosity and therefore the volatile organic compound (VOC) of paint, and sometimes to improve flexibility, weatherability, and adhesion of the coat. However, it is very difficult to analyze aliphatic epoxy resins using the HPLC method. As mentioned in the "Introduction," most aliphatic epoxy resins are UV insensitive and hence are not detectable by the commonly used UV detector in HPLC. One may use a reflective index (RI) detector to analyze aliphatic



*Trademark of The Dow Chemical Company

FIG. 8—*HPLC of solid epoxy resins with various molecular weights.*

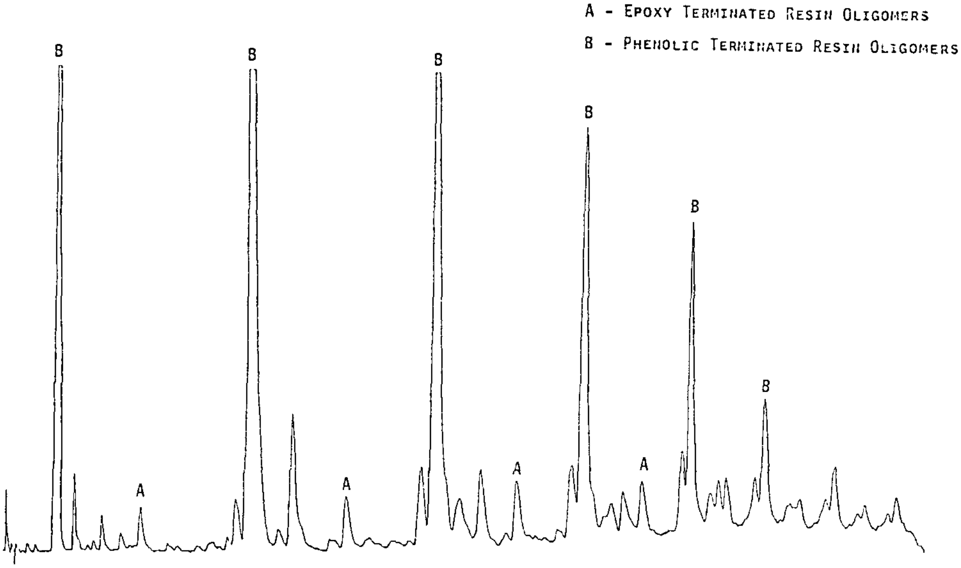


FIG. 9—*HPLC analysis of advanced phenolic resin.*

epoxy resins but must sacrifice a certain degree of separation capability. This is due to the fact that when a RI detector is used, multiple solvent gradient systems are no longer applicable and the analysis must be run under isocratic conditions. The HPLC resolution for any multicomponent resin in general is not satisfactory under the isocratic conditions.

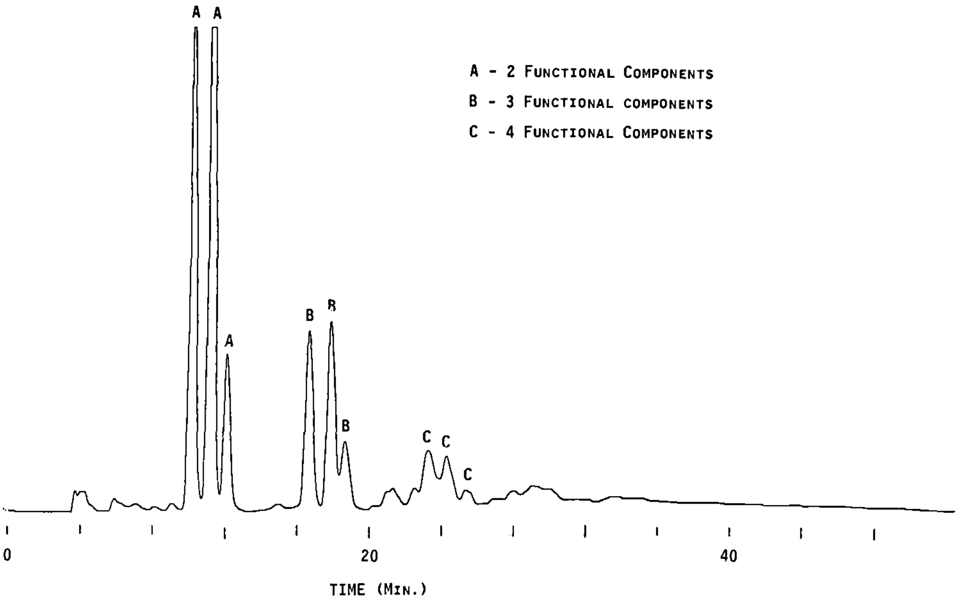


FIG. 10—*HPLC analysis of novolac epoxy resin (D.E.N. 431).*

However, in order to improve the UV sensitivity, one may incorporate chromophores onto the aliphatic backbone to make the resin detectable by the UV detector. Furthermore, this technique of making UV sensitive derivatives is also employed by HPLC analysts to characterize nonepoxy paint materials [*48*].

Applications

Effect of Resin Alpha-Glycol

Among the components in LER, resin alpha-glycol (see Fig. 4) is the most interesting species which could affect viscosity of both LER and its advanced solid epoxy resins in different directions (Fig. 12). Increase of alpha-glycol level would increase the viscosity of LER. This is probably due to the strong nature of hydrogen-bonding of the glycol group. On the other hand, increase of alpha-glycol level in LER would decrease the viscosity of the advanced epoxy products possibly through a chain termination mechanism.

With the combination of hydrogen bonding and chain termination characteristics, alpha-glycol resin has been recognized as a very unique but interesting component. It could affect paint performances, such as adhesion, flexibility, etc., in a quantitative way. For example, Fig. 13 demonstrates the effect of increase of alpha-glycol resin on wet adhesion of a high Mw epoxy resin with a phenolic curing agent coated on a tin-free substrate. The adhesion strength is measured by T-peel method using an Instron (see procedure in the section entitled "Experimental"). For epoxy producers and paint manufacturers, HPLC again is a powerful tool to measure the alpha-glycol level for monitoring the raw material quality (see Fig. 14 for the alpha-glycol measurement in LER via HPLC method).

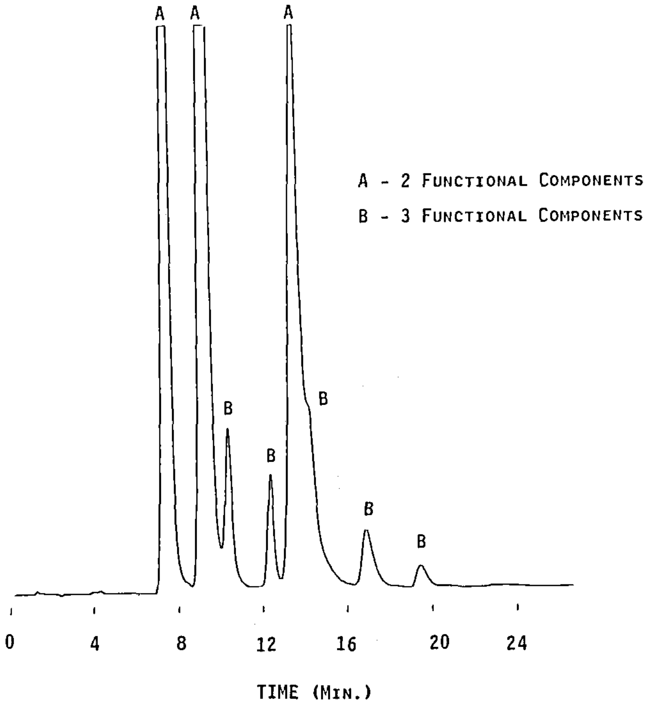


FIG. 11—*HPLC analysis of novolac precursor (low Mw).*

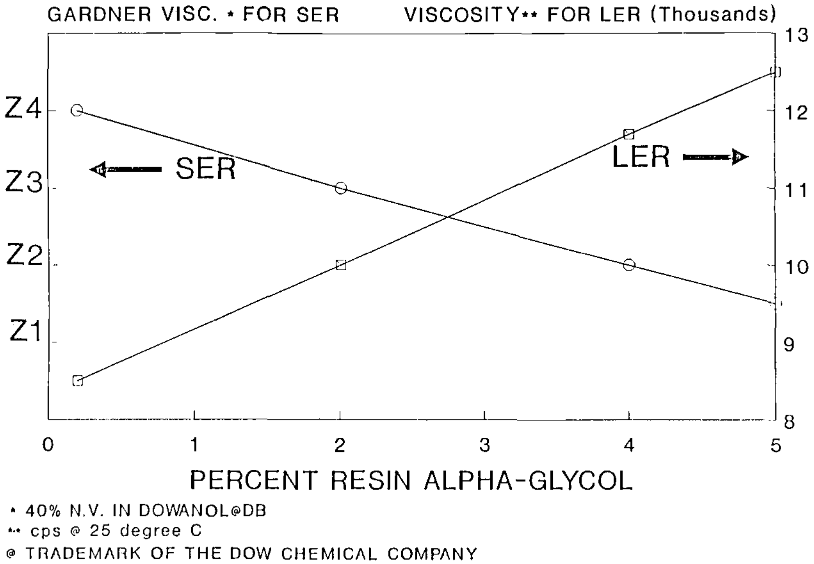


FIG. 12—*Effect of resin alpha-glycol (effect on viscosity of LER or SER).*

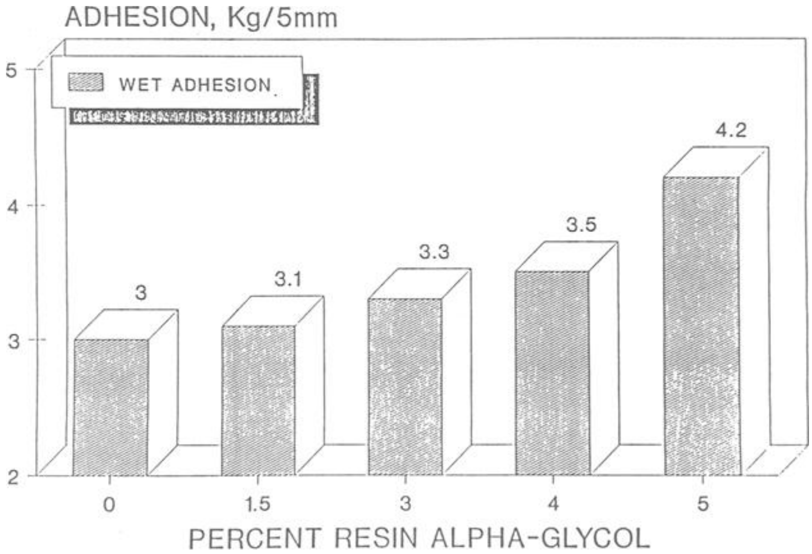


FIG. 13—*Effect of resin alpha-glycol (effect on wet adhesion).*

Effect of Hydrolyzable Chloride

Hydrolyzable chloride is another important component in LER. This reactive functional group has a small but detectable effect on adhesion over the average range of hydrolyzable chloride found in most commercial LERs (Table 1). HPLC analysis offers a quick and reliable tool to monitor the level of hydrolyzable chloride for controlling the quality.

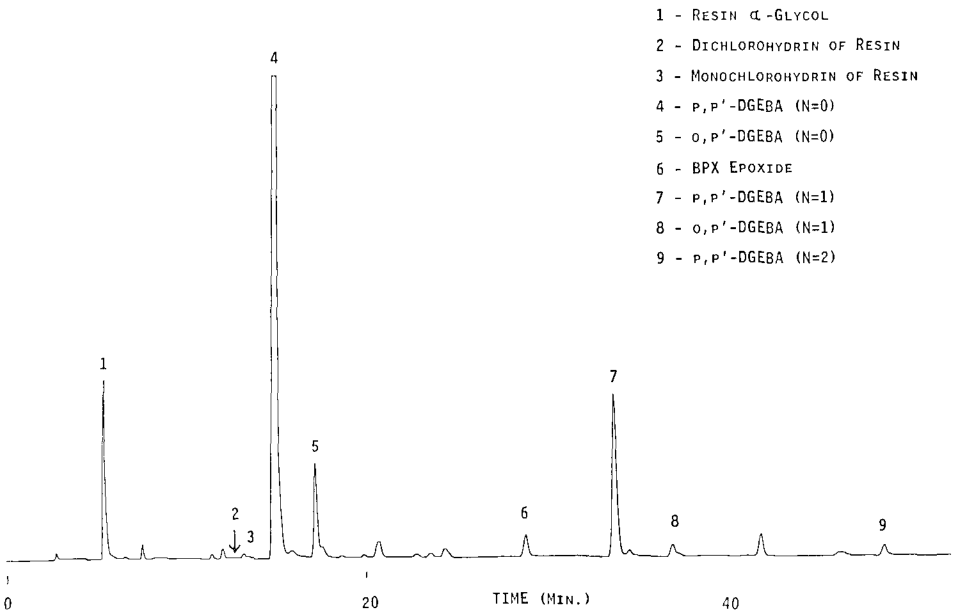


FIG. 14—*HPLC analysis of liquid epoxy resin (D.E.R. 331).*

Effect of O,P'-Isomer

The other reactant beside LER in the fusion advancement reaction is bisphenol A, which comes commercially in several grades. The major component is p,p'-bisphenol A with a minor level (less than 5%) of its isomeric coproduct, o,p'-bisphenol A. In our work (Table 2), we found that the level of ortho,para' isomer in the LER used in the advancement

TABLE 1—*Effect of hydrolyzable chloride on adhesion.*

Hydrolyzable Chloride, ppm	Adhesion, kg/5 mm	
	Dry	Wet
240	7.0	3.7
500	6.8	3.8
750	6.6	4.0

TABLE 2—*Effect of ortho,para bisphenol A.*

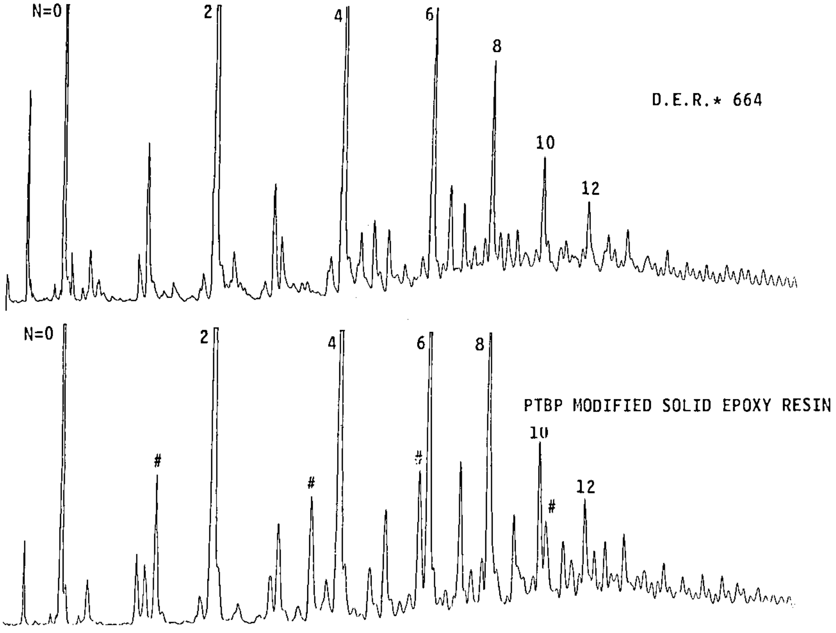
% O,P in Epoxy	% O,P' in Bis A	EEW	Mw	Adhesion, kg/5 mm	
				Dry	Wet
3.3	0.3	3500	15 500	6.7	3.9
3.3	3.6	3300	14 000	4.8	3.2
12.8	0.3	3330	14 100	5.0	3.6
12.8	12.8	2300	7 700	N/A	N/A

NOTE: N/A = Not Applicable due to incomplete polymerization.

reaction had considerably less effect on adhesion than did the amount of o,p'-bisphenol A in the bisphenol A used. Apparently, the lower reactivity of the sterically hindered ortho-substituted phenol effectively causes that portion of the bisphenol A molecules to act as monofunctional with respect to epoxide. Monofunctionality affects the advancement reaction as shown by the product made from high (12.8%) o,p'-isomer level in bisphenol A. Again, HPLC is probably the only suitable analytical means to quantitatively measure the o,p'-isomer in both bisphenol A and LER.

Effect of End-group Capping on Viscosity

In order to reduce paint viscosity to improve flow-out property or to meet the regulatory VOC requirement, epoxy coating resins often are modified by capping with some monofunctional phenols, e.g., p-tert. butylphenol (PTBP). The modification with PTBP capping normally can cut the viscosity significantly. For instance, Fig. 15 shows the HPLC peaks of PTBP (<1%) capped components (as labelled) of a modified resin with a viscosity (cone/plate at 150°C) of 579 versus 680 cSt for the nonmodified resin. Dramatic effect of viscosity reduction can be obtained with a higher level of capping, e.g., some commercial products contains 5 to 10% PTBP capped oligomers. HPLC is the ideal analytical means for measuring capped components.



- p-t-Butyl Phenol Capped Resin Oligomers

*Trademark of The Dow Chemical Company

FIG. 15—*HPLC analysis of p-t-butyl phenol (PTBP) modified solid epoxy resin.*

Summary

A general overview of the HPLC techniques for analysis of epoxy resins has been presented in this paper. Three categories of epoxy resins, i.e., liquid (including both bisphenol A based and aliphatic), solid, and novolac epoxy resin, are included in the discussion. Among the conventional analytical methods, including both instrumental and wet methods, HPLC is recognized as the best choice based on its speed, reliability, and accuracy of analysis. However, in order to obtain good resolution of all the components of interest, analysis procedures must be modified in many cases by the individuals to obtain the desired separations.

In this paper, we also have demonstrated that the different components of epoxy resins can be responsible for the success or failure in the performance of coating formulations. For example, the resin alpha-glycol could affect significantly the adhesion strength of paints. Other examples were also given to exhibit the superiority of HPLC for component identifications as well as for establishment of performance relationship with the components.

References

[*1*] Kuo, C., Provder, T., Holsworth, R. M., and Kah, A. F. in *Liquid Chromatography of Polymers and Related Materials*, Vol. 3, Dekker, New York, 1981, p. 169.

[*2*] Twichell, J. E., Walker, J. Q., and Maynard, J. B., *Journal of Chromatographic Science*, Vol. 17, 1979, p. 259.

[*3*] Dark, W. A., Conrad, E. C., and Crossman Jr., L. W., *Journal of Chromatography*, Vol. 91, 1974, p. 247.

[*4*] Van der Maeden, F. P. B., Biemond, M. E. F., and Janssen, P. C. G. M., *Journal of Chromatography*, 1978, pp. 149 and 539.

[*5*] Zucconi, T. D. and Humphrey, J. S., *Polymer Engineering and Science*, Vol. 16, 1976, p. 11.

[*6*] Hagnauer, G. L. and Dunn, D. A., *Industrial Engineering Chemistry, Product Research and Development*, 1982, p. 68.

[*7*] Hagnauer, G. L. and Dunn, D. A., *Proceedings*, 12th National SAMPE Technical Conference, 1980, p. 648.

[*8*] Hagnauer, G. L., *Polymer Composites*, Vol. 2, 1980, p. 81.

[*9*] Crabtree, D. J. and Hewitt, D. B., *Liquid Chromatography of Polymers and Related Materials*, Vol. 1, Dekker, New York, 1977, p. 63.

[*10*] Mestan, S. A. and Morris, C. E. M., *Reviews in Macromolecular Chemical Physics*, C24 (1), Marcel Dekker, Inc., 1984, pp. 117–172.

[*11*] Fedtke, M. and Taenzer, W., *Journal Fuer Praktische Chemie*, Vol. 324, No. 3, 1982, p. 429.

[*12*] Scheuing, D. R., *Journal of Coatings Technology*, Vol. 57, No. 723, 1985, pp. 47–53.

[*13*] Henrids-Eckerman and Laijoki, T., *Analyst*, Vol. 113, February 1988, pp. 239–242.

[*14*] Woodlee, F. R., *Proceedings*, 430th National SAMPE Symposium, 1985, pp. 471–478.

[*15*] Ishi, D. and Takeuchi, T., *Journal of Chromatography*, Vol. 255, 1983, pp. 349–358.

[*16*] King, J. J. et al., *Proceedings*, 427th National SAMPE Symposium, May 1982, pp. 163–177.

[*17*] Epprt, G. and Liebscher, G., *Journal of Chromatography*, Vol. 238, 1982, pp. 399–407.

[*18*] Fedtke, M. and Tanzer, W., *Journal Fuer Praktische Chemie*, Band 324, 1982,S., pp. 429–442.

[*19*] Thomas, G. R. et al., *Proceedings*, Natl. SAMPE Symp. Exhib., Vol. 24, No. 1, pp. 458–505.

[*20*] Eggimann, D. W., Brand, J. C., and Elliott, C. K., *Proceedings*, Natl. SAMPE Symp., Vol. 26, 1981, pp. 304–313.

[*21*] Schenk, C. and Kayen, A. H. M., *Proceedings*, Cong. FATIPEC, Vol. 15Th, No. 3, pp. 345–60.

[*22*] Hagnauer, G. L., NTIS Report No. AD-A080 221, National Technical Information Service, U.S. Department of Commerce, November 1979.

[*23*] Dark, W. A., Conrad, E. C., and Crossman, L. W., *Journal of Chromatography*, Vol. 91, 1974, pp. 247–260.

[*24*] Hadad, D. K. in *Liquid Chromatography of Polymers and Related Materials III*, Marcel Dekker, New York, pp. 157–167.

[*25*] Lai, S. T. and Sangermano, L., *Journal of Chromatography*, Vol. 321, 1985, pp. 325–333.

[*26*] Belton, D. J. and Sullivan, E., *Journal of Applied Polymer Science*, Vol. 31, 1986, pp. 1309–1326.

[27] Hanus, J. et al., *Plaste und Kautschuk,* 27. Jahrgang, Heft 2, 1980, pp. 75–77.

[28] Maslov, V. A., Grozdov, A. G., and Kutepov, D. F., *Polymer Science U.S.S.R.,* Vol. 24, No. 8, 1982, pp. 2034–2039.

[29] Szap, P., Kesse, I., and Klapp, J., *Journal of Liquid Chromatography,* Vol. 1, No. 1, 1978, pp. 89–96.

[30] Lee, H. and Neville, K. in *Handbook of Epoxy Resins,* McGraw-Hill, New York, 1982, Chapt. 4, pp. 4–1 to 4–70.

[31] May, C. A. in *Epoxy Resins—Chemistry and Technology,* Marcel Dekker, New York, 1988, Chapts. 13 & 14, pp. 1049–1172.

[32] McKinley, W. A., Popovich, D. J., and Layne, T., *American Laboratory,* August 1980, pp. 37–47.

[33] Majors, R. E., *Journal of Chromatographic Science,* Vol. 18, 1980, pp. 488–511.

[34] Rabel, F. M., *Journal of Chromatographic Science,* Vol. 18, 1980, pp. 394–408.

[35] Walton, H. F., *Analytical Chemistry,* Vol. 52, 1980, pp. 15R–27R.

[36] Cooke, N. H. C. and Olsen, K., *Journal of Chromatographic Science,* Vol. 18, 1980, pp. 512–524.

[37] Meek, J. L., *Analytical Chemistry,* Vol. 52, 1980, pp. 1370–1371.

[38] Lurie, I. S., *American Laboratory,* October 1980, pp. 35–42.

[39] McNair, H. M., *American Laboratory,* May 1980, pp. 33–44.

[40] DeStefano, A. P., Goldberg, A. P., Larmann, J. P., and Parris, N. A., *Industrial Research and Development,* April 1980, pp. 99–103.

[41] Assenza, S. P. and Brown, P. R., *Journal of Liquid Chromatography,* Vol. 13, No. 1, 1980, pp. 41–59.

[42] Bruins, P. F., Ed., *Epoxy Resin Technology,* Interscience, New York, 1968.

[43] Hagnauer, G. L., *Industrial Research and Development,* Vol. 23, No. 4, 1981, p. 128.

[44] Shiono, S., Karino, I., Ishimura, A., and Enomoto, J., *Journal of Chromatography,* Vol. 193, 1980, p. 243.

[45] Sheih, P. S. and Massingill, J. L., *Journal of Coatings Technology,* Vol. 61, No. 781, 1990, pp. 25–30.

[46] Massingill, J. L. and Sheih, P. S., *Journal of Coatings Technology,* Vol. 61, No. 781, 1990, pp. 31–39.

[47] Sheih, P. S. and Whiteside, R. C., *Proceedings,* Preceedings 15 of XVth International Conference in Organic Coatings Science and Technology, Athens, Greece, 1989, pp. 359–377.

[48] Scheuing, D. R., *Chromatography Review (Spectra Physics),* Vol. 6, No. 1, January 1980.

Cheng-Yih Kuo[1] *and Theodore Provder*[1]

Application of Size Exclusion Chromatography to Polymers and Coatings

---

REFERENCE: Kuo, C.-Y. and Provder, T., "**Application of Size Exclusion Chromatography to Polymers and Coatings,**" *Analysis of Paints and Related Materials: Current Techniques for Solving Coatings Problems, ASTM STP 1119,* American Society for Testing and Materials, Philadelphia, 1992, pp. 57–81.

ABSTRACT: The newer coatings technologies of waterborne, high solids, powder, and radiation curable coatings generally require high molecular weight latex polymers or strategically designed low molecular weight polymers, oligomers, and reactive additives. The design of these resin materials requires molecular weight distribution (MWD) information in the very high and very low molecular weight ranges which are accessible by size exclusion chromatography (SEC). In addition, there is a need for compositional distribution information as a function of molecular weight, particularly for oligomers; absolute MWD information, particularly for water-soluble polymers; and chain-branching information for high molecular weight polymers.

In this paper, the SEC separation mechanism, molecular weight calibration methods including the use of hydrodynamic volume, data treatment methods, and polymer chain-branching determination will be discussed. The use of molecular size sensitive detectors (viscometer, light scattering) and compositional sensitive detectors (UV-visible, IR) will be discussed in the context of illustrative qualitative and quantitative examples. The practice of high resolution SEC analysis of oligomers will be discussed and illustrated with problem-solving examples.

KEY WORDS: size exclusion chromatography, SEC, gel permeation chromatography, GPC, polymers, coatings, oligomers, molecular weight, molecular weight distribution, MWD, refractometer, laser light scattering, viscometer, photodiode array detector, Fourier transform infrared, FTIR, waterborne, high solids, powder, chain branching

Over the last twelve years, new coatings technologies such as high solids, powder, waterborne, and radiation curable coatings have been developed to meet the challenges of: (a) governmental regulations in the areas of ecology [volatile organic compounds (VOC) emission]; (b) long-term increasing costs of energy and petroleum-based solvents; (c) more active public consumerism; and (d) the continual need for cost-effective high performance coatings in a highly competitive and global business environment. These new coatings technologies require the use of water as the major solvent with water soluble or high molecular weight latex polymers or the use of strategically designed low molecular weight polymers, oligomers, and reactive additives, which when further reacted produce high molecular weight and crosslinked polymers. Knowledge of the molecular weight and molecular weight distribution (MWD) of the polymer components in a coatings system is essential for the optimization of polymer design for specific end-use properties. Since its introduction over two decades ago, gel permeation chromatography (GPC) [*1*] or size exclusion chromatography (SEC) has become an important and practical tool for the determination of the MWD of

---

[1] Scientist and principal scientist, respectively, The Glidden Co., part of ICI Paints World Group, Research Center, 16651 Sprague Road, Strongsville, OH 44136.

polymers. Numerous studies have been published on the use of SEC in plastics, elastomeric, and coatings systems including a number of monographs [*2–15*]. With the advent of high efficiency columns, the resolution in the lower molecular weight region (molecular weights in the range of 200 to 10 000) has been greatly improved and the speed of analysis increased. These features make high performance SEC (HPSEC) an indispensable characterization tool for the analysis of oligomers and polymers in environmentally acceptable coatings systems.

SEC Separation Mechanism

Size exclusion chromatography separates the polymer molecules by their molecular size or "hydrodynamic volume" in solution. The separation occurs as the polymer molecules elute through one or more columns packed with a porous support. Smaller molecules are retained in the pores to a greater degree than the larger molecules. As a result the largest size molecule (or the molecule having the greatest hydrodynamic volume) elutes from the column first followed by the smaller molecules. The volume of liquid at which a solute elutes from a column or the volume of liquid corresponding to the retention of a solute on a column is known as the retention volume (V_R) and is related to the physical parameters of the column, such as interstitial (void) volume and internal pore volume.

The dependence of molecular size in solution upon retention volume is schematically illustrated in Fig. 1. The void volume V_0 corresponds to the total exclusion of solute molecules from the pores. The excluded solute molecules are significantly larger than the largest available size pores. Between V_0 and V_T the solute molecules are selectively separated based on their molecular size in solution. Beyond the total column volume V_T, separation will not be achieved by a liquid exclusion chromatography mechanism. If molecules appear to separate beyond V_T, they are being retained on the column support by an affinity mechanism. The fundamental aspects of the SEC separation mechanism have been treated theoretically

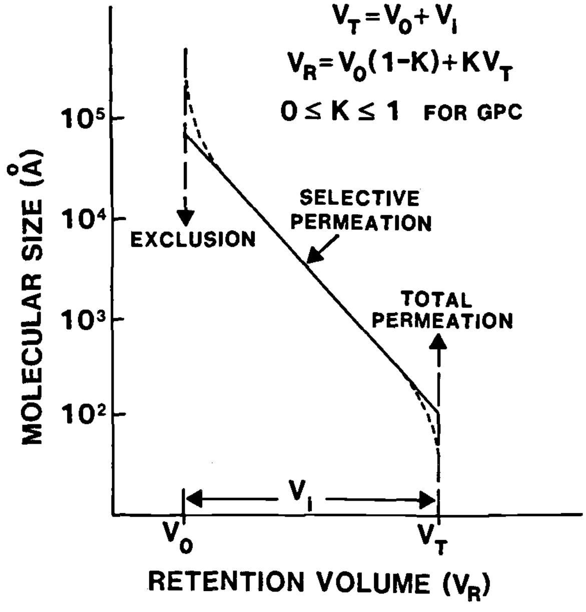


FIG. 1—*Illustrative SEC calibration curve.*

by Casassa et al. [*16–20*], Giddings [*21*], and Yau et al. [*22,23*]. These treatments are based on an equilibrium distribution of species between the mobile phase in the interstitial volume and the species in the pore volume of the column support.

Instrumentation

The essential components of the instrumentation are a solvent reservoir, a solvent delivery system (pump), sample injection system, packed columns, a detector(s), and a data processing system.

The heart of the instrumentation is the fractionation column where the separation takes place. The most common packing material used has been a semirigid cross-linked polystyrene gel. Developments in column technology have made the low efficiency, large particle size (37 to 75 μm) packing material obsolete. Currently, almost all the available SEC columns are packed with the high efficiency, microparticulate packings (<10 μm). Recent state-of-the-art developments on column packings have been described by Majors [*24*]. An up-dated listing of such type of packing materials is included in a recent overview on SEC [*25*].

The concentration of the polymer molecules eluting from SEC columns is continuously monitored by a detector. The most widely used detector in SEC is the differential refractometer (DRI), which measures the difference in refractive index between solvent and solute. Other detectors commonly used for SEC are functional group detectors: ultaviolet (UV) and infrared (IR), and absolute molecular weight detectors: low angle laser light scattering (LALLS) and in-line continuous viscometers. Applications of these detectors to SEC analysis will be discussed later in the Multiple Detector section. Other detectors also being used are the densimeter [*26–34*], the mass detector [*35–41*], and photodiode array UV-visible spectrophotometer and multiangle laser light scattering (MALLS) [*42–44*].

Calibration

In order to convert a chromatogram into a molecular weight distribution curve, a calibration curve relating molecular weight to retention volume is required. Narrow MWD standards (polydispersity, $\overline{M}_w/\overline{M}_n$, is usually less than 1.1) of the polymer of interest are used to generate retention volume curves. A one to one correspondence of peak retention volume with peak molecular weight, $\overline{M}_p$, is made. The peak retention volume is usually assigned to be $\sqrt{\overline{M}_w \cdot \overline{M}_n}$ for narrow MWD polymers. By plotting log $\overline{M}_p$ versus retention volume, a primary molecular weight calibration curve is generated. The disadvantage of this method is that quite often well-characterized narrow MWD polymer fractions of interest are not readily obtainable or require extensive laboratory time for their generation.

There are other methods for generating absolute MWD curves without resorting to polymer fractionation. One of these methods uses broad MWD standards to generate the molecular weight calibration curve [*45–57*]. Other methods involve the use of the hydrodynamic volume concept. Polymers having different chemical structures or polymers having the same chemical structures but different chain configurations (linear versus different types of branching) will have unique calibration curves. The SEC separation mechanism is based upon molecular size in solution (not molecular weight) or hydrodynamic volume. Therefore, if a parameter related to the hydrodynamic volume is used to generate calibration curves, a common calibration curve for a variety of polymers will be obtained. Benoit and coworkers [*58*] first proved the experimental validity of this concept by generating calibration curves consisting of a plot of the product of the instrinsic viscosity, [η], and weight average molecular weight, $\overline{M}_w$ versus retention volume. With commercially available polystyrene standards, such curves are readily generated. One can use experimental and/or mathematical techniques

[*59*] to obtain secondary molecular weight calibration curves from the hydrodynamic volume calibration curve. Figure 2 shows the schematic procedures for obtaining the secondary molecular weight calibration curve from on-line SEC/viscometer data.

Two refinements involving the use of hydrodynamic calibration curves are: (1) Rudin's equation [*60*], which accounts for the reduction of effective hydrodynamic volume of high molecular weight polymers with finite concentration; (2) Hamielec and Ouano's finding [*61*] that the hydrodynamic volume is the product of intrinsic viscosity and $\overline{M}_n$ instead of $\overline{M}_w$. This refinement is of importance when applying hydrodynamic volume considerations to molecular branching models for highly branched and heterogeneous polymers. Transformation of the raw chromatogram into various molecular weight average, differential, and cumulative distribution curves was described by Pickett [*62*] in one of his early papers. To numerically fit the calibration curve, various approaches have been used, i.e., polynomial, Yau-Malone equation [*63*], and sum of exponentials. Detailed discussion of these treatments can be found in Balke's book [*64*].

With all the calibration options available, the primary molecular weight calibration curve is still the most widely used calibration method in the coatings industry.

Instrument Spreading Correction

MWD curves calculated from SEC are generally broader than the true or absolute MWD curves due to instrumental spreading of the experimental chromatogram. Thus, the molecular weight averages calculated from the experimental chromatograms can be significantly different from the absolute molecular weight averages. The instrument spreading in SEC has been attributed to axial dispersion and skewing effects. Several computational procedures [*65–76*] have been reported in the literature to correct for these effects. In each method a specific shape for the chromatogram of an ideal monodisperse species or narrow MWD sample is assumed.

Tung [*77*] has shown that the normalized observed SEC chromatogram, $F(v)$, at retention volume v is related to the normalized SEC chromatogram corrected for instrument broadening, $W(y)$, by means of the shape function $G(v,y)$ through the relation

$$F(v) = \int_{-\infty}^{\infty} G(v - y)w(y)dy \tag{1}$$

Provder and Rosen [*68*], applying Tung's equation and the "method of molecular weight averages" in conjunction with a linear calibration curve obtained, corrected molecular weight averages from the uncorrected values. The "method of molecular weight averages" has been included in ASTM Test Method for Molecular Weight Averages and Molecular Weight Distribution of Polystyrenes by Liquid Exclusion Chromatography (Gel Permeation Chromatography-GPC) (D 3536-76) to correct for instrument spreading effects.

For the high performance microparticulate organic gel columns, the need for instrument spreading corrections is minimum. However, for the porous silica columns the need to correct for instrument spreading still exists. Yau and coworkers [*69*] used the following equations to correct the spreading effect of the bimodal porous silica columns

$$\overline{M}_n = \frac{D_1 \exp[(D_2\sigma)^2/2]}{\Sigma F(V)\exp(D_2V)} \tag{2}$$

$$\overline{M}_w = \left[\exp \frac{-(D_2\sigma)^2}{2}\right] \Sigma F(v)D_1 \exp(-D_2v) \tag{3}$$

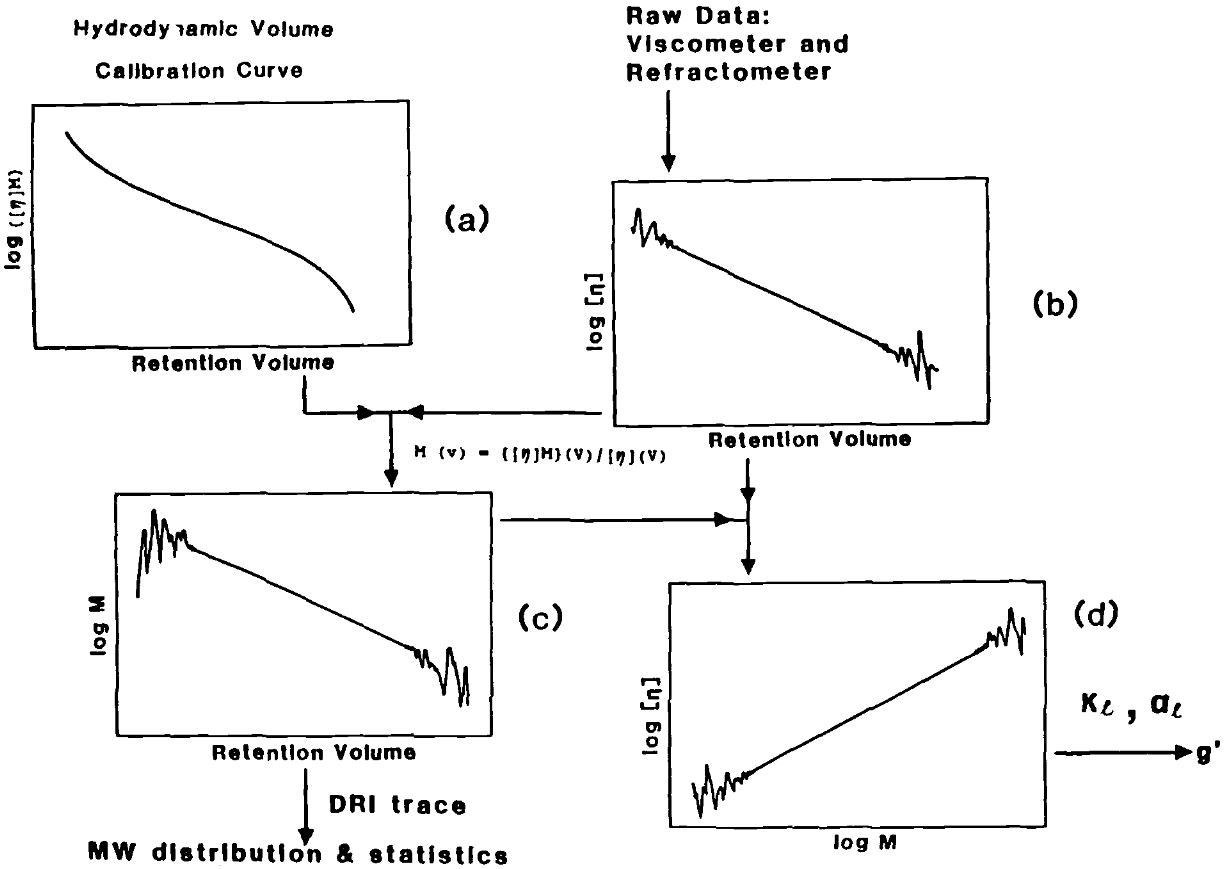


FIG. 2—*Data reduction scheme for analysis of DRI/viscometer chromatograms.*

where σ^2 is the variance of the Gaussian instrument spreading function and a measure of peak broadening, and D_1,D_2 are the intercept and slope of the linear calibration curve. Hamielec et al. [*70–71*] extended these situations to a nonuniform Gaussian spreading function and a nonlinear molecular weight calibration curve.

Multiple Detectors

Most size exclusion chromatographs use a DRI as a detector to monitor the concentration curves of samples eluting from the columns. This type of detector is highly sensitive and versatile and can monitor exceedingly low sample concentrations in a variety of solvents. However, it has several disadvantages which prevent it from being a "universal detector." At low and intermediate molecular weights, the specific refractive index increment at a given sample concentration is dependent upon the molecular weight [*78–79*]. For homopolymers, this difficulty can be circumvented by constructing a response factor curve versus molecular weight. For multicomponent polymer systems, there is the additional complexity of the dependence of the specific refractive index increment upon the composition of the polymer system. In principle, if the structural features of the polymer system were known, response factor curves for a given multicomponent system could be constructed from a knowledge of atomic and bond refractions [*80*]. However, this is a very impractical approach for real polymer systems.

Most coatings materials are complex multicomponent systems covering the low to intermediate molecular weight range. The use a of differential refractometer detector in the practice of SEC provides useful routine screening information with regard to the approximate molecular weight distribution of these samples. However, little or no information can be inferred with regard to the compositional distribution as a function of molecular weight. To obtain this type of information on polymers in the past, SEC fractions have been collected and analyzed by infrared spectroscopy. In addition to being a tedious and time-consuming method, a rather crude analysis of compositional distribution as a function of molecular weight is obtained [*81–82*]. To get maximum benefit from the SEC technique in terms of obtaining absolute molecular weight distributions and refined compositional distributions as a function of molecular weight, specific functional group detectors coupled on-line to the SEC are required.

SEC/DRI/UV/IR

There have been a number of studies reported in the literature concerning the use of on-line functional group detectors [*83–101*] for SEC. The following examples show how SEC with multiple detectors can be used in a qualitative manner. Figure 3 shows an SEC/DRI/IR/UV chromatogram for a copolymer of methyl methacrylate (MMA) and vinyl acetate (VA) (25/75). Comparison of the SEC/IR trace with the SEC/DRI trace shows the difference in the ratio of the low retention volume to high retention volume peaks. The DRI detector has a different response to VA functionality than the MMA functionality at low retention volumes (high molecular weight). Although there are no UV active monomers present in the polymer, there is a UV detector response to the benzoyl peroxide initiator fragments attached to polymer chain ends. The difference in curve shape for the SEC/UV trace compared to the SEC/IR and SEC/DRI traces over the common retention volume range is indicative of a high degree of branching in this polymer. This is to be expected since vinyl acetate is known to produce branched polymers when made by emulsion polymerization techniques as was this copolymer of vinyl acetate. From this type of analysis of chain end distributions, valuable information about polymer chain-branching can be obtained.

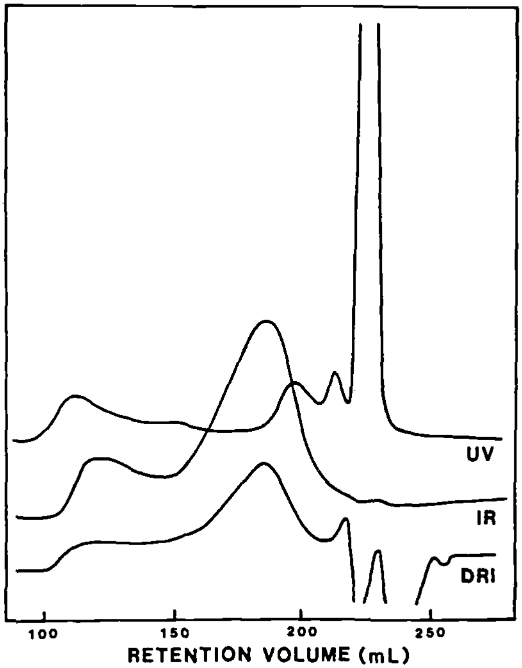


FIG. 3—*SEC/DRI/IR/UV chromatogram of copolymer MMA/VA (25/75) (reprinted with permission from Ref* 91).

Figure 4 shows the SEC/UV/IR trace of a blend of a styrene/acrylic/acid terpolymer resin and a melamine resin. It is seen that there are three distinct peaks in the SEC/UV trace for this blend. The SEC/UV/IR traces shows that the peak at ~185 mL corresponds to the polymer backbone; the middle peak at ~205 mL is associated with the melamine resin; and the third peak at ~220 mL has a strong UV absorbing characteristic and is acidic in nature and may well be caused by reaction by-products between catalyst, solvent, and monomers. The melamine resin is melt blended with the terpolymer resin. This chromatogram indicates that physical mixing occurs. The SEC/IR/UV information shown in this example is quite helpful in establishing proper blending conditions.

Figure 5 shows the SEC/UV and SEC/IR traces of PMMA samples [*102*] which were photopolymerized with different concentrations of photosensitizer (0.05×10^{-2} *M*, 0.08×10^{-2} *M*, 0.25×10^{-2} *M*, and 0.5×10^{-2} *M*). The photosensitizer used was 4,4′ bis-(diethyl amino) benzophenone (DEABP). From the UV traces it is seen that the photosensitizers are chemically bound to the polymer chains. The results also seem to indicate that a greater number of sensitizer fragments reside in the lower molecular weight regions. A considerable amount of free sensitizer can be detected by the UV detector (retention volume ~210 mL) when the initial concentration of the sensitizer is above 0.08×10^{-2} *M*. The other auxiliary peaks beyond the retention volume of 200 mL could be due to some oligomeric components or solvent. The SEC/UV trace at retention volumes less than 200 mL are polymer chains having sensitizer fragments attached to the chain ends. Thus the UV trace provides a distribution of polymer chain ends in these samples. Values of $\overline{M}_n$ and $\overline{M}_w$ can be calculated by means of the hydrodynamic volume approach. These results show that the molecular weight of PMMA decreases with increasing concentration of sensitizer. This is expected from the kinetics of conventional free-radical polymerization. Earlier results of the same

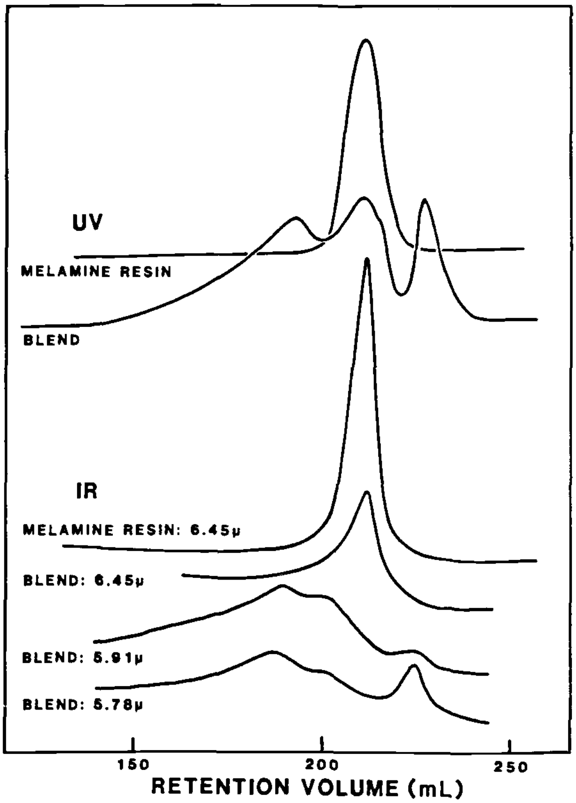


FIG. 4—*SEC/UV/IR chromatogram of a blend of a styrene/acrylic/acid terpolymer resin and a melamine resin (reprinted with permission from Ref* 91).

samples run on an SEC/DRI instrument did not show this systematic trend of molecular weights of PMMA as a function of DEABP concentration. The DRI detector picked up contributions from all the existing components which may not be PMMA, such as those which show up at retention volumes greater than 200 mL. These low molecular weight impurities distorted the chromatograms with respect to molecular weight distribution calculations. Consequently, the calculated molecular weights and molecular weight distributions would be erroneous. This illustrates one of the advantages of using the SEC/IR traces. In addition, there are no negative peaks in the SEC/IR traces as there are in the DRI trace. The absence of these negative peaks allows much better definition of the low molecular weight baseline cut-off point. Also, the IR detector is not as sensitive to room temperature fluctuations as is the DRI and, therefore, the SEC/IR trace baseline will have better long-term stability. The same considerations with regard to better baseline definition and long-term stability apply to the SEC/UV traces.

The main problem with on-line IR detector is the spectral interference caused by the organic solvents used as eluents. This limitation prevented the dispersive IR detector from the widespread use in SEC characterization. With the advent of Fourier transform IR (FTIR), the speed and sensitivity of obtaining spectra have been greatly improved. However, these advantages of FTIR did not alleviate the solvent interference problem when conventional flow-through cell technology is used. Recently, a new type of flow-through cell based on attenuated total reflectance (ATR) has been commercialized. This cylindrical internal

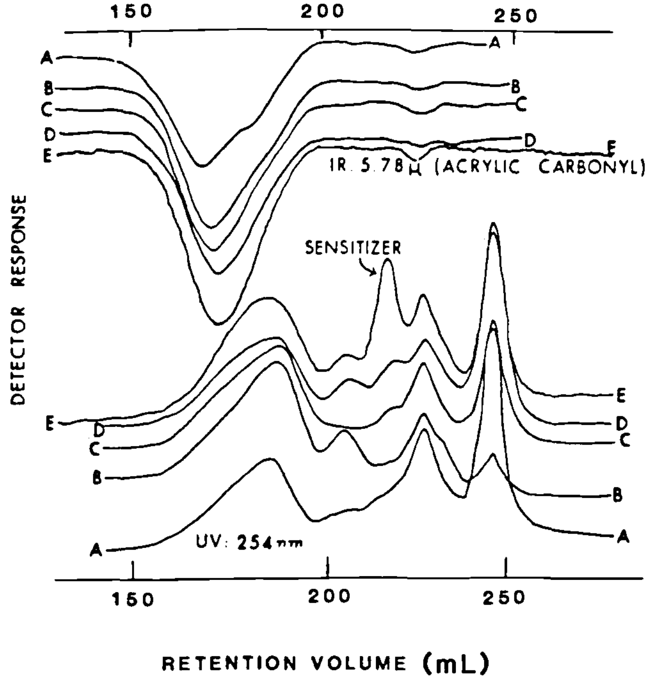


FIG. 5—*SEC/UV/IR chromatograms of photopolymerized PMMA for* [*DEABP*]*: A is* 5 × 10^{-4} M; *B is 8* × 10^{-4} M; *C is 12* × 10^{-4} M; *D is 25* × 10^{-4} M, *E is 50* × 10^{-4} M *(reprinted with permission from Ref* 91*).*

reflectance cell (CIRCLE) has been used mostly for HPLC [95] for on-line analysis. In our laboratory, we tested this accessory for SEC on-line detection. With triglycine sulfate (TGS) as an IR detector, the concentration of effluent coming out of the SEC column was not high enough to obtain good spectra. Mathias [96] reported similar negative results for the use of a CIRCLE cell for aqueous SEC. Mercury cadmium telluride (MCT), which is a much more sensitive IR detector than TGS, might provide sufficiently improved signal-to-noise to make FTIR detection in SEC more viable.

Another way to reduce the solvent interference in a flow-through cell is to use deuterated solvents. However, this may not be practical. More recently, supercritical fluid chromatography (SFC) has been revitalized and developed into commercial instrumentation where pressurized CO_2 is used as the eluent. The combination of SFC and FTIR appears to be more promising than SEC/FTIR.

Photodiode array detection (PAD) is a fairly new development in UV-VIS detection in liquid chromatography. It can simultaneously monitor all wavelengths (190 to 600 nm) in the spectrum in contrast to the conventional single wavelength or slow wavelength scanning UV-VIS detectors. The stored data can be retrieved for postrun data manipulations. In addition to the conventional chromatographic analysis, PAD provides additional data with regard to the spectral information contained in the sample. The features of PAD [*103*] can include: (1) *Spectrum analysis:* This mode monitors spectral regions at various retention times across a peak or within a given analysis. The ability to look at several (up to six) spectral regions across one peak provides an indication of peak purity. The ability to monitor several (up to six) different spectral regions within a chromatogram allows the analyst to compare various components to discern easily any spectral similarities or differences. (2)

Spectrum index plot: Spectral points of peak maxima, slope, and valley can be automatically plotted for spectral comparisons to help confirm peak identity and purity. (3) *Three-dimensional plot:* Four angles can be chosen to display a 3-D plot of the chromatogram. The analyst can review 45° left and right, and 90° left and right, and be confident that all areas of the chromatograms have been displayed. (4) *Contour plot:* This mode provides a topographical look at the chromatogram to provide still another view of the peak. This method of viewing the concentric rings of concentration shows areas of peak asymmetry and indicates peak purity. PAD is useful in monitoring compositional heterogeneity as a function of molecular weight. Figure 6 shows a contour plot of an acrylic copolymer, and Fig. 7 is the corresponding spectrum index plot. Figure 8 shows an example of using PAD to estimate the styrene content of a SAN copolymer [*104*].

Although there are severe limitations in the use of DRI and there are many favorable attributes for functional detectors, DRI is still the most widely used detector in the coatings field due to its simplicity.

Quantitative Compositional-Molecular Weight Distribution Considerations

The previous examples demonstrated that crucial qualitative information can be obtained about the composition of components in multicomponent copolymers and blends. Coatings systems, typically, contain three to six components with some present as minor constituents. To quantitatively determine compositional heterogeneity and/or distribution as a function of molecular weight is a rather formidable task for such complicated systems. In addition, there are some complexities associated with using multiple detectors for determining the compositional heterogeneity of copolymer, as discussed by Mori and Suzuki [97] and Bressau

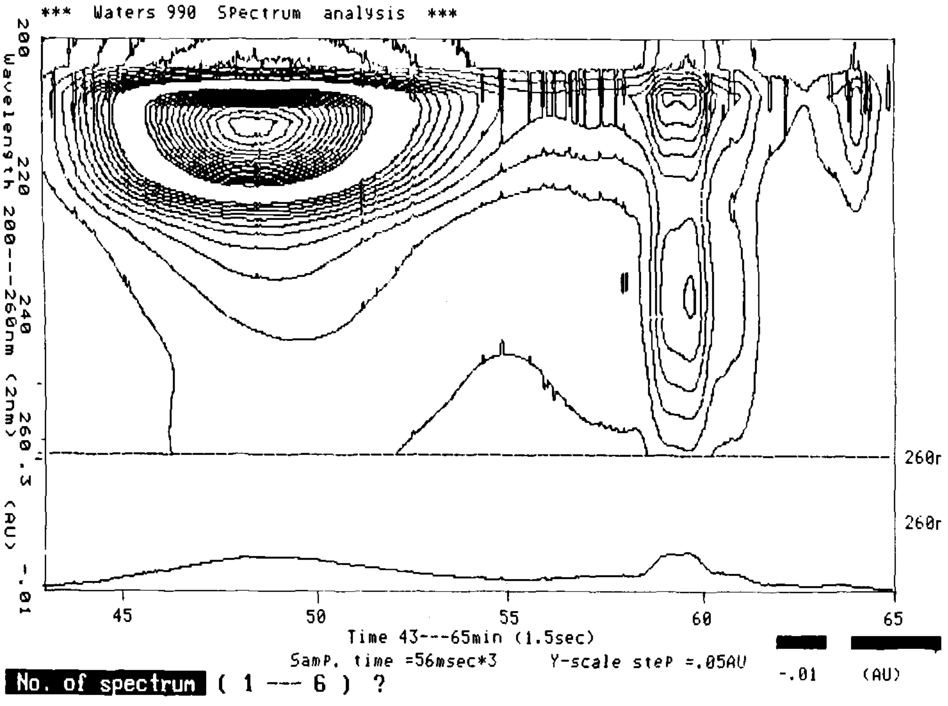


FIG. 6—*Contour plot from the Waters 990 photodiode detector of a GMA acrylic resin.*

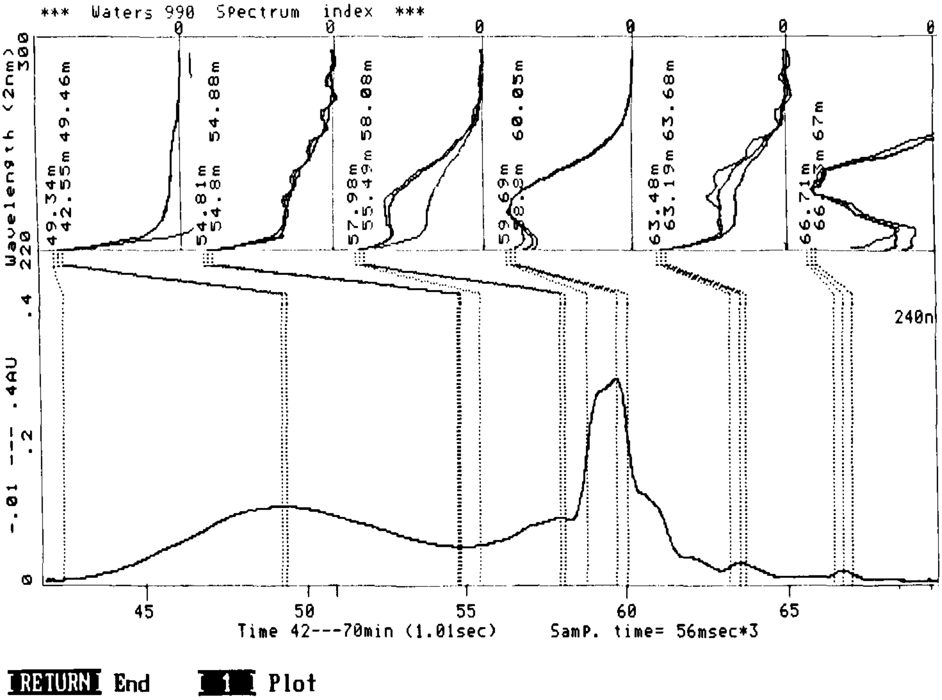


FIG. 7—*Spectrum index plot from the Waters 990 photodiode array detector of a GMA acrylic resin.*

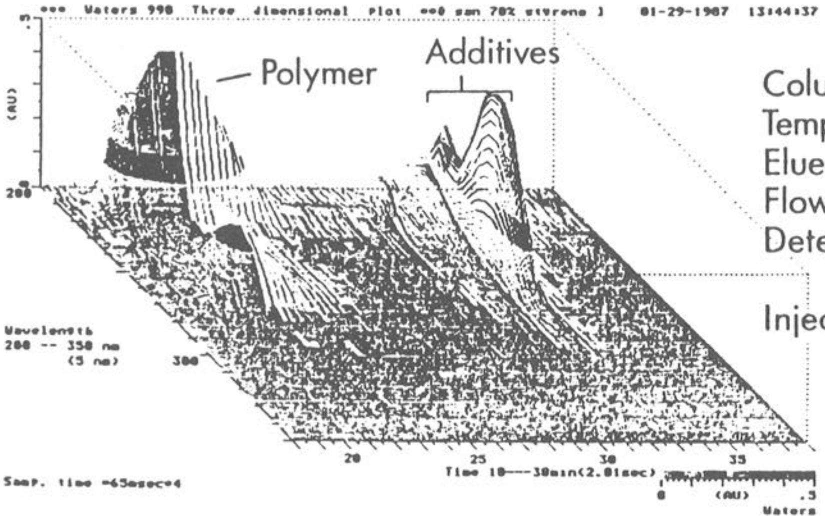
[*101*]. These complexities include accounting for: (a) dead volume corrections, (b) hyperchromic shifts of copolymer detection wavelengths, (c) variance of monomer component absorptivity in the homopolymer to the copolymer, (d) validity of the copolymer molecular weight scale or hydrodynamic volume calibration approach, and (e) mismatch of detector sensitivities in either the low or high molecular weight ranges of the chromatogram. To experimentally determine the individual response factors, generally the homopolymers of the components are monitored by the appropriate detector at several concentrations [*84*,*87*]. The slope of the detector response (area under the appropriate SEC/detector trace) versus concentration (grams), which should be linear, is then the response factor for that component.

When the total polymer response is known as a function of retention volume, the molecular weight distribution can be obtained in the usual manner with the appropriate molecular weight calibration curve. The molecular weight calibration curve can be obtained: (a) by using the Runyon [*87*] copolymer molecular weight scale approach, or (b) by using a hydrodynamic volume approach if the Mark-Houwink constants for the polymer of interest are known or can be determined, or (c) by using a hydrodynamic volume approach in conjunction with an on-line viscosity detector.

SEC/LALLS/MALLS

One of the absolute molecular weight detectors finding increasing usage is the low angle laser light scattering (LALLS) detector [*105–109*]. The unique features of the SEC/LALLS include: (a) simultaneous generation of the absolute molecular weight calibration curve and generation of the absolute molecular weight distribution by using a DRI and in conjunction with a LALLS, (b) being an excellent detector for aqueous SEC because it can generate an

Three dimensional plot of a SAN with 70 percent styrene



Columns: Waters Ultrastyragel™ Linear (2)
Temperature: 45°C
Eluent: THF
Flow rate: 1.0 ml/min.
Detection: Waters 990 Photodiode Array,
Waters 410 Differential Refractometer
Inject volume: 225 μl of a 0.1% w/v solution

FIG. 8—*Three-dimensional plot of an SAN sample (reprinted with permission from Ref* 104).

absolute molecular calibration curve, (c) its use for high temperature measurement, especially for polyolefins, and (d) being sensitive to very high molecular weight polymers, e.g., microgel. LALLS detection can sense a high molecular weight component that sometimes escapes detection with an IR or DRI detector. SEC/LALLS also has been used for the detection of shear degradation of polymers in SEC columns [*110*], simultaneous calibration of molecular weight separation and column dispersion [*111*], measurement of Mark-Houwink parameters [*112*], determination of molecular weight and compositional heterogeneity of block copolymers [*113*], and in obtaining branching information in homopolymers and copolymers [*114–124*]. However, in using SEC/LALLS the analyst needs to be aware of some data analysis considerations: (a) specific refractive index increment, *dn/dc*, varies with molecular weight for low molecular weight polymers and is dependent on the composition of the copolymers; (b) virial coefficients depend on molecular weight; (c) transient noise spikes caused by bleeding of packing materials or elution of dust particles can occur; (d) there can be a sensitivity mismatch between LALLS and DRI (e.g., inadequate sensitivity in low molecular weight regions and detection of microgel in high molecular weight regions); (e) instrumental peak broadening can occur in the scattering cell; and (f) SEC/LALLS provides only qualitative indications of polymer chain branching.

A recent development in light scattering detection is the multiangle laser light scattering detector (MALLS/DAWN®) commercialized by Wyatt Technology [*125*]. MALLS measures the intensity of light scattered at 15 angles simultaneously for the determination of absolute molecular weights and sizes, as well as important information about particle structures and distribution. Figure 9 shows an example of SEC/MALLS illustrating the responses from DRI and MALLS for a three component polystyrene (PS) mixture [*149*]. It is seen that like LALLS, MALLS is more sensitive to higher molecular weight components. Figure 10 shows the variations of scattering intensities with angular position and retention volume. The radius of gyration (r_g) can be obtained from the angular dissymmetry [*125*].

SEC/Viscometer

Another on-line SEC detector which can provide both absolute molecular weight statistics as well as branching information is the viscosity detector. A discrete viscometry technique [*126–135*] involving the coupling of a Ubbelohde-type viscometer to measure the efflux time of each fraction was reported in early 1970. The disadvantage of this type of viscometer is that it is not a truly continuous detector. With the speed and reduced column volumes and lower sample concentrations associated with modern high performance SEC, this type of viscosity detector is not practical. In 1972, Ouano [*136*] developed a unique on-line viscometer which used a pressure transducer to monitor the pressure drop across a capillary continuously. More recently Lesec [*137–139*] and coworkers described a similar and simpler on-line viscosity detector. In the authors' laboratory, a differential transducer has been used to monitor the pressure drop across a section of capillary tubing as the polymer fractions elute from the SEC column. The experimental apparatus and performance evaluation were described previously [*140,141*]. In 1984, the first commercially available continuous viscosity detector for SEC was introduced by Viscotek [*142,143*]. The main component is the Wheatstone bridge configuration consisting of four balanced capillary coils. Most recently Abbott and Yau [*144*] described the design of a differential pressure transducer capillary viscometer, which is comprised of two capillary tubes, one for eluting sample solution and one for eluting solvent. The advantage of this device is that the measured signal is independent of flow rate and temperature fluctuations. A new commercial viscosity detector recently was introduced by Millipore Waters Chromatography. This detector is based on the work reported in the literature by Lesec and coworkers, and by Kuo, Provder, Koehler et al. [*140,141,145*]. The

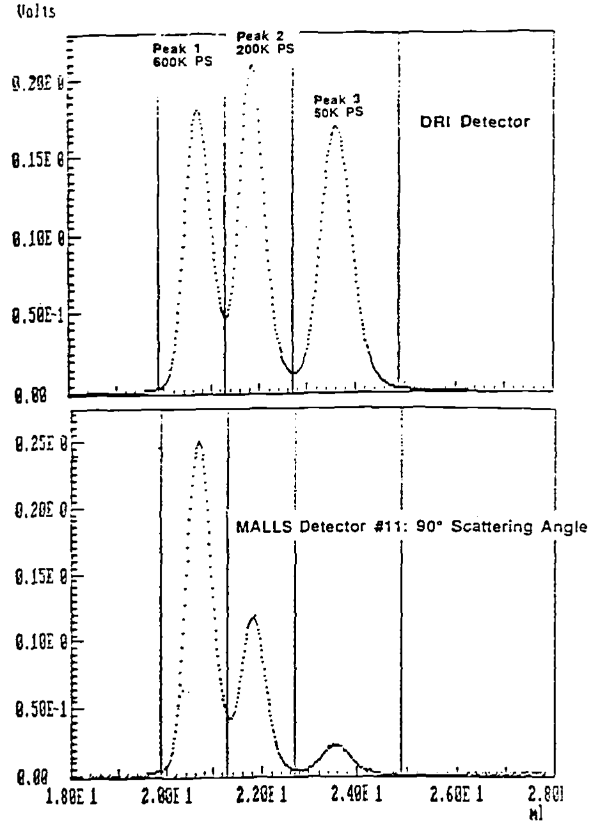


FIG. 9—*SEC/MALLS of a three-components PS mixture (reprinted with permission from Ref* 149).

performance characteristics of the hardware and evaluation of the software were the subjects of two papers presented at a recent GPC symposium [*146,147*].

Like SEC/LALLS, the viscosity detector is sensitive to high molecular weight fractions as shown in Fig. 11 for a three-component PS mixture. It is seen that the viscometer is more responsive to the higher molecular weight component. The usefulness of the SEC/Viscometer method is exemplified by the study of branched polymers. Figure 12 shows the log $[\eta]$ versus log $\overline{M}_w$ plots for two randomly branched polyvinyl acetate samples obtained from the SEC/viscometer technique. The deviation from linearity in the high molecular weight region can be clearly seen. Upon comparing the intrinsic viscosity with that of the linear counterpart at the same molecular weight, the branching index, g', can be obtained as a function of molecular weight. It also was concluded that the sample in Fig. 12*b* is more branched than the sample in Fig. 12*a*. In addition, the SEC/viscometer coupling can provide absolute molecular weight averages, bulk intrinsic viscosity, and Mark-Houwink parameters from a single SEC experiment. A paper dealing with the detailed description and the evaluation of the data treatment for an SEC/viscometer system can be found in a recent monograph [*145*]. Also, SEC/viscometer has been used to estimate the polymer tacticity [*148*] and determination of the radius of gyration (r_g) [*149*] as well as determination of absolute $\overline{M}_n$ [*150*]. Yau [*149*] also reported combining an on-line osmometer with a viscometer for GPC detection to determine absolute $\overline{M}_n$, polymer branching, and conformation. An analyst using

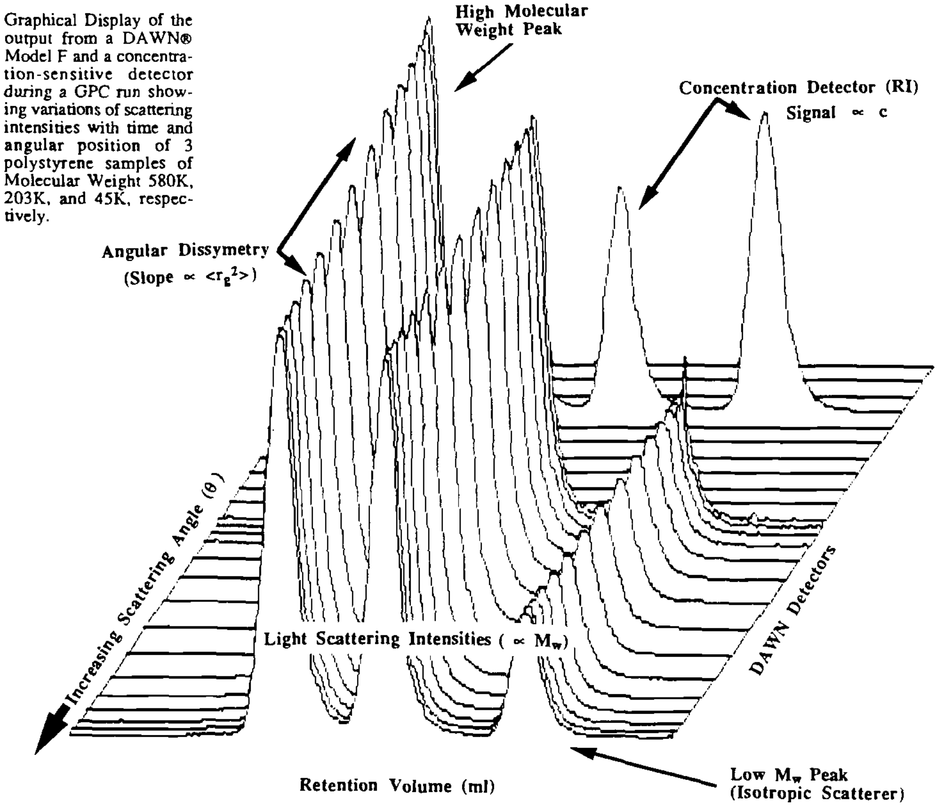


FIG. 10—*Angular dependence of SEC/MALLS intensities (reprinted with permission from Ref* 125).

an SEC/viscometer should be aware of the following operational parameters which can produce errors in the data: (a) flow variations caused by pump pulsations, temperature fluctuations, and restrictions in SEC columns as well as in the connecting tubing; (b) mismatch between the flow rate setting and actual delivered flow rate which can cause concentration errors; (c) finite dead volume between detectors which can produce a data offset between the DRI and viscometer detector; (d) sensitivity mismatch between the viscometer and the DRI detectors in the high and low molecular weight regions.

Oligomer Applications

The emergence of new coatings technologies such as high solids, powder, water-borne, and radiation curable coatings as a response to governmental regulations has led to the development of resin systems where the measurement of the oligomer and low molecular polymer MWD is critically important in order to control the properties of these coatings systems. Recently the HPSEC technique, using high efficiency columns, has been shown to provide the necessary resolution in the low molecular weight region of interest for the above coatings systems. The high efficiency columns result from the use of high pore volumes and narrow particle size distribution of microparticulate packing materials. The efficiency of a column is measured by plate count. For a typical HPSEC column with 10 μm or less particle packing, the plate count is usually in the order of 40 000 plates/m in contrast to about 1 500

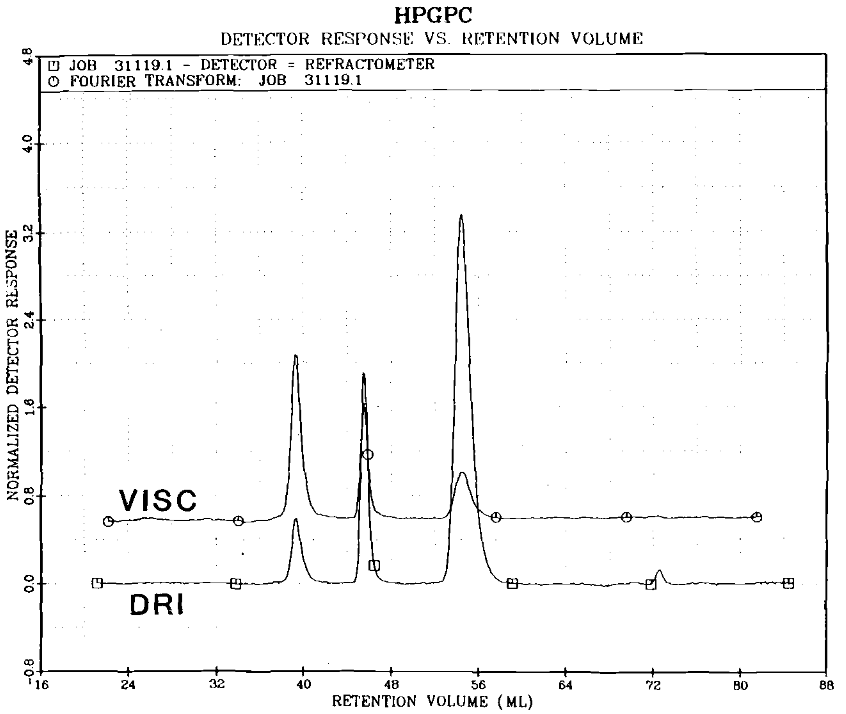


FIG. 11—*DRI/VISC traces of a three-components PS mixture.*

plates/m for conventional columns (37 to 75 μm particles). The ability of a column to separate two adjacent peaks is expressed by the specific resolution R_S as derived by Bly [*151*]. For oligomer and small molecule applications, R_S values are usually obtained from various pairs of *n*-alkanes as reported in the literature [*152–154*] for a variety of HPSEC columns from various vendors. The effect of operational variables (e.g., flow rate, particle size, column length, temperature, mobile phase, etc.) has been studied by various groups [*155–158*]. In general, the column plate height decreases (efficiency increases) with decreasing flow rate until an optimum flow rate is achieved in accordance with the Van Deemter equation [*159*]. Consequently, to obtain high resolution, the flow rate should be kept as low as possible. For practical purpose, using THF as mobile phase, the flow rate is usually set at 1 mL/min. The column efficiency also depends on the particle size of the packings as shown by Vivilecchia and coworkers [*156*]. Kato et al. [*158*] showed the effect of flow rate, particle size, and column length on the column plate count.

With the advent of high efficiency columns, HPSEC has become an indispensable characterization and problem-solving tool for oligomer analysis in environmentally acceptable coatings systems [*153,160,161*]. Specific applications include (a) quality control of supplier raw materials, (b) guiding resin synthesis and processing and (c) correlating oligomer distribution with end-use properties. The following are two of the examples.

Figure 13 shows the HPSEC chromatograms of two polyester resin samples. One sample (A) had good "shelf stability," while the other sample (B) was unstable on standing over a two-week period. It is seen from the chromatograms that the peak, which eluted at retention volume ~30.5 mL, was present in excessive amounts for Sample B as compared to Sample

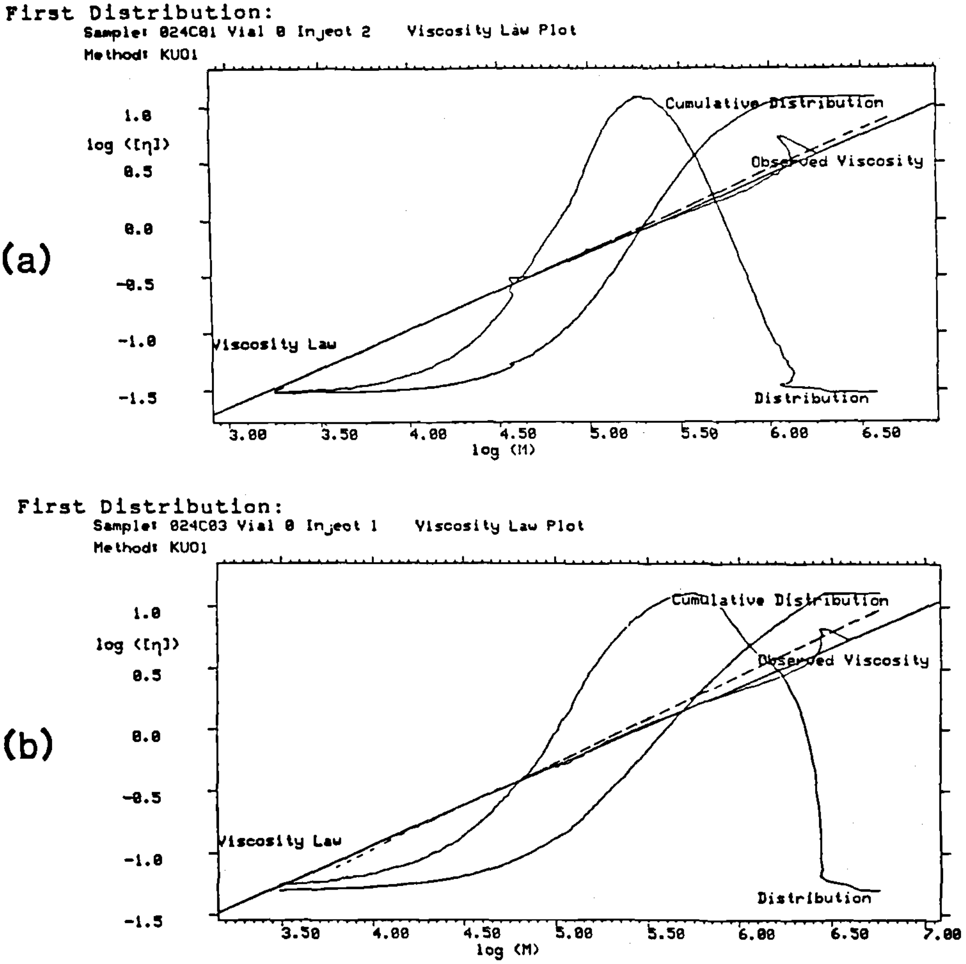


FIG. 12—*MWD and viscosity law for two polyvinyl acetate samples (PVA_c#1 and PVA_c#3) (reprinted with permission from Ref* 147).

A. The component(s) under this peak for Sample B crystallized on standing, causing haze, and then precipitated. Identification of the presence and the amount of the component(s) under this peak will help resin chemists to control and eliminate the instability problem.

In powder coatings, some of the most frequently used curing agents are blocked isocyanate crosslinkers. It is well known that the level of moisture present in the coreactants will affect the MWD and properties of the resulting crosslinker. This is due to the high reactivity of the $N=C=O$ functionality. Figure 14 shows the chromatograms of three isocyanate crosslinkers made with different amounts of added water present in the reactor. The one with 0% water added was a control. The other two samples were made with 0.5 and 2% of water being deliberately added as a coreactant. The weight percent was based on the weight of one of the major coreactants. It is seen from the chromatograms that the molecular weight distribution of the isocyanate crosslinkers made in the presence of added water is different from that of the control sample. In addition to the building up of the molecular weight, the

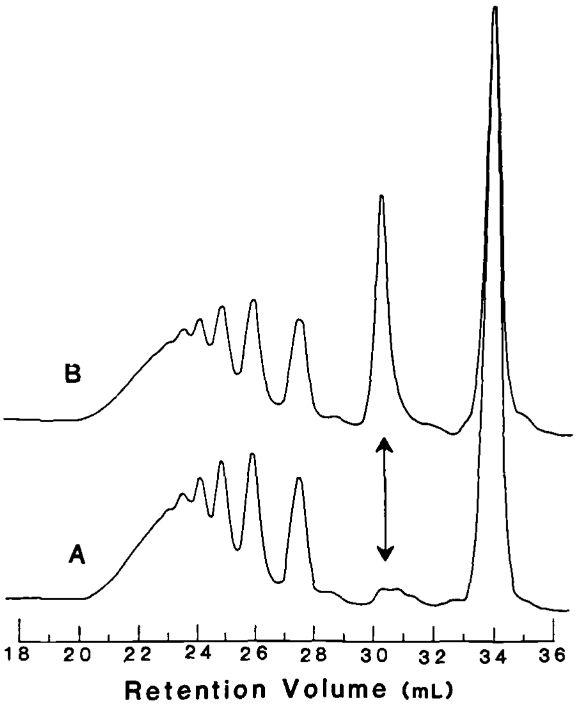


FIG. 13—*SEC chromatograms of two high solids polyesters (reprinted with permission from Ref* 153*)*.

level of the component eluted at retention volume ~27 mL is increasing with the amount of water added. A previous study showed that the presence of this component in excessive amounts was one of the reasons why this type of isocyanate crosslinker is overly reactive.

Future Trends and Needs

In the area of column technology, the development and commercialization of the columns for ultra high molecular weight ranges (MW > 10^6) are needed. There is a need for enhanced SEC/viscometer sensitivity of oligomers and small molecules. For SEC/UV, diode array spectrometry providing a simultaneous multiwavelength scan will be advantageous for providing detailed compositional information for polymers with UV active chromophores. Using a Fourier transform infrared (FTIR) spectrometer for on-line polymer composition determination and identification would expand SEC capability to a significantly greater extent. Current literature available for the application of FTIR to SEC in an on-line mode is quite limited [*162–164*]. In addition to the high cost of the FTIR, the main obstacle is the availability of a suitable flow-through cell to overcome mobile phase spectral interference and low solute concentration. For complex polymers, the technique of orthogonal chromatography [*165–167*] or cross-fractionation chromatography [*168–175*] should be explored. For oligomers, supercritical fluid chromatography (SFC) [*176–180*] has a great potential. Chromatographic methods for gel content determination now are more feasible with LALLS and viscometric detectors and should be reexamined [*181–185*].

Over the next ten years, significant progress on the detection problem in compositional analysis will be made. There is still a need for improved analysis capability in the ultra high

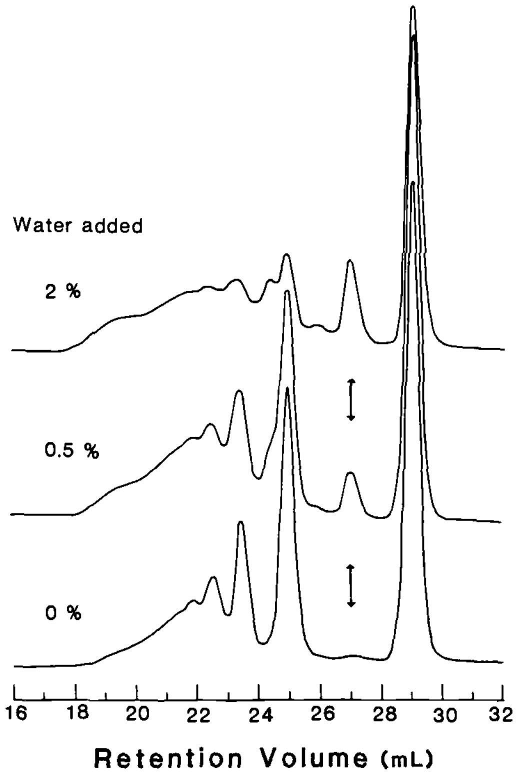


FIG. 14—*SEC chromatograms of three blocked isocyanate crosslinkers (reprinted with permission from Ref* 153*).*

molecular weight range. Improvements in detector sensitivity, column technology, and the application of chemometrics to SEC analysis will facilitate in this area. In addition, recent advancements occurring in thermal field flow fractionation (ThFFF) [*186–197*] show great promise. This technique is being advanced by J. C. Giddings and coworkers of the University of Utah and J. Kirkland and W. W. Yau of E. I. DuPont de Nemours and Co.

This overview covers only nonaqueous SEC. For the theory, practice, and applications of aqueous SEC, the reader is referred to the literature [*198–208*].

Summary

This paper has presented a review of the SEC separation mechanism, molecular weight calibration methods, and instrument spreading correction methods. Examples were shown for the application of multiple detectors to the determination of absolute molecular weight distribution of polymers, compositional distribution as a function of molecular weight of copolymers, and branching information for nonlinear polymers. Examples also were shown where HPSEC can be used for guiding polymer synthesis and processing, correlating oligomer distribution with end-use properties, and monitoring the quality of supplier raw materials. In recent years, HPSEC has become an indispensable characterization and problem-solving tool for the analysis of oligomers and polymers in the plastics, rubbers, and coatings industries. The information generated by means of the HPSEC technique has significantly aided polymer chemists and coatings formulators to tailor-make coatings systems to meet specific end-use properties.

References

[*1*] Moore, J. C., *Journal of Polymer Science*, Part *A-2*, Vol. 2, 1964, p. 285.
[*2*] Hunt, B. J. and Holding, S. R., Eds., *Size Exclusion Chromatography*, Blackie, London, 1989.
[*3*] Provder, T., Ed., "Detection and Data Analysis in Size Exclusion Chromatography," *ACS Symposium Series*, No. 352, American Chemical Society, Washington, DC, 1987.
[*4*] Balke, S. T., *Quantitative Column Liquid Chromatography—A Survey of Chemometric Methods*, Elsevier, NY, 1984.
[*5*] Provder, T., Ed., "Size Exclusion Chromatography—Methodology and Characterization of Polymers and Related Materials," *ACS Symposium Series*, No. 245, American Chemical Society, Washington, DC, 1984.
[*6*] Janca, J., Ed., "Steric Exclusion Liquid Chromatography of Polymers," *Chromatographic Science Series*, Vol. 25, Marcel Dekker, Inc., NY, 1984.
[*7*] Cazes, J., Ed., "Liquid Chromatography of Polymers and Related Materials III," *Chromatographic Science Series*, Vol. 19, Marcel Dekker, Inc., NY, 1981.
[*8*] Cazes, J. and Delamare, V., Eds., "Liquid Chromatography of Polymers and Related Materials II," *Chromatographic Science Series*, Vol. 13, Marcel Dekker, Inc., NY, 1980.
[*9*] Provder, T., Ed., "Size Exclusion Chromatography (GPC)," *ACS Symposium Series*, No. 138, American Chemical Society, Washington, DC, 1980.
[*10*] Yau, W. W., Kirkland, J. J., and Bly, D. D., *Modern Size Exclusion Liquid Chromatography*, Wiley-Interscience, NY, 1979.
[*11*] Cazes, J., Ed., "Liquid Chromatography of Polymers and Related Materials I," *Chromatographic Science Series*, Vol. 8, Marcel Dekker, Inc., NY, 1977.
[*12*] Ezrin, M., Ed., "Polymer Molecular Weights," *Advances In Chemistry Series*, No. 125, American Chemical Society, Washington, DC, 1973.
[*13*] Altgelt, K. H. and Segal, L., Eds., *Gel Permeation Chromatography*, Marcel Dekker, Inc., NY, 1971.
[*14*] Determann, H., *Gel Chromatography*, Springer Verlag, Berlin, 1968.
[*15*] Johnson, J. F. and Porter, R. S., Eds., "Analytical Gel Permeation Chromatography," *Journal of Polymer Science*, Vol. C, Polymer Symposia No. 21, NY, 1967.
[*16*] Casassa, E. F., *Journal of Polymer Science*, Part B, Vol. 5, 1967, p. 773.
[*17*] Casassa, E. F. and Tamami, Y., *Macromolecules*, Vol. 2, 1969, p. 14.
[*18*] Casassa, E. F., *Separation Science*, Vol. 6, 1971, p. 305.
[*19*] Casassa, E. F., *Journal of Physical Chemistry*, Vol. 75, 1971, p. 3929.
[*20*] Casassa, E. F., *Macromolecules*, Vol. 9, 1976, p. 182.
[*21*] Giddings, J. C., Kucera, E., Russell, C. P. and Myers, M. N., *Journal of Physical Chemistry*, Vol. 78, 1968, p. 4397.
[*22*] Yau, W. W., Malone, C. P., and Fleming, S. W., *Journal of Polymer Science*, Part B, Vol. 6, 1968, p. 803.
[*23*] Yau, W. W. and Malone, C. P., *Polymer Preprints, American Chemical Society, Division of Polymer Chemistry*, Vol. 12, No. 2, 1971, p. 797.
[*24*] Majors, R. E., *Journal of Chromatographic Science*, Vol. 18, 1980, p. 488.
[*25*] Kuo, C. and Provder, T. in "Detection and Data Analysis in Size Exclusion Chromatography," T. Provder, Ed., *ACS Symposium Series*, No. 352, 1987, p. 1.
[*26*] Leopold, H. and Trathnigg, B., *Die Angewandte Makromolekulare Chemie*, Vol. 68, 1978, p. 185.
[*27*] Francois, J., Jacob, M., Grubisic-Gallot, Z. and Benoit, H., *Journal of Applied Polymer Science*, Vol. 22, 1978, p. 1159.
[*28*] Trathnigg, B. and Leopold, H., *Die Makromolekulare Chemie, Rapid Communication*, Vol. 1, 1980, p. 569.
[*29*] Trathnigg, B., *Die Makromolekulare Chemie*, Vol. 89, 1980, p. 73.
[*30*] Kratky, O., Leopold, H., and Stabinzer, H., *Zatschrift faer Angewandte Physik*, Vol. 7, 1969, p. 273.
[*31*] Trathnigg, B., *Die Angewandte Makromolekulare Chemie*, Vol. 89, 1980, p. 65.
[*32*] Trathnigg, B. and Jorde, C., *Journal of Chromatography*, Vol. 24, 1982, p. 147.
[*33*] Elsdon, W. L., Goldwasser, J. M. and Rudin, A., *Journal of Polymer Science, Polymer Chemistry Edition*, Vol. 20, 1982, p. 3271.
[*34*] Boyd, D., Narasimlan, V., Huang, R. Y. M. and Burns, C. M., *Journal of Applied Polymer Science*, Vol. 29, 1984, p. 595.
[*35*] Charlesworth, J. M., *Analytical Chemistry*, Vol. 50, 1978, p. 1414.
[*36*] Applications Report, Applied Chromatography Systems, Ltd., 1984.
[*37*] Morris, E. E. M. and Grabovac, I., *Journal of Chromatography*, Vol. 189, 1980, p. 259.

[38] Bartle, K. D. and Zander, M., *Erodel Kohle*, Vol. 36, No. 1, 1983, p. 15.
[39] Bartle, K. D., Taylor, N., Mulligan, M. J., Mills, D. G., and Gibson, C., *Fuel*, Vol. 62, 1983, p. 118.
[40] Huang, S. and Barth, H. G., Proceedings 43rd SPE Technical Conference, *Plastics*, Vol. 85, 1985, p. 1277.
[41] Grinshpun, V. and Rudin, A., *Journal of Applied Polymer Science*, Vol. 32, 1986, p. 4303.
[42] Wyatt, P. J., Jackson, C., and Wyatt, G. K., *American Laboratory*, Vol. 20, No. 5, 1988, p. 86.
[43] Wyatt, P. J., Jackson, C., and Wyatt, G. K., *American Laboratory*, Vol. 20, No. 6, 1988, p. 108.
[44] Jackson, C., Nidsson, L. M., and Wyatt, P. J., *Journal of Applied Polymer Science, Applied Polymer Symposium Edition*, Vol. 43, 1989, p. 99.
[45] Cantow, J. J. R., Porter, R. S. and Johnson, J. F., *Journal of Polymer Science*, Part A-1, Vol. 5, 1967, p. 1391.
[46] Weiss, A. R. and Cohn-Ginsberg, E., *Journal of Polymer Science*, Part A-2, Vol. 8, 1970, p. 148.
[47] Wild, L., Ranganath, R., and Ryle, T., *Journal of Polymer Science*, Part A-2, Vol. 9, 1971, p. 2137.
[48] Swartz, T. D., Bly, D. D., and Edwards, A. S., *Journal of Applied Polymer Science*, Vol. 16, 1972, p. 3353.
[49] Abdel-Alim, A. H. and Hamielec, A. E., *Journal of Applied Polymer Science*, Vol. 18, 1974, p. 297.
[50] Balke, S. T., Hamielec, A. E., LeClair, B. P. and Pearce, S. L., *Industrial and Engineering Chemistry, Product Research and Development*, Vol. 8, 1969, p. 54.
[51] Frank, F. C., Ward, I. M. and Williams, T., *Journal of Polymer Science*, Part A-2, Vol. 6, 1968, p. 1357.
[52] Friis, N. and Hamielec, A. E., *Advances in Chromatography*, J. C. Giddings, E. Grushka, R. A. Keller, and J. Cazes, Eds. Vol. 13, 1975, p. 41.
[53] Yau, W. W., Stoklosa, H. J., and Bly, D. D., *Journal of Applied Polymer Science*, Vol. 21, 1977, p. 1911.
[54] Provder, T., Woodbrey, J. C., and Clark, J. H., *Separation Science*, Vol. 6, 1971, p. 101.
[55] Hamielec, A. E. and Omorodion, S. N. E., *ACS Symposium Series*, No. 138, T. Provder, Ed., American Chemical Society, Washington, DC, 1980, p. 183.
[56] Kubin, M., *Journal of Applied Polymer Science*, Vol. 27, 1982, p. 2933.
[57] Kubin, M., *Journal of Liquid Chromatography*, Vol. 7(S-1), 1984, p. 41.
[58] Benoit, H., Grubisic, Z., and Rempp, P., *Journal of Polymer Science*, Part B, Vol. 5, 1967, p. 753.
[59] Provder, T., Clark, J. H. and Drott, E. E., *Advances in Chemistry Series*, Vol. 125, 1973, p. 117.
[60] Rudin, A. and Wagner, R. A., *Journal of Applied Polymer Science*, Vol. 20, 1976, p. 1483.
[61] Hamielec, A. E. and Ouano, A. C., *Journal of Liquid Chromatography*, Vol. 1, 1978, p. 111.
[62] Pickett, H. E., Cantow, M. J. R. and Johnson, J. F., *Journal of Applied Polymer Science*, Vol. 10, 1966, p. 917.
[63] Yau, W. W. and Malone, C. P., *Journal of Polymer Science, Polymer Letters Edition*, Vol. 5, 1967, p. 663.
[64] Balke, S. T. in *Quantitative Column Liquid Chromatography; a Survey of Chemometric Methods*, Elsevier, NY, 1984, p. 204.
[65] Hess, M. and Kratz, R. F., *Journal of Polymer Science*, Part A-2, Vol. 4, 1966, p. 731.
[66] Pickett, H. E., Cantow, M. J. R. and Johnson, J. F., *Journal of Polymer Science*, Part C, No. 21, 1968, p. 67.
[67] Balke, S. T. and Hamielec, A. E., *Journal of Applied Polymer Science*, Vol. 13, 1969, p. 1381.
[68] Provder, T. and Rosen, E. M., *Separation Science*, Vol. 5, 1970, p. 437.
[69] Yau, W. W., Stoklosa, H. J., and Bly, D. D., *Journal of Applied Polymer Science*, Vol. 21, 1977, p. 1911.
[70] Hamielec, A. E., *Journal of Liquid Chromatography*, Vol. 3, 1980, p. 381.
[71] Hamielec, A. E., Ederer, H. J. and Ebert, K. H., *Journal of Liquid Chromatography*, Vol. 4, 1981, p. 1697.
[72] Halvorson, H. R. and Ackers, G. K., *Journal of Polymer Science*, Part A-2, Vol. 9, 1971, p. 245.
[73] Pierce, P. E. and Armonas, J. E., *Journal of Polymer Science*, Part C, No. 21, 1968, p. 23.
[74] Timm, D. C. and Rachow, J. W., *Journal of Polymer Science, Polymer Chemistry Edition*, Vol. 13, 1975, p. 1401.
[75] Biesenberger, J. A. and Ouano, A., *Journal of Applied Polymer Science*, Vol. 14, 1970, p. 471.
[76] Adesanya, B. A., Yen, H. C., Timm, D. C. and Plass, N. C., *Organic Coatings and Applied Polymer Science Proceedings*, Vol. 48, 1983, p. 870.
[77] Tung, L. H., *Journal of Applied Polymer Science*, Vol. 10, 1966, p. 375.

[*78*] Barrall, E. M., Cantow, M. J. R. and Johnson, J. F., *Journal of Applied Polymer Science*, Vol. 12, 1968, p. 1373.

[*79*] Law, R. D., *Journal of Polymer Science*, Part A-1, Vol. 7, 1969, p. 2097.

[*80*] Daniels, F. and Alberty, R. A., *Physical Chemistry*, John Wiley & Sons, Inc., NY, 1966, p. 674.

[*81*] Bartosiewics, R. L., *Journal of Paint Technology*, Vol. 39, 1967, p. 28.

[*82*] Anderson, D. G. and Isakson, K. E., *Polymer Preprints*, Vol. 11, No. 2, 1970, p. 1190.

[*83*] Rodriguez, F., Kulakowski, R. A. and Clark, O. K., *Industrial and Engineering Chemistry Product Research and Development*, Vol. 5, 1966, p. 121.

[*84*] Terry, S. L. and Rodriguez, F., *Journal of Polymer Science*, Part C, No. 21, 1968, p. 191.

[*85*] Ross, J. H. and Casto, M. E., *Journal of Polymer Science*, Part C, No. 21, 1968, p. 143.

[*86*] Ross, J. H. and Shank, R. L., *Polymer Preprints*, Vol. 12, No. 3, 1971, p. 812.

[*87*] Runyon, J. R., Barnes, D. E., Rudd, J. F. and Tung, L. H., *Journal of Applied Polymer Science*, Vol. 13, 1969, p. 2359.

[*88*] Adams, H. E., *Separation Science*, Vol. 6, No. 2, 1971, p. 259.

[*89*] Chang, F. S., *Journal of Chromatography*, Vol. 55, 1971, p. 67.

[*90*] Mirabella, Jr., F. M., Barrall, II, E. M. and Johnson, J. F., *Journal of Applied Polymer Science*, Vol. 20, 1976, p. 581.

[*91*] Provder, T. and Kuo, C., *Organic Coatings and Plastics Chemistry Preprints*, Vol. 36, No. 2, 1976, p. 7.

[*92*] Stojanov, C., Shirazi, Z. H., and Audu, T. O. K., *Chromatographia*, Vol. 11, 1978, p. 63.

[*93*] Stojanov, Ch., Shirazi, Z. H., and Audu, T. O. K., *Chromatographia*, Vol. 11, 1978, p. 274.

[*94*] Mori, S., *Journal of Chromatography*, Vol. 157, 1978, p. 75.

[*95*] Sabo, M., Gross, J., Wang, J. S., Rosenberg, I. E., *Analytical Chemistry*, Vol. 57, 1985, p. 1822.

[*96*] Mathias, L. J., Scan Time, *Spectra Tech*, No. 3, January/February 1984.

[*97*] Mori, S. and Suzuki, T., *Journal of Liquid Chromatography*, Vol. 4, 1981, p. 1685.

[*98*] Elgert, K. F. and Wohlschiess, R., *Die Agnewandte Makromolekulare Chemie*, Vol. 51, 1977, p. 87.

[*99*] Balke, S. T. and Patel, R. D., in "Size Exclusion Chromatography (GPC)," T. Provder, Ed., *ACS Symposium Series*, No. 138, 1980, pp. 149–82.

[*100*] Garcia-Rubio, L. H., Hamielec, A. E. and MacGregor, J. F., *ACS Symposium Series*, No. 203, C. D. Craver, Ed., 1983, p. 310.

[*101*] Bressau, R., in *Liquid Chromatography of Polymers and Related Materials II*, J. Cazes and X. Delamare, Eds., Marcel Dekker, NY, 1979, p. 73.

[*102*] McGinniss, V. D., Provder, T., Kuo, C. and Gallopo, A., *Macromolecules*, Vol. 11, 1978, p. 393.

[*103*] Del Rios, J., *Journal of Analysis and Purification*, March 1986, p. 22.

[*104*] Polymer Notes: Waters Chromatography Division, Millipore Corporation, Vol. 2, No. 1, 1988.

[*105*] Ouano, A. C. and Kaye, W., *Journal of Polymer Science, Polymer Chemistry Ed.*, Vol. 12, 1974, p. 1151.

[*106*] McConnell, M. L., *American Laboratory*, Vol. 10, No. 5, 1978, p. 63.

[*107*] Jordan, R. C., *Journal of Liquid Chromatography*, Vol. 3, 1980, p. 439.

[*108*] MacRury, T. B. and McConnell, M. L., *Journal of Applied Polymer Science*, Vol. 24, 1979, p. 651.

[*109*] Malihi, F., Kuo, C., and Provder, T., *Journal of Applied Polymer Science*, Vol. 29, 1984, p. 925.

[*110*] Rooney, J. G. and Ver Strate, G. in *Liquid Chromatography of Polymers and Related Materials III*, J. Cazes, Ed., Marcel Dekker, NY, 1981, p. 207.

[*111*] He, Z.-D., Zhang, X.-C., and Cheng, R.-S., *J. of Liquid Chromatography*, Vol. 5, 1982, p. 1209.

[*112*] Grinshpun, V. and Rudin, A., *Die Makromolekulare Chemie Rapid Communication*, Vol. 6, 1985, p. 219.

[*113*] Dumelow, T., Holding, S. R., Maisey, L. J., and Dawkins, J. V., *Polymer*, Vol. 27, 1986, p. 1170.

[*114*] Hamielec, A. E., Ouano, A. C., and Nebenzahl, L. L., *Journal of Liquid Chromatography*, Vol. 1, 1978, p. 527.

[*115*] Jordan, R. C. and McConnell, M. L. in "Size Exclusion Chromatography (GPC)," T. Provder, Ed., *ACS Symposium Series*, Vol. 138, 1980, pp. 107–129.

[*116*] Axelson, D. E. and Knapp, W. C., *Journal of Applied Polymer Science*, Vol. 25, 1980, p. 119.

[*117*] Agarwal, S. H., Jenkins, R. J., and Porter, R. S., *Journal of Applied Polymer Science*, Vol. 27, 1982, p. 113.

[*118*] Jordan, R. C., Siler, S. F., Sehon, R. D. and Rivard, R. J. in "Size Exclusion Chromatography Methodology and Characterization of Polymers and Related Materials," T. Provder, Ed., *ACS Symposium Series*, No. 245, 1984, p. 295.

[*119*] Roovers, J. and Toporowski, P. M., *Macromolecules*, Vol. 14, 1981, p. 1174.

[*120*] Roovers, J., Hadjichristidis, N., and Fetters, L. J., *Macromolecules*, Vol. 16, 1983, p. 214.

[*121*] Rudin, A., Grinshpun, V., and O'Driscoll, K. F., *Journal of Liquid Chromatography*, Vol. 7, 1984, p. 1009.

[*122*] Grinshpun, V., Rudin, A., Russell, K. E., and Scammell, M. V., *Journal of Polymer Science, Polymer Physics Edition*, Vol. 24, 1986, p. 1171.

[*123*] Hamielec, A. E. and Meyers, H., in *Developments in Polymer Characterization—5*, J. V. Dawkins, Ed., Applied Science Publishers, NY, 1986, p. 95.

[*124*] Hjertberg, T., Kulin, L.-I., and Sorrik, E. *Polymer Testing*, Vol. 3, 1983, p. 267.

[*125*] Company Brochure: Wyatt Technology Corporation, Santa Barbara, CA, 1990.

[*126*] Meyerhoff, G., *Die Makromolekulare Chemie*, Vol. 118, 1968, p. 265.

[*127*] Goedhart, D., and Opschoor, A., *Journal of Polymer Science, Part A-2*, Vol. 8, 1970, p. 1227.

[*128*] Meyerhoff, G., *Separation Science*, Vol. 6, 1971, p. 239.

[*129*] Grubisic-Gallot, Z., Picot, M., Gramain, P., and Benoit, H., *Journal of Applied Polymer Science*, Vol. 16, 1972, p. 2931.

[*130*] Gallot, Z., Marais, L., and Benoit, H., *Journal of Chromatography*, Vol. 83, 1973, p. 363.

[*131*] Servotte, A. and DeBruille, R., *Die Makromolekulare Chemie*, Vol. 176, 1975, p. 203.

[*132*] Park, W. S. and Graessley, W. W., *Journal of Polymer Science, Polymer Physics Edition*, Vol. 15, 1977, p. 71.

[*133*] Constantin, D., *European Polymer Journal*, Vol. 13, 1977, p. 907.

[*134*] Janca, J. and Kolinsky, S. J., *Journal of Chromatography*, Vol. 132, 1977, p. 187.

[*135*] Janca, J. and Pokorny, S., *Journal of Chromatography*, Vol. 134, 1977, p. 273.

[*136*] Ouano, A. C., *Journal of Polymer Science*, Vol. A-1, No. 10, 1972, p. 2169.

[*137*] Lesec, J. and Quivoron, C., *Analysis*, Vol. 4, 1976, p. 399.

[*138*] Letot, L., Lesec, J. and Quivoron, C., *Journal of Liquid Chromatography*, Vol. 3, 1980, p. 427.

[*139*] Lecacheux, D., Lesec, J. and Quivoron, C., *Journal of Applied Polymer Science*, Vol. 27, 1982, p. 4867.

[*140*] Malihi, F. B., Koehler, M. E., Kuo, C., and Provder, T., *Proceedings*, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Paper No. 806, 1982.

[*141*] Malihi, F. B., Kuo, C., Koehler, M. E., Provder, T., and Kah, A. F., "Size Exclusion Chromatography Methodology and Characterization of Polymers and Related Materials," T. Provder, Ed., *ACS Symposium Series*, No. 245, 1984, p. 281.

[*142*] Haney, M. A., U. S. Patent 4,463,598, 1984.

[*143*] Haney, M. A., *Journal of Applied Polymer Science*, Vol. 30, 1985, p. 3037.

[*144*] Abbott, S. D. and Yau, W. W., U. S. Patent 4, 578, 990, 1 April 1986.

[*145*] Kuo, C., Provder, T., Koehler, M. E., and Kah, A. F., "Detection and Data Analysis in Size Exclusion Chromatography," T. Provder, Ed., *ACS Symposium Series*, No. 352, 1987, p. 130.

[*146*] Ekmanis, J., *Proceedings*, 1989 International GPC Symposium, 1–4 Oct. 1989, pp. 1–25.

[*147*] Kuo, C., Provder, T., and Koehler, M. E., *Proceedings*, 1989 International GPC Symposium, 1–4 Oct. 1989, pp. 54–79.

[*148*] Yau, W. W., Han, M. C., and Barth, H. G., *Proceedings*, 1989 International GPC Symposium, 1–4 Oct. 1989, pp. 573–583.

[*149*] Yau, W. W., *Proceedings*, 1989 International GPC Symposium, 1–4 Oct. 1989, pp. 80–143.

[*150*] Goldwasser, J. M., *Proceedings*, 1989 International GPC Symposium, 1–4 Oct. 1989, pp. 150–157.

[*151*] Bly, D. D., *Journal of Polymer Science*, Part C., No. 21, 1968, p. 13.

[*152*] Krishen, A. and Tucker, R. G., *Analytical Chemistry*, Vol. 99, 1977, p. 898.

[*153*] Kuo, C., Provder, T., Holsworth, R. M., and Kah, A. F., *Chromatography Science Series*, Vol. 19, 1981, p. 169.

[*154*] Chiantore, O. and Guaita, M., *Journal of Liquid Chromatography*, Vol. 9, 1986, p. 1341.

[*155*] Little, J. N., Waters, J. L., Bombaugh, K. J., and Pauplis, W. J., *Separation Science*, Vol. 5, 1970, p. 765.

[*156*] Vivilecchia, R. V., Cotter, R. L., Limpert, R. J., Thimot, N. Z., and Little, J. N., *Journal of Chromatography*, Vol. 99, 1974, p. 407.

[*157*] Yau, W. W., Kirkland, J. J., Bly, D. D., and Stoklosa, H. J., *Journal of Chromatography*, Vol. 125, 1976, p. 219.

[*158*] Kato, Y., Kido, S., Yamamoto, M. and Hasimoto, T., *Journal of Polymer Science, Polymer Physics Edition*, Vol. 12, 1974, p. 1339.

[*159*] Van Deemter, J. J., Zuiderweg, F. J., and Klinkenberg, A., *Chemical Engineering Science*, Vol. 5, 1956, p. 271.

[*160*] Kuo, C. and Provder, T., in "Size Exclusion Chromatography (GPC)," T. Provder, Ed., *ACS Symposium Series*, Vol. 138, 1980, pp. 207–224.

[*161*] Kuo, C., Provder, T., and Kah, A. F., *Paint and Resin*, Vol. 53, No. 2, 1983, p. 26.

[*162*] Vidrine, D. W., *Journal of Chromatography Science*, Vol. 17, 1979, p. 477.
[*163*] Brown, R. S., Hausler, D. W., Taylor, L. T. and Carter, R. C., *Analytical Chemistry*, Vol. 53, 1981, p. 197.
[*164*] Folster, U. and Herres, W., Farbe and Lack, Vol. 89, 1983, p. 417.
[*165*] Balke, S. T., Separation and Purification Methods, Vol. 11, 1982, p. 1.
[*166*] Balke, S. T. and Patel, R. D., *Advanced Chemistry Series*, Vol. 203, 1983, p. 281.
[*167*] Balke, S. T., "Detection and Data Analysis in Size Exclusion Chromatography," T. Provder, Ed., *ACS Symposium Series*, No. 352, 1987, p. 59.
[*168*] Inagaki, H., Tanaka, T., *Pure and Applied Chemistry*, Vol. 54, 1982, p. 309.
[*169*] Teramachi, S., Hasagawa, A., Yoshida, S., *Macromolecules*, Vol. 16, 1983, p. 542.
[*170*] Glöckner, G. and Koningsveld, R., *Die Makromolekulare Chemie, Rapid Communication*, Vol. 4, 1983, p. 529.
[*171*] Glöckner, G., van den Berg, J. H. M., Meijerink, N. L. J., Scholte, T. G., and Koningsveld, R., *Journal of Chromatography*, Vol. 317, 1984, p. 615.
[*172*] Glöckner, G., Stickler, M., and Wunderlich, W., *Journal of Applied Polymer Science*, Vol. 37, 1989, p. 3147.
[*173*] Glöckner, G., Stejskal, J., and Kratochvil, P., *Die Makromolekulare Chemie*, Vol. 190, 1989, p. 427.
[*174*] Glöckner, G. in *Comprehensive Polymer Science*, Vol. 1, C. Booth and C. Price, Eds., Pergamon Press, Oxford, 1989.
[*175*] Mori, S., *Analytical Chemistry*, Vol. 60, 1988, p. 1125.
[*176*] Jentoft, R. E. and Fouw, T. H., *Journal of Polymer Science*, Polymer Letters, Vol. 7, 1969, p. 811.
[*177*] Schmitz, F. P. and Klesper, E., *Polymer Bulletin*, Vol. 5, 1981, p. 603.
[*178*] Fjeldsted, J. C., Jackson, W. P., Peaden, P. A. and Lee, M. L., *Journal of Chromatography Science*, Vol. 21, 1983, p. 222.
[*179*] Hirata, Y. and Nakata, F., *Journal of Chromatography*, Vol. 295, 1984, p. 315.
[*180*] White, C. M. and Houck, R. K., *High Resolution Chromatography and Chromatography Communications*, Vol. 9, 1986, p. 4.
[*181*] Gaylor, V. F., James, H. L. and Herdering, J. P., *Journal of Polymer Science*, Vol. 13, 1975, p. 1575.
[*182*] Williamson, T. J., Gaylor, V. F., and Piirma, I., ACS Symposium Series, Vol. 138, 1980, p. 77.
[*183*] Hellman, M. Y., Bowmer, T., and Taylor, G. N., *ACS Organic Coatings and Plastics Chemistry Preprints*, Vol. 45, 1981, p. 126.
[*184*] Malihi, F. B., Kuo, C. and Provder, T., *Journal of Liquid Chromatography*, Vol. 6, 1983, p. 667.
[*185*] Brower, L., Trowbridge, D., Kim, D., Mukherjee, P., Seeger, R., and McIntyre, D., *ACS Symposium Series*, No. 352, 1987, p. 155.
[*186*] Thompson, G. H., Myers, M. N., and Giddings, J. C., *Analytical Chemistry*, Vol. 41, 1969, p. 1219.
[*187*] Hovingh, M. E., Thompson, G. H., and Giddings, J. C., *Analytical Chemistry*, Vol. 42, 1970, p. 195.
[*188*] Myers, M. N., Caldwell, K. D., and Giddings, J. C., *Separation Science*, Vol. 9, 1974, p. 47.
[*189*] Giddings, J. C., Martin, M., and Myers, M. N., *Journal of Chromatography*, Vol. 158, 1978, p. 419.
[*190*] Giddings, J. C., Myers, M. N., and Janca, J., *Journal of Chromatography*, Vol. 186, 1979, p. 37.
[*191*] Martin, M., and Reynaud, R., *Analytical Chemistry*, Vol. 52, 1980, p. 2293.
[*192*] Janca, J., and Kleparnik, K., *Separation Science Technology*, Vol. 16, 1981, p. 657.
[*193*] Kirkland, J. J. and Yau, W. W., *Macromolecules*, Vol. 18, 1985, p. 2305.
[*194*] Kirkland, J. J. and Yau, W. W., *Journal of Chromatography*, Vol. 353, 1986, p. 95.
[*195*] Kirkland, J. J., Rementer, S. W., and Yau, W. W., *Analytical Chemistry*, Vol. 60, 1988, p. 610.
[*196*] Kirkland, J. J., Rementer, S. W., and Yau, W. W., *Journal of Applied Polymer Science*, Vol. 38, 1989, p. 1383.
[*197*] Giddings, J. C., *Chemical and Engineering News*, Vol. 34, 10 Oct. 1988.
[*198*] Barth, H. and Regnier, F., *Journal of Chromatography*, Vol. 192, 1980, p. 275.
[*199*] Barth, H., *Analytical Biochemistry*, Vol. 124, 1982, p. 191.
[*200*] Kim, C. J., Hamielec, A. E. and Benedek, A., *Journal of Liquid Chromatography*, Vol. 5, 1982, p. 425.
[*201*] Cooper, A. R. and Van DerVeer, D. S., *Journal of Liquid Chromatography*, Vol. 1, 1978, p. 693.

[*202*] Rollings, J. E., Bose, A., Caruthers, J. M., Tsao, G. T. and Okos, M. R. in "Polymer Characterization Spectroscopic, Chromatographic, and Physical Instrumental Methods," C. D. Craver, Ed., *Advances in Chemistry Series*, No. 203, 1983, p. 345.
[*203*] Levy, I. J. and Dubin, P. L., *Industrial and Engineering Chemistry, Product Research and Development*, Vol. 21, 1982, p. 59.
[*204*] Dubin, P. L., *American Laboratory*, January 1983, p. 60.
[*205*] Muller, G. and Yonnet, C., *Die Makromolekulare Chemie, Rapid Communication*, Vol. 5, 1984, p. 197.
[*206*] Omorodin, S. N. E., Hamielec, A. E. and Brash, J. L., *ACS Symposium Series,* No. 138, 1980, p. 267.
[*207*] Hashimoto, T., Sasaki, H., Aiura, M. and Kato, Y., *Journal of Polymer Science*, Polymer Physics Ed., Vol. 16, 1978, p. 1789.
[*208*] Barth, H., *ACS Symposium Series*, No. 352, 1987, p. 29.

A. Monroe Snider, Jr.[1]

X-Ray Techniques for Coatings Analysis

REFERENCE: Snider, A. M. Jr., "**X-Ray Techniques for Coatings Analysis,**" *Analysis of Paints and Related Materials: Current Techniques for Solving Coatings Problems, ASTM STP 1119*, American Society for Testing and Materials, Philadelphia, 1992, pp. 82–104.

ABSTRACT: X-ray diffraction (XRD) and X-ray fluorescence spectrometry (XRFS) are powerful, well-established tools used by analytical chemists in many areas of technology. However, their potential in the coatings industry has not been fully exploited. XRD is convenient for the identification of diverse crystalline solids encountered in paint research laboratories and production plants. It is particularly well suited for use in the identification and quantitative analysis of crystalline pigments and extenders, either alone or when present in pastes or paint. XRFS is useful as a stand-alone technique for elemental analysis and as a complementary tool for use with other analytical techniques. X-ray spectrometers typically can analyze all elements with an atomic number of about 11 and higher, but some units can reach as low as atomic number 5. XRFS spans the concentration range from parts per million to high percentages for most elements in liquid or solid samples. Dedicated XRFS units, much lower in cost than scanning spectrometers, can be set up to detect and quantify one or a few specific elements. Portable XRFS units are available for field investigations. A survey of the principles, applications, and limitations of XRD and XRFS is given.

KEY WORDS: X-ray diffraction, X-ray fluorescence spectrometry, paint, coatings, pigment, elemental analysis

X-ray techniques are among the oldest instrumental techniques in common use today. The beginning of X-ray analysis can be traced back to the discovery by von Laue in 1912 that X-rays possess characteristics of waves [*1*]. Moseley recognized the relationship between the wavelength of X-ray emissions and the identity of the element emitting the X-rays and the correlation between the amount of an element in a mixture and the intensity of the spectral lines of the element [*2,3*]. His 1913 publication of the first X-ray spectra laid the foundation of modern X-ray spectrometry. In 1913 W. L. Bragg provided a simple mathematical explanation for the position of spots produced on photographic film by X-rays diffracted from crystalline material [*4*]. The equation, now known as the Bragg equation, is the foundation of X-ray diffraction and plays a vital role in X-ray spectrometry. It was realized that each crystalline substance has a unique repeating three-dimensional array of atoms and produces a unique X-ray diffraction pattern [*5*]. Thus, diffraction patterns can be used as "fingerprints" for identification of crystalline phases. Since the early beginnings, instrumentation available for X-ray diffraction and X-ray spectrometry has continually improved in both analytical capability and operating convenience. X-ray analysis has progressed from being a laborious tool used by physicists engaged in basic research to a quick and convenient technique used in many disciplines. The progress of the development is documented in numerous treatises [*6–9*] and reviews [*10–14*]. However, despite the long history and widespread acceptance of X-ray techniques, their use in the coating industry has been limited. Even today, many paint manufacturers do not use X-ray techniques for analysis.

---

[1] Senior research associate, PPG Industries, Inc., Pittsburgh, PA 15238.

Nevertheless, X-ray techniques have great potential as a tool for analyzing organic coatings, coatings components, and impurities and for investigating coatings problems. The use of X-ray diffraction for qualitative and quantitative analysis of pigments in paint has been championed by Scott and other workers [*14–17*]. The relatively small number of pigments and extenders commonly used in paint aids their identification by X-ray diffraction. An analyst equipped with a library of reference diffraction patterns for about 25 to 30 common pigments and extenders can, by comparison of the patterns of test samples with the reference patterns, identify all pigments and extenders in about 90% of all paints commonly encountered [*16*]. The remainder may be identified by systematic comparison of the patterns of test samples with patterns listed in published compilations of X-ray diffraction data, such as the Powder Diffraction File (PDF) of the Joint Committee on Powder Diffraction Standards (JCPDS) [*18*]. The JCPDS PDF is available in several forms that include, in part, bound volumes, microfiche, and LASER-read compact disk. The compact disk read only memory (CD-ROM) system has been described by Jenkins [*19*]. Computerized X-ray diffraction units and personal computer-based search systems now available permit rapid identification of crystalline phases. Klug and Alexander discussed and illustrated with examples the use of the JCPDS PDF for identification of crystalline material [*20*]. They also discussed complications and limitations of the PDF method. Methods suitable for quantitative analysis of pigments and extenders in the paint have been detailed by Chung and other workers [*21–25*].

X-ray fluorescence spectrometry, sometimes more strictly called secondary-emission spectrometry, is extremely useful in the analysis of coatings and coatings components. All X-ray fluorescence spectrometers share the common principle that X-rays are directed onto the specimen to excite secondary emission of X-rays, i.e., X-ray fluorescence, which consists of wavelengths characteristic of the element or elements that comprise the specimen. The emitted X-rays are sorted into components of different wavelength by diffraction from a crystal or identified as photons of different energies by an electronic sorting system after reaching the detector. The use of X-ray spectrometry for qualitative and quantitative analysis has been discussed in detail by Bertin [*6,7*].

X-Ray Diffraction in Coatings

Physical Basis

X-ray diffraction experiments are performed by irradiating a specimen of crystalline or polycrystalline material with a beam of X-rays of known wavelength and determining the angle 2θ between the incident beam and each of the diffracted beams of X-rays and measuring the intensity of each of the diffracted beams. Diffraction occurs only at discrete angles defined by the Bragg equation

$$n\lambda = 2d \sin \theta$$

where

n = a positive integer (usually one, representing the difference in path, expressed in wavelengths of X-rays, traveled by X-rays "reflected" from adjacent layers of atoms),
λ = the wavelength of the X-rays used,
d = the perpendicular distance between parallel layers of atoms of a set of lattice planes, and
θ = the angle between the incident X-ray beam and the lattice plane [*20*].

The wavelength of the X-rays is determined by the choice of target material in the X-ray tube, usually copper. A crystal monochrometer or absorption filter is used to prevent unwanted wavelengths of X-rays, such as K_α X-rays, from contributing to the diffraction pattern. Bragg angle θ is half of the diffraction angle, 2θ, which is determined experimentally. The distance between parallel planes of atoms may be calculated using the Bragg equation. The distance, *d*, is determined by the diameter of atoms comprising the crystal, the three-dimensional arrangement of the atoms in the crystal, and the set of lattice planes in the crystal that produced the "reflection" of X-rays. Each crystal structure produces a unique set of d-spacings. Detailed discussions of the Bragg equation and the physical basis of X-ray diffraction are available in treatises by Klug and Alexander [*20*].

In X-ray diffraction analysis, the specimen is placed in the primary beam of a diffractometer; both the diffraction angle and the intensity of each diffraction peak are measured. Diffractometers use either an electronic detector or photographic film to indicate the position of the diffracted beams of X-rays. Most diffraction units in industrial laboratories today use an electronic detector, usually a proportional counter. In this case, the specimen is placed in a holder located at the center of the diffraction system. The detector slowly sweeps around an arc at a fixed distance from the specimen. While the detector moves through an angle two-theta, the specimen rotates about the same axis through an angle theta. The intensity of diffracted X-rays is plotted as a function of angle two-theta by a recorder or the equivalent information is stored in computer files for later processing. Figure 1 shows the diffraction patterns of three pigments.

A relatively new variation of the electronic detector is the position-sensitive detector (PSD) that uses an arc-shaped solid state detector to sense both the position and intensity of the diffracted radiation. The PSD is stationary during data collection, but may intermittently move to different locations on the goniometer circle, as required, so that its surface can sample the intensity of X-rays at all two-theta positions of interest.

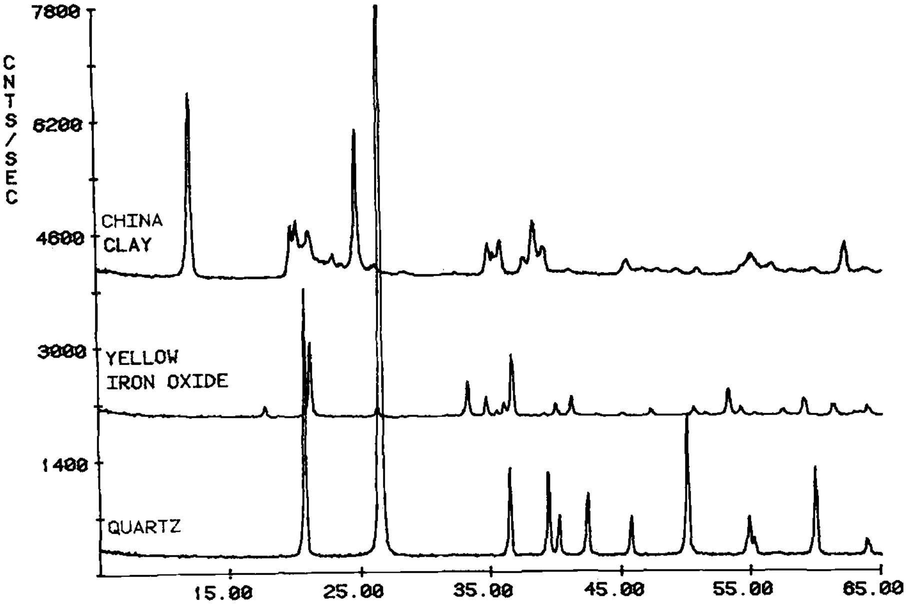


FIG. 1—*Diffraction patterns of three pigments.*

Diffraction patterns can also be recorded photographically, with the Debye-Sherrer camera being the camera most commonly used in industrial laboratories. The Debye-Sherrer camera utilizes a strip of photographic film mounted on the inner surface of a cylindrical holder to record X-rays diffracted from the specimen mounted at the center. The film records X-rays diffracted over a two-theta range of nearly 360°. The d-spacing of arcs caused by exposure of the film to diffracted X-rays can be calculated from the position of the arcs on the film. Relative intensities of the diffracted X-ray beams can be evaluated by measuring the degree of darkening of the corresponding arcs on the film by an optical density measurement or by visual comparison to standards.

Diffractometers that use electronic X-ray detectors offer the advantages of automation, convenience, and speed. The advantage of the Debye-Sherrer camera is the ability to collect a diffraction pattern of very small samples.

Experimental Procedure

Common samples encountered in the coatings industry and their mode of mounting in a scanning diffractometer are as follows:

Sample	Method of Mounting
Powder	Apply flat in holder or sprinkle on film of petroleum jelly or amorphous glue on holder.
Liquid paint or grind paste	Prepare drawdown film on amorphous plastic. Cut specimen to fit holder.
Paint chip	Cut specimen to fit holder or scrape off portion of interest, pulverize, and run as powder.
Paint on panel	Cut specimen to fit holder or cut to same dimension as holder and run without holder.

It may not be possible to collect diffraction patterns of usable intensity from drawdowns of paint that have low pigment content. In these cases, pigment analysis by X-ray diffraction can be accomplished by first removing the pigment from the paint by centrifugation. The pigment plug is then dried, ground, and run as a powder. Quantitative results obtained from the plug, however, may not be reliable because of differences in the sedimentation rate of different pigments during centrifugation.

Conventional scanning techniques can be applied with ease to 2.5 g of powder sample or, when necessary, to as little as about 0.1 g.

The Debye-Sherrer camera is useful when the sample is too small for a conventional scanning diffraction unit. Small amounts of powder, as little as 1 mg, can be loaded into a thin-walled glass capillary or mixed with noncrystalline glue and rolled to form a filament after hardening. The capillary or filament is mounted in the center of the camera where it rotates to present a more nearly random orientation of crystallites to the incident X-ray beam. A single small chip or crystal may be analyzed by gluing it to the end of a glass capillary and exposing it to X-rays in the Debye-Sherrer camera.

Qualitative Analysis

Characteristic Patterns—Identification of pigments, extenders, and other crystalline phases by X-ray diffraction is accomplished by matching the peaks of the diffraction pattern of a sample under analysis with the sets of diffraction peaks exhibited by reference samples of known composition. X-ray diffraction provides no chemical information about a test sample other than the identification of each crystalline phase present. Persons experienced in the analysis of paints usually employ a procedure for qualitative analysis consisting of the following two parts. First, the diffraction pattern is inspected for the presence of sets of peaks that are characteristic of commonly used pigments and extenders, or other phases suspected of being present. Sets of peaks found in the pattern that are suspected of resulting from common components are compared to the peaks on reference diffraction patterns. The comparison may be done directly by comparing diffraction patterns or indirectly by comparing the d-spacings and relative intensities calculated from reference patterns. Identification of some or all components may sometimes be achieved by this procedure. This approach is most useful when the analyst, on the basis of information available from other sources such as elemental analysis, the appearance, knowledge of the intended use of the paint, or past experience, suspects the presence of certain crystalline components. Second, peaks that were not identified by the first approach are subjected to a systematic search using compilations of X-ray diffraction data, such as the JCPDS Powder Diffraction File.

Figures 1 and 2 show the X-ray diffraction patterns of six common paint pigments. For brevity, the term pigment will be used to mean both pigments and extenders. The pigments are readily distinguished from each other and from all other crystalline material on the basis of the two-theta positions of the peaks and by the relative intensities of the peaks. The patterns were collected under identical conditions from powder specimens. The difference in intensity of the patterns of the different pigments is of importance in quantitative analysis, discussed in the section entitled "Quantitative Analysis," and has a bearing on the ease of detection of pigments at low concentrations in qualitative analysis.

Figure 3 shows diffraction patterns of dried paint films of two test paints of known composition. Each crystalline component in the paint film contributes its own set of peaks to pattern, with the position and relative intensity unaltered by the other components. Noncrystalline resin components produce only a broad, weak hump in the baseline. Some

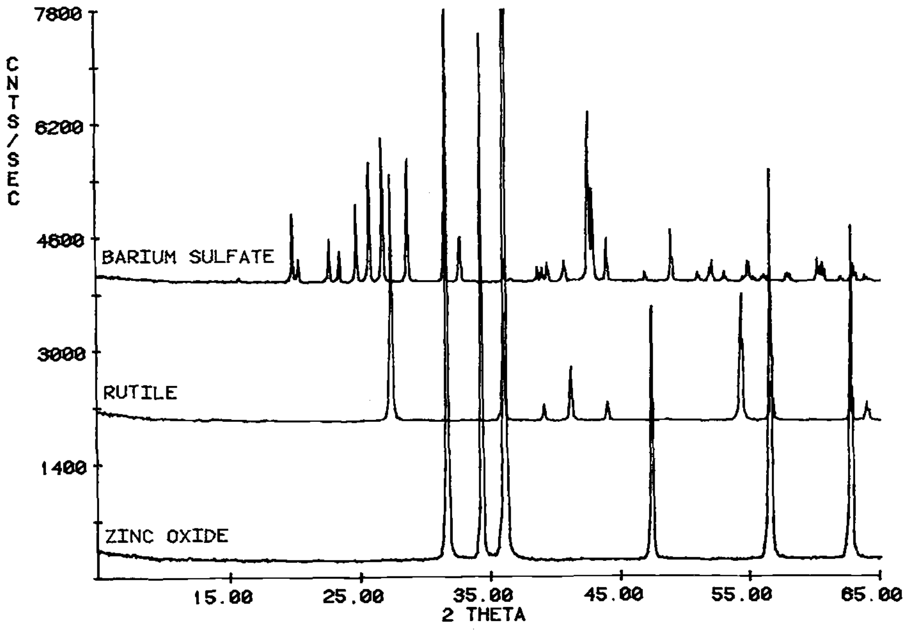


FIG. 2—*Diffraction patterns of three pigments:* (a) *tan solvent-borne alkyd paint;* (b) *white acrylic latex.*

of the crystalline components of the two paints represented by Fig. 3 can be identified by comparison with the patterns of individual pigments in Figs. 1 and 2.

Table 1 lists 36 pigments and extenders commonly used in paint, along with the d-spacings and relative intensities of their five most intense diffraction peaks. This table, compiled from the JCPDS Powder Diffraction File, should aid one in identifying common components. The pigments are listed in order of the d-spacing of the strongest peak. The d-spacing of the strongest peak is listed in the first column, and the next four strongest peaks of each phase are listed in decreasing order of their d-spacings. The subscripts state the relative intensity of each peak rounded off to the nearest integer, with the intensity of the strongest peak taken as 10 and represented by "X," as done by JCPDS.

To use Table 1 in a systematic manner in interpreting a diffraction pattern, the analyst determines the d-spacing of the peaks at the high d-spacing end of the pattern of the sample under analysis and then searches the first column of Table 1 for apparent matches. When an apparent match is found for a peak, the pattern of the test sample is inspected for the presence of the remainder of the peaks listed in the same row of Table 1. The absence from the pattern of any one of the listed peaks is sufficient reason for rejection of the suspected component. Possible exceptions to this rule for rejection are pigments with platelet or needle-shaped particles which may have one or more peaks "missing" because of nonrandom orientation of the particles. The JCPDS file number for the phase is listed in the last column. The file number may then be used to locate the full set of diffraction data provided by JCPDS compilations. Using the JCPDS data, all peaks attributed to the identified component may be marked on the pattern of the test sample. The identification process is then repeated with unassigned peaks in the pattern, working progressively from the peaks with the highest d-spacing, particularly the strongest ones, to the peaks with low d-spacing.

In an alternate use of Table 1, the analyst searches the list for crystalline phases suspected to be present in the test sample. If the strongest peaks listed in Table 1 for the suspected

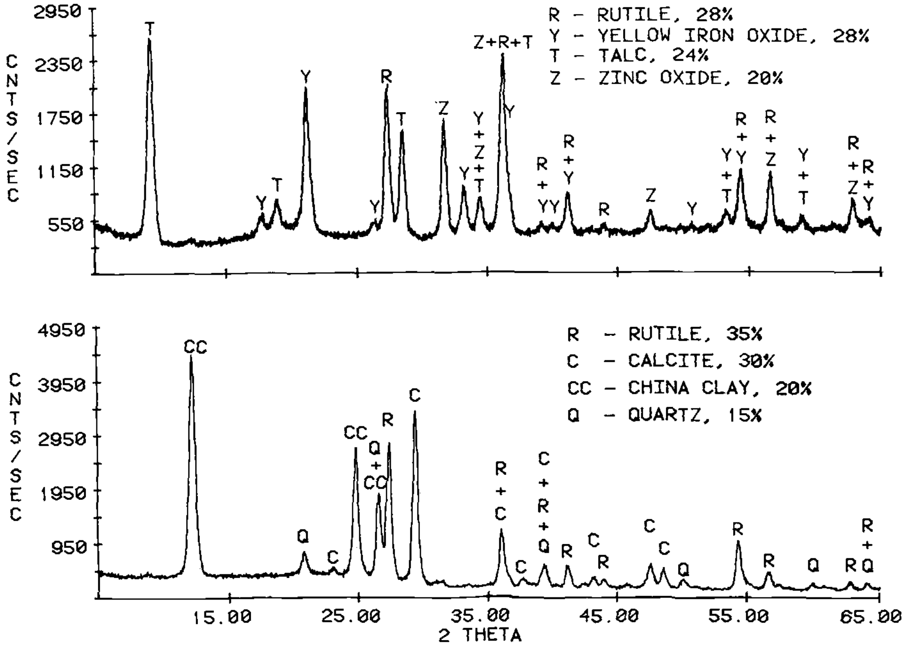


FIG. 3—*Diffraction pattern of two test paints.*

TABLE 1—*Common pigments and extenders for paint.*

d-Value and Intensity[a]					Name	Formula	JCPDS File No.
17.6_x	9.0_5	4.49_8	3.58_4	1.504_6	Bentonite[b]	$Na_{0.3}(AlMg)_2Si_4O_{10}(OH)_2 \cdot H_2O$	12-219
10.1_x	4.49_9	3.66_6	3.36_x	2.565_9	Mica[b]	$KAl_2Si_3AlO_{10}(OH)_2$	7-25
9.34_x	4.66_9	3.116_x	2.476_7	1.870_4	Talc[b]	$Mg_3Si_4O_{10}(OH)_2$	13-558
7.63_x	4.283_x	3.065_8	2.873_5	2.685_4	Gypsum	$CaSO_4 \cdot 2H_2O$	33-311
7.36_x	4.56_5	3.66_8	2.451_7	1.531_7	Chrysotile-20rcl	$Mg_3Si_2O_5(OH)_4$	25-645
7.31_x	4.57_5	3.65_7	2.27_3	1.535_5	Chrysotile-2Mcl	$Mg_3Si_2O_5(OH)_4$	31-808
7.17_x	4.366_6	4.186_5	3.579_8	2.495_5	Kaolinite[b]	$Al_2Si_2O_5(OH)_4$	14-164
4.568_x	9.12_6	4.410_2	3.460_3	2.853_7	Zinc phosphate[b]	$Zn_3(PO_4)_2 \cdot H_2O$	37-465
4.18_x	2.69_4	2.45_5	2.19_2	1.72_2	Yellow iron oxide	$FeO(OH)$	29-713
4.040_x	3.136_1	2.841_1	2.487_1	2.486_0	Crystobalite	SiO_2	39-1425
3.52_x	2.370_2	1.892_4	1.700_2	1.667_2	Anatase	TiO_2	21-1272
3.445_x	3.319_7	3.103_x	2.121_8	2.106_8	Barium sulfate	$BaSO_4$	24-1035
3.39_x	6.32_2	2.986_8	2.840_4	2.269_2	Chrome orange	$Pb_2(OH)_2CrO_4$	8-437
3.38_x	2.903_5	2.787_5	2.632_3	1.755_3	Red lead	Pb_3O_4	8-19
3.342_x	4.257_2	2.457_1	1.818_1	1.542_1	Quartz	SiO_2	33-1161
3.310_x	3.129_8	2.926_9	1.9103_8	1.7642_5	Zinc sulfide	ZnS	36-1450
3.28_x	4.96_3	4.38_3	3.48_6	3.03_7	Lead chromate	$PbCrO_4$	8-209
3.260_x	9.79_6	5.771_2	4.251_2	3.130_5	Lead oxide sulfate hydrate	$Pb_4O_3SO_4 \cdot H_2O$	29-781

3.260_x	3.452_8	3.006_6	2.543_6	2.308_5	Strontium chromate	$SrCrO_4$	15-356
3.247_x	2.487_5	2.188_3	1.687_6	1.624_2	Rutile	TiO_2	21-1276
3.22_x	4.89_3	4.72_3	3.12_x	2.668_2	Moly orange	$Pb(Cr_{19}Mo_{11})O_4$	19-685
3.160_x	3.583_8	3.367_6	2.068_6	1.761_5	Cadmium yellow	CdS	6-314
3.142_x	4.571_2	3.494_3	3.174_2	3.118_8	Antimony oxide	Sb_2O_3	11-689
3.030_x	3.852_3	2.284_2	2.094_3	1.8726_3	Calcite	$CaCO_3$	24-27
2.886_x	2.192_3	2.015_2	1.804_2	1.786_3	Dolomite	$CaMg(CO_3)_2$	11-78
2.700_x	3.684_3	2.519_7	1.8406_4	1.6941_5	Red iron oxide	Fe_2O_3	33-664
2.666_x	3.633_8	2.480_x	2.176_4	1.672_9	Chrome oxide green	Cr_2O_3	6-504
2.623_x	4.47_6	4.25_6	3.61_9	3.29_9	Lead carbonate hydroxide	$Pb_3(CO_3)_2(OH)_2$	13-131
2.609_x	7.02_9	3.31_9	3.08_9	2.896_7	Zinc yellow	$K_2Zn_4(CrO_4)_2 \cdot 3H_2O$	8-202
2.5503_x	2.8766_3	2.3846_7	1.6361_4	1.4376_4	Copper chromium oxide	$CuCr_2O_4$	34-424
2.543_x	2.984_4	2.109_2	1.624_3	1.491_4	Tan iron oxide	$ZnFe_2O_4$	22-1012
2.532_x	2.967_3	2.0993_2	1.6158_3	1.4845_4	Black iron oxide	Fe_3O_4	19-629
2.476_x	2.814_6	2.603_4	1.625_3	1.477_3	Zinc oxide	ZnO	36-1451
2.443_x	2.864_7	2.026_2	1.56024	1.424_4	Cobalt aluminum oxide	$CoAl_2O_4$	10-458
2.338_x	2.024_5	1.431_2	1.221_2	0.9289_1	Aluminum metal[b]	Al	4-787
2.091_x	2.473_5	2.308_4	1.687_3	1.342_3	Zinc metal[b]	Zn	4-831

[a] Subscripts represent the relative intensity (rounded to the nearest integer) of the diffraction peaks of a phase, with the most intense peak taken as 10 and represented by "X."

[b] Particles of this material frequently exhibit preferred orientation in paint films, thus causing the observed relative intensitives to differ significantly from intensities listed in this table.

component are present in the diffraction pattern of the test sample, then the analyst notes the JCPDS file number and proceeds as described in the previous paragraph.

The JCPDS *Common Phases* volume provides an alphabetical listing by name of about 2600 commonly encountered crystalline phases, their formula, the d-spacing of the three strongest peaks, and their JCPDS file number. This reference is an extremely useful starting point in peak identification when one knows or suspects the presence of certain phases in the test sample.

Peaks that remain unassigned after the information in Table 1 and *Common Phases* has been used must be identified by means of the JCPDS Powder Diffraction File and either the Hanawalt or Fink search methods or other search system. The Hanawalt method is based on the three strongest peaks in the diffraction pattern. The Fink method is based on the eight strongest diffraction peaks of each phase without use of intensity information. The Fink index lists each phase eight times with a cyclic permutation of the eight peaks. Instructions in the Hanawalt and Fink search manuals should be studied carefully before attempting to use either method [*18*]. Use of a compact disk containing the JCPDS Powder Diffraction File and a personal computer can greatly speed searches.

Limitations—Qualitative analysis by X-ray diffraction has two principal limitations. First, different substances may have similar diffraction patterns, at least in part. Misidentification can occur when the sample contains several crystalline phases producing a complex pattern and diffraction is the only technique being used for analysis. Examples of potentially confusing coincidences or near coincidences are the strongest peaks of red lead, quartz, and zinc sulfide, with d-spacings of 3.38, 3.34, and 3.31 A, respectively, and a secondary peak of barytes at 3.319 A. Many other similar peaks can be found for common pigments in Table 1.

The speed with which an analysis can be done and the reliability of the outcome can be greatly improved if information is available about what elements and functional groups are present in the sample. Optical emission and X-ray fluorescence spectroscopy are convenient techniques for qualitative elemental analysis. Infrared spectroscopy can provide functional group information and, through spectral matching, may provide independent corroboration of pigment identification.

Quantitative Analysis

Quantitative analysis by X-ray diffraction is based on the principle that the intensity of a diffraction pattern of a crystalline substance is directly proportional to the concentration of that substance in the sample. This relationship and several complicating factors, including absorption of X-rays by the sample, are discussed in detail by Klug and Alexander [*20*]. Using the "matrix flushing" method devised by Chung as a simplified alternative to the Klug and Alexander method, the *relative* concentration of crystalline components in a mixture can be determined without knowledge of the absorption coefficient [*21,22*]. This approach is based on the fact that all components under analysis are in the same matrix and thus are equally influenced by X-ray absorption. The intensity of X-rays diffracted from a component i is given by the equation

$$I_i = k_i X_i$$

where

k_i = a constant that depends on component i and the apparatus, and
X_i = the mole fraction of component i.

The ratio of the intensity of X-rays diffracted from two components i and R is given by the equation

$$\frac{I_i}{I_R} = \frac{k_i}{k_R}\frac{X_i}{X_R}$$

where

k_R = a constant that depends on component R and the apparatus, and
X_R = the mole fraction of component R.

The constants k_i and k_R indicate the relative efficiency of two materials in diffracting X-rays from given sets of crystallographic planes into the detector of the diffractometer. The relative value of k_i and k_R can be determined from the equation

$$\frac{k_i}{k_R} = \frac{I_i}{I_R}$$

by measuring the intensity of X-rays diffracted from two crystalline components i and R in a 1:1 binary mixture. Quantitative analysis of a multicomponent mixture requires that the identity of all components be known. One component is arbitrarily chosen as an internal reference, R. Binary 1:1 by weight mixtures are prepared with the reference component and each of the other components. The intensity ratio I_i/I_R of a peak, usually the strongest, of each component is then measured. The ratio of the intensities of the diffraction peaks defines the k_i/k_R of each pair of components. Instead of using the ratio k_i/k_R, the author recommends using the reciprocal K_R/K_i, referred to in this work as a "K-factor" or in works by some authors as a "reference intensity ratio." If the intensity of the chosen diffraction peak of each component is multiplied by the corresponding K-factor and the resultant set of quotients normalized to yield a sum of 100, then the final set of numbers will be the relative weight percents of the crystalline components.

Two important points about quantitation by X-ray diffraction analysis should be noted. First, the results do not include noncrystalline components such as carbon black, amorphous silica, or highly processed clays. Second, the results do not represent percent by weight on either a dry film or a liquid paint basis. The absolute weight percent of crystalline pigments and extenders can be determined by a variation of the above method that includes the use of an internal standard [*21,23*]. The relative percent by weight derived from the method above can be converted into percent on a dry film or liquid paint basis if appropriate total pigment content has been determined by another method and no amorphous pigment is present.

Accuracy, in relative percent, and standard deviation of analyses by the Chung and similar methods were 5% or better in studies by Chung, Goehner, and Karlak and Burnett [*22–24*]. Table 2 summarizes the results of a study, by the author, of the accuracy and precision of X-ray diffraction for the analysis of pigments in paints prepared for the study.

Limitations—Quantitative analysis of pigments by X-ray diffraction is sometimes handicapped by one or more of the following problems. First, the degree of crystalline regularity of particles of some pigments, especially silica and clays, may differ depending on the source and the nature of the processing that they have received. A factor contributing to variability of the apparent crystallinity is the amount of substitution of "foreign" ions in the crystalline lattice. An example is the substitution of magnesium for calcium in calcite and strontium for barium in barytes. Thus, a given amount of pigment in a test sample may diffract X-rays more or less strongly than the supposedly equivalent pigment sample used to establish the K-factor. An article by Davis et al. provides a valuable listing of reference intensity

TABLE 2—*Precision and accuracy of X-ray diffraction for the analysis of pigments in cured paint films.*[a]

		Percent Composition		Relative Percent	Standard Deivation of Observed Composition	
Formulation	Pigments	Actual	Observed	Error	Absolute	Relative
1	Rutile	65.4	60.6	−7.3	1.21	1.85
	Calcite	34.6	39.3	+13.6	1.22	3.53
2	Yellow iron oxide	70.0	69.7	−0.43	1.02	1.46
	Rutile	30.0	30.3	+1.0	1.02	3.40
3	Rutile	40.0	34.1	−14.8	1.22	3.05
	Barytes	30.0	34.3	+14.3	1.35	4.50
	Yellow iron oxide	20.0	21.8	+9.0	1.47	7.35
	Zinc oxide	10.0	9.9	−1.0	1.38	13.8

[a] Based on twelve independent analyses of each sample done on six days. Instrument conditions: 0.02° step size, 1.0-s count time per step, copper target operated at 40 kV and 50 mA.

ratios (versus corundum) for many common pigments and illustrates the variability of reference intensity ratios for pigments from different sources [25]. Second, pigments particles that are platelet or acicular in shape tend to assume preferred orientations in a paint film as the paint dries. If the extent of preferred orientation of the particles in the test sample and in the reference sample used to establish the K-factor differs, then quantitation based on the K-factor is incorrect. Mica and aluminum flakes commonly exhibit preferred orientation. Third, the peaks used to generate the K-factors may, in the test sample, be overlapped by peaks of other components, thus requiring the use of weaker and less reliable peaks as the basis of quantitation.

Efforts to improve the accuracy and convenience of quantitative analysis by X-ray diffraction are continuing. An article by Smith et al. describes an approach to quantitation that uses the full diffraction pattern of a specimen and contains references to similar work by other investigators [26]. Methods based on the use of the full pattern alleviate problems that result from preferred orientation of crystallites and overlap of peaks.

Applications of X-Ray Diffraction Analysis

Pigment Analysis—X-ray diffraction analysis is the most direct way to determine the identity and purity of pigments, whether in assessing the quality of pigments from established suppliers or in evaluating pigment from a potential new supplier. Crystalline impurities contribute "extra" peaks to diffraction patterns, differences that may be readily seen in patterns of pigment powders alone or in grind pastes. X-ray analysis has long been established as the method of choice for determination of the amount of anatase in rutile [ASTM Test Method for Ratio of Anatase to Rutile in Titanium Dioxide Pigments by Use of X-Ray Diffraction (D 3720)]. The widespread use of diffraction in the pigment industry attests to its utility in that field.

Questions concerning the identity or amount of pigments in paint can be more conveniently and definitively answered by X-ray diffraction than by any other technique. Visual comparison of diffraction patterns or, when necessary, quantitative analysis can be used to determine whether errors in pigment composition account for the difference in performance, color, or gloss of "good" and "bad" paint. Diffraction analysis is one of the basic tools that may be used to verify whether a paint that exhibits poor performance is the correct paint and comes from the correct supplier. The differences in the two patterns in Fig. 4, one for a good paint and one from a poorly performing suspect paint, along with differences in resin and solvent determined by other techniques, proved that the suspect paint obtained by a paint user from a discount supplier was not identical to the good paint from the usual supplier.

Metal Pretreatment and Other Thin Coatings—In addition to its utility for determining bulk composition, X-ray diffraction can be used to determine the identity and amount of pretreatment on metal or, in general, crystalline coatings on a substrate. Figure 5 shows the characteristic part of the diffraction patterns of two common types of pretreatment, hopeite and scholtzite, on zinc galvanized steel. Coating thickness or pretreatment weight can be determined by comparison of the intensity of one or more peaks of the species of interest with the same peaks exhibited by standard samples.

Crystallinity of Polymers—The percent crystallinity of a polymeric solid, i.e., the amount of polymer chains that exists in domains of crystalline regularity compared to the amount of chains in regions of disorder, can influence bulk properties [*20*]. In particular, excessive crystallinity can increase brittleness, which, in a coating, is manifested as reduced flexibility and impact resistance and increased susceptibility to stress cracking. Although many polymers used in the coatings industry are predominately amorphous, some polymers such as polyethylene, poly(ethylene terephthalate), and poly(ethylene isophthalate) have significant crystalline character. Figure 6 shows contrasting diffraction patterns of polypropylene with high and low degree of crystallinity, differences induced by differences in thermal history. Johnson illustrated with poly(ethylene terephthalate) an X-ray diffraction method for determination of the degree of crystallinity of a polymer based on comparison of the intensity

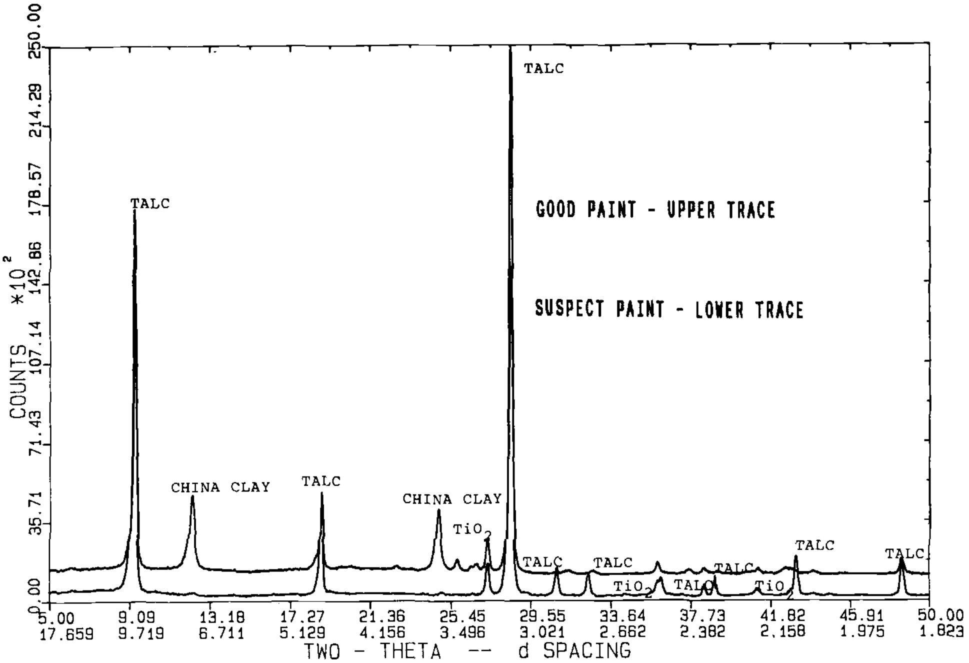


FIG. 4—*X-ray diffraction patterns of drawdowns of two paints, one known to be good, one of suspect identity.*

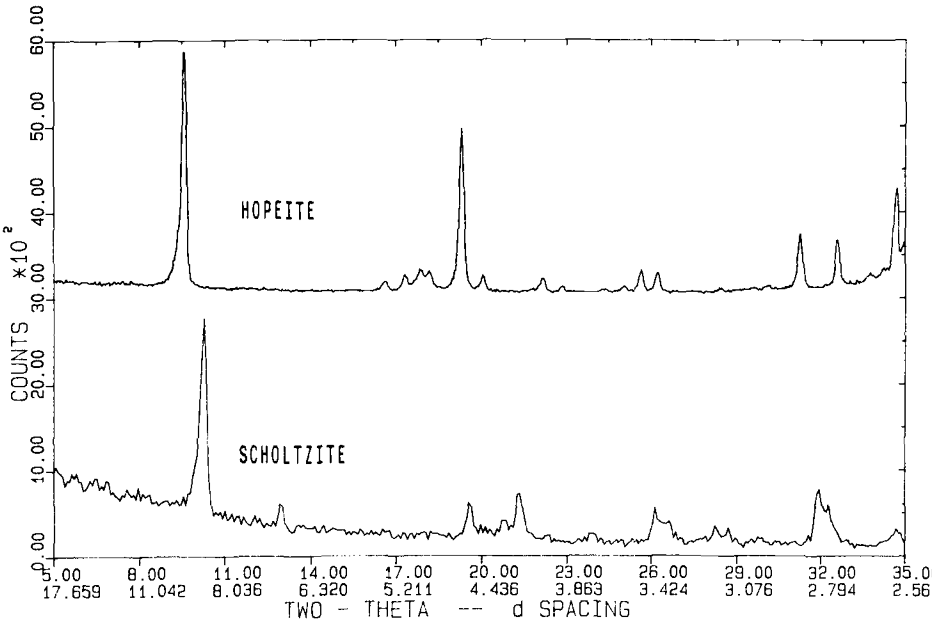


FIG. 5—*X-ray diffraction patterns of hopeite and scholtzite pretreatment on zinc-galvanized steel. The principle peaks of zinc are beyond the right end of the pattern.*

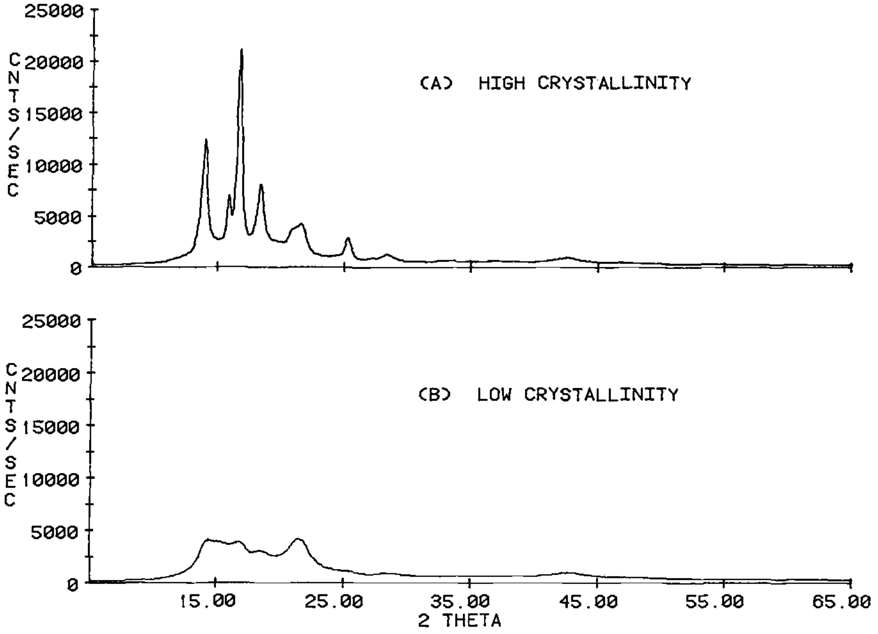


FIG. 6—*X-ray diffraction patterns of polypropylene with different degrees of crystallinity.*

of the sharp peaks produced by coherent scattering of X-rays by the crystalline regions to the intensity of the broad "halo" produced by incoherent scatter of X-rays by the amorphous regions [*27*]. Chung and Scott used the same concept and their "matrix flushing" principle to devise a convenient way to determine the crystallinity of polymers [*28*]. In the latter approach, the degree of crystallinity of a two-phase crystalline-amorphous system is determined by the equation

$$X_c = \frac{1}{1 + kI_a/I_c}$$

where

X_c = the weight fraction of crystalline domains,
I_a = the integrated intensity of the broad amorphous halo,
I_c = the integrated intensity of a diffraction peak of the crystalline phase, and
k = a constant relating the intensity of a crystalline peak to the intensity of the amorphous halo (determined from a sample of known crystallinity).

Particle Size—The size of crystallites, in the size range of less than 1000 A, can be determined from the width of their X-ray diffraction peaks through use of the Scherrer equation [*20*]

$$L = \frac{K\lambda}{B \cos \theta}$$

where

L = the mean crystalline size,
λ = the wavelength of X-rays used,
B = the diffraction broadening of the peak,
θ = half the Bragg angle of the peak maximum, and
K = a physical constant related to the shape of the crystallites and the manner of defining B and L.

De Angelis and coworkers have used the method to determine the mean size and size distribution of NiO on alumina and silica [*29*]. Areas of potential application in the coatings industry are the determination of the size of crystallites of pretreatment on metal and crystallites in polycrystalline polymers.

X-Ray Fluorescence Spectrometry

Physical Basis

When X-ray photons of sufficient energy are beamed onto a specimen, some of the photons are absorbed in a process that causes ejection of electrons from core atomic orbitals. The vacancies thus created in the inner orbitals are then filled by electrons from outer orbitals. The transitions of electrons from outer to inner orbitals are accompanied by the release of X-rays in a process called X-ray fluorescence [*6,7*]. The wavelengths of the fluorescent X-rays are greater than the wavelength of the incident X-rays. Of importance in analysis is the fact that every element emits fluorescent X-rays at characteristic wavelengths. The spectra are plotted as intensity as a function of either energy, wavelength, or two-theta angle, the latter referring to the position of the diffraction crystal used in some instruments to separate the wavelengths.

Types of X-ray Fluorescence Spectrometers

Scanning Spectrometers—Scanning X-ray fluorescence spectrometers permit the acquisition of spectra spanning a broad wavelength or energy range. They are versatile instruments for both qualitative and quantitative analysis. Scanning spectrometers, all using X-rays from Coolidge-type tubes, can be further classified as either wavelength or energy dispersive.

Wavelength-dispersive (WLD) instruments produce a spectrum by using a crystal to diffract the fluorescent X-rays, a single wavelength at a time, onto a detector that measures their intensity. By rotating the crystal through an angle defined as theta as the detector moves around an arc through angle two-theta, only those X-rays that satisfy the Bragg equation reach the detector. The resultant spectrum is usually plotted as intensity as a function of two-theta angle, but could in principle be plotted as intensity as a function of wavelength. Through the use of several crystals, each effective for a certain span of wavelengths, a broad range of wavelengths can be scanned.

Instruments based on energy-dispersive X-ray spectroscopy (EDXS) permit all wavelengths of the fluorescence to reach the detector simultaneously and use a pulse-height-discriminator to electronically classify the energy of the X-ray photons that strike the detector.

Descriptions and comparisons of the two types of spectrometers have been provided by Campbell [*30*]. Compared to EDXS units, the WLD spectrometers generally offer far superior resolution and lower limits of detection. EDXS instruments provide much faster acquisition of multielement survey spectra and are usually lower in cost. Scanning spectrometers are convenient for qualitative elemental analysis and are broadly versatile for quantitative analysis.

Dedicated Spectrometers—Dedicated X-ray fluorescence spectrometers, available at much lower cost than the scanning spectrometers, permit quantitative analysis of a single element or a few selected elements. Most of the dedicated units, and all of the lowest priced ones, use a radioactive isotope rather than an X-ray tube as the source of radiation to excite the specimen. In the case of single element analyzers, the isotope source and operating conditions are chosen to give best performance for analysis of a specific element of interest. Compared to scanning spectrometers, dedicated units have the advantage of lower cost and simplicity of operation. They are well-suited for routine analysis in either research laboratory or production plant.

Portable X-ray fluorescence units, either single or multiple element, with or without self-contained power supplies, are available for uses that require mobility.

Experimental Procedures

Specimens may be any solid or liquid that can be placed in specimen holders suitable for the spectrometer. Specimen preparation methods have been discussed by Bertin and Leyden [*6,31*]. Liquid or powder is placed in a disposable plastic cup, the bottom of which is covered with a thin plastic film that transmits X-rays. (Liquids and powder are most conveniently analyzed in spectrometers that irradiate the specimen from below. For instruments of the opposite configuration, the specimen cup must be filled so that there is no bubble when the cup is inverted in the analysis chamber.) For qualitative analysis, paint chips may be placed directly in the specimen cup and drawdowns of paint on metal-free plastic sheet, such as Mylar, may be cut to fit the specimen holder. For quantitation, powers may be pressed into disks in a binding agent such as orthoboric acid, granular cellulose, or graphite or cast as pellets after dissolution in molten flux such as lithium tetraborate or lithium metaborate. Two grams or more of specimen is preferred for routine quantitative analysis. Qualitative analysis can be done on as little as a few milligrams of specimen.

Specimens are analyzed under vacuum whenever possible to prevent absorption of X-rays by the atmosphere in the analysis chamber. However, liquids and powders must be run under helium or air to prevent spatter.

Qualitative Analysis

X-ray fluorescence spectrometry using a modern unit is probably the most convenient technique available for qualitative elemental analysis of solids and liquids. Most instruments are capable of detecting all elements of the periodic table from sodium to uranium. Some instruments have ranges that extend down in atomic number as far as boron. However, the limit of detection rises rapidly as the atomic number decreases below that of sodium. X-ray fluorescence spectrometry is applicable to elements present in a wide range of concentrations from 100% down to a few parts per million in favorable cases. Elements in a specimen can be identified by the position of the peaks on the spectrum expressed as energy (kilovolts), two-theta angle, or wavelength. Peak identification tables can be found in manuals provided by manufacturers of the spectrometers or in treatises on X-ray spectrometry [*6*]. Many modern spectrometers, especially EDXS units, have computer programs that can automatically identify elements in a specimen.

In addition to being an independent analytical tool, X-ray fluorescence spectrometry can facilitate analysis by other methods. Survey spectra recorded by scanning X-ray fluorescence units are useful for determining what elements are present in a sample prior to quantitative analysis by atomic absorption spectrometry or ion chromatography, or by X-ray fluorescence itself.

Figure 7 shows part of an X-ray fluorescence survey spectrum (collected using a wavelength-dispersive instrument) of a drawdown of the tan paint used to produce the diffraction pattern in Fig. 3(*a*). Note the corroborative nature of element content indicated by the spectrum in Fig. 7 and the identity of the pigments determined from the diffraction pattern in Fig. 3*a*. For comparison, Fig. 8 is an X-ray fluorescence survey spectrum, recorded by means of an energy-dispersive instrument, of the same sample used to record the spectrum in Fig. 7.

Quantitative Analysis

The principles of quantitative analysis by X-ray fluorescence spectrometry have been discussed in detail by numerous workers including Bertin [*6*]. The basic equations indicate that the intensity of the fluorescent X-rays is proportional to the amount of element that produced the X-rays, but is influenced by the density and absorption coefficient of the specimen and other factors. Nevertheless, the linear proportionality between analyte concentration and fluorescence intensity indicates that common analytical methods such as standard addition can be readily employed in X-ray spectrometry. Direct comparisons of concentration can also be made between samples that differ only in the amount of analyte of interest. Various analytical methods based on sets of standards have been devised to permit multielement quantitative analysis. Most research-type scanning X-ray fluorescence spectrometers can now be purchased with computers and programs for use of such programs.

In quantitative analysis of liquid samples, X-ray fluorescence spectrometry, compared to atomic absorption or plasma emission spectrometry, offers the advantage of being able to handle samples with: (1) higher concentrations of analyte without use of large dilution factors and attendant inaccuracy; (2) matrices that are ill-suited for aspiration into nebulizers; and (3) elements that are not easily detected by flame or plasma photometric techniques.

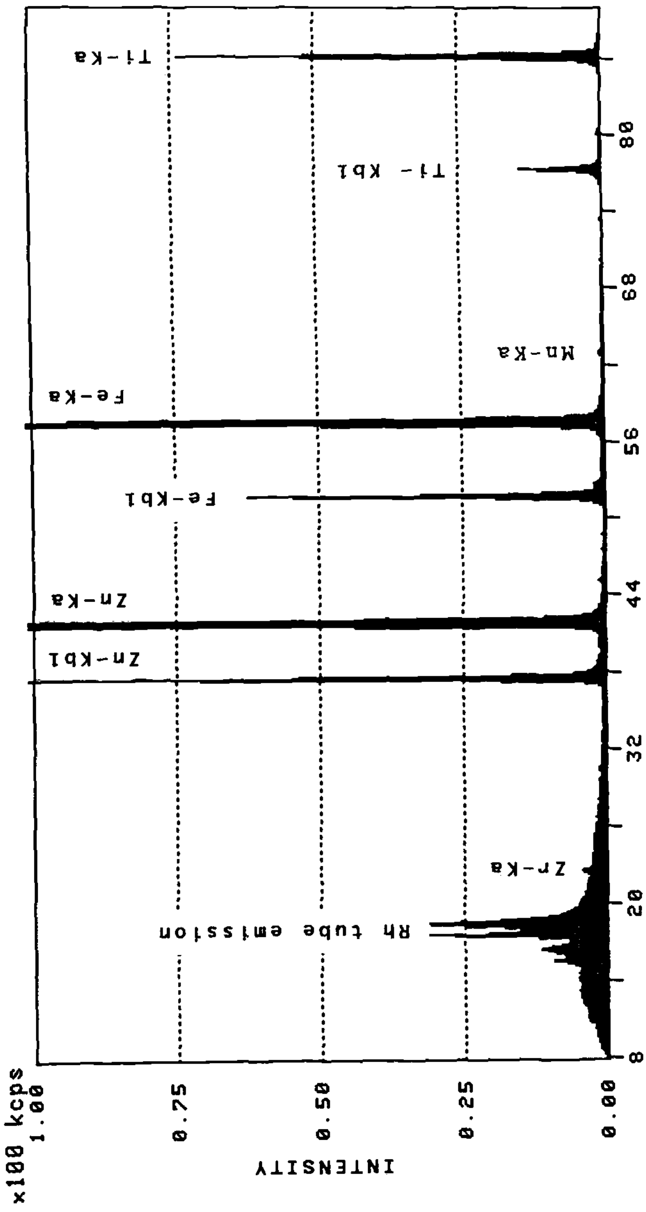


FIG. 7—*Part of a WLD X-ray fluorescence spectrum of paint containing rutile, yellow iron oxide, talc, and zinc oxide.*

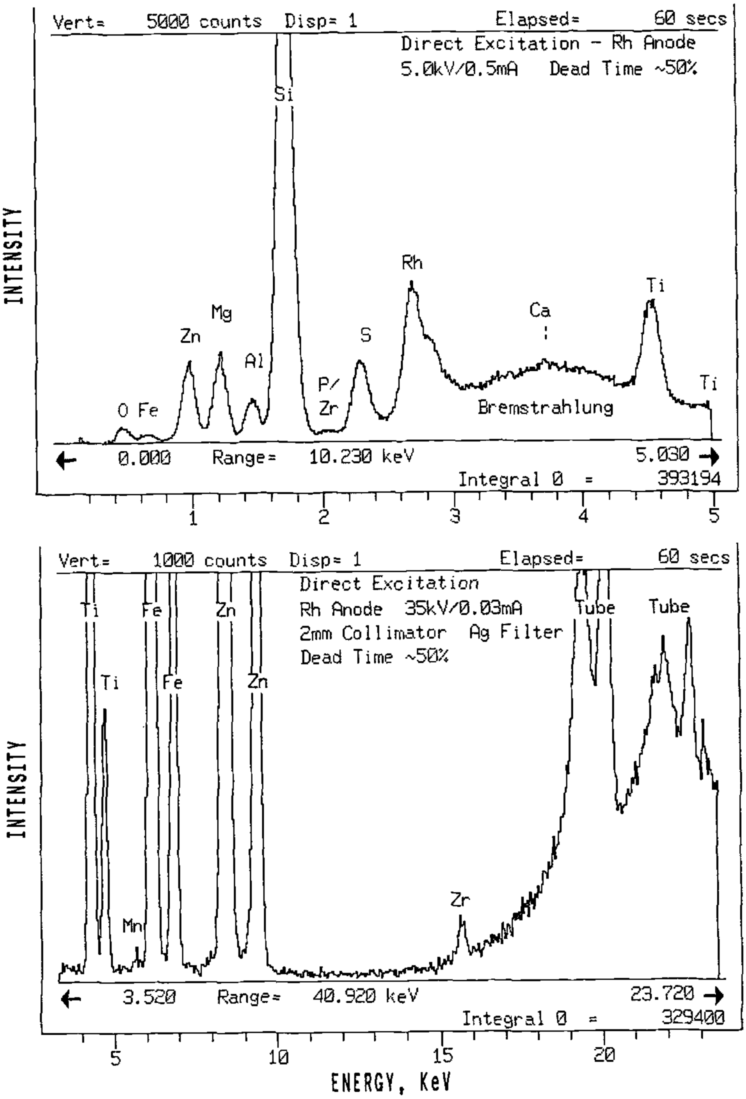


FIG. 8—*X-ray fluorescence spectrum, recorded using an energy dispersive spectrometer, of the paint used for Fig. 7.*

Applications of X-ray Fluorescence Spectrometry

Support for X-ray Diffraction Analysis—X-ray fluorescence spectroscopy is a powerful tool to aid or corroborate qualitative analysis done by X-ray diffraction. Knowledge of what elements are present in a sample may be helpful in suggesting phases for consideration in the initial stage of diffraction search-match operations and in discriminating phases with similar diffraction patterns. For example, an analyst relying on X-ray diffraction alone may fail to identify zinc oxide when present in paint in small amounts if its strongest peak at 2.476 A is overlapped by a peak of rutile at 2.487 A or talc at 2.476 A, particularly when the latter two phases are major components. X-ray fluorescence spectroscopy also offers the benefit of detection limits in the parts per million range for most elements, compared to 1 to 10% for some combinations of phases in X-ray diffraction. Laboratories that are not equipped with X-ray diffraction instrumentation sometimes resort to the practical but risky expedient of using X-ray elemental analysis alone or in combination with information from infrared spectroscopy to infer the identity of crystallinity phases. On this basis the analyst may conclude that the presence of zinc, iron, titanium, strontium, and chromium indicate the presence of zinc oxide, iron oxide, titanium dioxide, and strontium chromate.

Figures 7 and 8 show the qualitative elemental information that can be obtained from X-ray fluorescence scans.

Analysis of Elements in Solution—Figure 9 shows a plot of data used in the quantitation of sulfur in an acidic aqueous solution by a standard addition method. The sample resulted from flushing a steel panel retrieved from outdoor exposure with citric acid and then concentrating the solution by evaporation. This example illustrates a general-purpose method.

Surface Analysis—Foreign substances may sometimes be detected on surfaces by X-ray fluorescence spectroscopy, eliminating the need to resort to X-ray photoelectron spectroscopy and other "surface analysis" techniques. To be detectable, the contaminant must contain an element that is not present in significant amounts in the surface itself. Figure 10 shows a silicon peak in the high resolution X-ray fluorescence scan of the surface of a piece of aluminum extrusion from which poorly adhering paint was peeled. Comparison of Figs. 10*a* and 10*b*, respectively, demonstrate that washing the peeled surface with hexane significantly reduced the amount of silicon present. The elevated silicon signal on a substrate to which paint adhered poorly and the ready removal of the silicon material by hexane suggested the presence of silicone oil. This suspicion was confirmed using analysis by microinfrared spectroscopy of residue left by evaporation of the hexane washings.

Detection of Bulk Contaminant—The low limit of detection of X-ray fluorescence spectroscopy makes it well suited for the detection of trace impurities, some of which may not

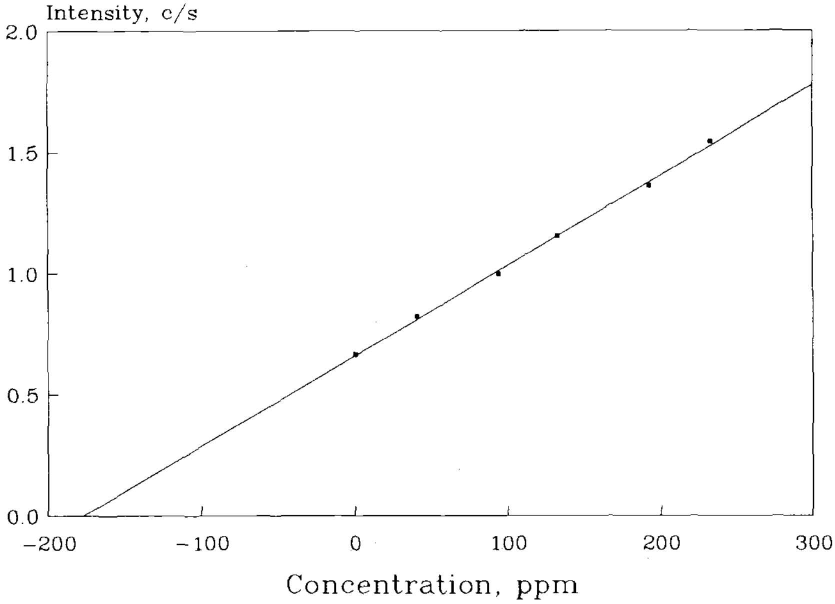


FIG. 9—*A plot of the intensity of the sulfur* K *peak as a function of the concentration of sulfur in the analysis of an aqueous solution by a standard addition method.*

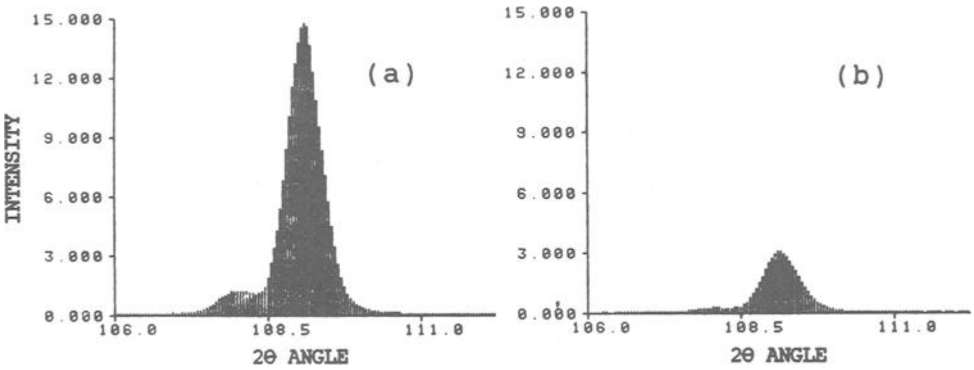


FIG. 10—*The* K-α *peak of silicon on extruded aluminum from which poorly adhering paint has been peeled:* (a) *peeled only;* (b) *peeled and washed with hexane.*

be detectable by any other means. There is the tacit requirement that the contaminant contain an element that is not a normal component of the sample. Although small amounts of impurity make no perceptible impact on the performance of a material, knowledge of the presence and amount of an impurity may be crucial in determining the cause of substandard performance. Table 3 summarizes data collected by X-ray fluorescence spectrometry in the investigation of a case in which silicone contamination was suspected as the cause of cratering exhibited by certain batches of water-borne paint. Quantitation was by a standard addition method. Although X-ray fluorescence spectrometry cannot distinguish between different silicon-bearing species, the higher level of silicon in batches of resin used in the crater-prone paint supports the suspicion that silicone caused the cratering. The data also indicate that a threshold concentration between 7 and 13 ppm silicon in the resin is needed to produce cratering in the paint produced from it.

Quality Control—Dedicated X-ray fluorescence units capable of determining the concentration of a single element have great utility in production plants for monitoring the composition of raw materials, intermediates, and products. One application is the monitoring of batches of paints to ensure compliance with federal regulations that limit lead content to no more than 600 ppm on the basis of nonvolatile content. A common technique for determining lead content has been atomic absorption spectroscopy using ASTM Test Method for Low Concentrations of Lead, Cadmium, and Cobalt in Paint by Atomic Absorption Spectroscopy (D 3335) or a similar method. X-ray fluorescence offers a quick alternative to atomic absorption spectroscopy, which is too laborious and time-consuming for routine plant use. Lead content of a sample of paint can be determined by placing a drawdown or

TABLE 3—*Concentration of silicon, determined by XRFS, in batches of resin used in batches of paint of known extent of cratering.*

Extent of Cratering	Concentration of Silicon, ppm
None	3
None	4
None	7
Bad	13
Bad	13
Worst	40

liquid specimen in the analysis chamber and directly reading either the content or signal count rate of lead. Dedicated X-ray fluorescence analyzer are available that give direct readout of concentration once a calibration curve has been established using samples of known concentration. The principal drawback of this method is the need for a separate calibration curve for every type of paint analyzed [*16*]. Differences in the paint composition, such as the type and amount of pigment, can influence the intensity of the lead signal. In addition, interference from other elements, such as bromine, can produce large errors in apparent lead concentration.

Figure 11 is a plot of lead count rate from ten consecutive batches of latex house paint measured with a Princeton Gamma-Tech M-100 X-ray fluorescence analyzer [*16*]. The count rate that corresponds to 0.06% lead, the legal limit, is indicated by a horizontal line, $x_{\text{Pb}0.06\%}$. To provide leeway for error, a lead concentration, L_{Pb} (less than the legal limit by an amount determined by the precision of the method), may be chosen as the highest "passing" count rate. The dotted line represents L_{Pb}. Any sample that gives a count rate between L_{Pb} and the legal limit is considered suspect. Suspect batches of paint should be analyzed by ASTM Method D 3335, or other independent method, to determine the concentration of lead. Batches with unacceptable lead content may be scrapped or "blended-off."

Dedicated X-ray analyzers have also been used to monitor the amount on rutile in batches of paint in production plants [*16*].

Detection of Lead in Residential Paint in situ—Concerns over the potential adverse health effects of lead in paint in residential buildings has prompted an interest in convenient, nondestructive methods of testing for lead. Fully portable X-ray analyzers capable of detecting lead pigmented paints on walls and other surfaces are commercially available. The analyzers reportedly can detect lead-containing paint beneath layers of lead-free paint, and some can provide direct readout of the amount of lead per unit area of paint surface [*32*]. The accuracy and precision are not well documented. The Department of Housing and Urban Development established a limit of 1.0 mg of lead per cm^2 of painted surface, a level detectable by portable analyzers.

X-ray Spectrometry/Scanning Electron Microscopy

The electrons striking the specimen in a scanning electron microscope not only produce an image, but induce the emission of X-rays. Through use of an energy-dispersive X-ray detector or a wavelength-dispersing analyzer, a spectrum of the X-rays emitted from the impacted area can be collected. This phenomenon, although not properly classified as X-ray *fluorescence* as it is sometimes mistakenly called, permits elemental analysis of the electron impact area. Through manipulation of the electron beam, the microscopist can perform qualitative and at least semiquantitative analysis of spots, lines, or broad areas of an image viewed with the microscope. Although probe techniques are not the subject of this paper, the kinship of the methods merit note. A scanning electron microscope equipped with an X-ray analyzer is probably the most useful tool available for examination of small defects in paint.

Summary

X-ray diffraction and X-ray fluorescence spectrometry, used alone or in combination, can provide valuable information about coatings, coating ingredients, impurities, and substrates. Sample preparation effort is minimal for both techniques. X-ray diffraction offers easy qualitative and quantitative analysis of crystalline materials in general and pigments in particular. X-ray fluorescence spectrometry is widely useful for qualitative analysis and, when suitable standards are used, for quantitative analysis. Attractive features of X-ray

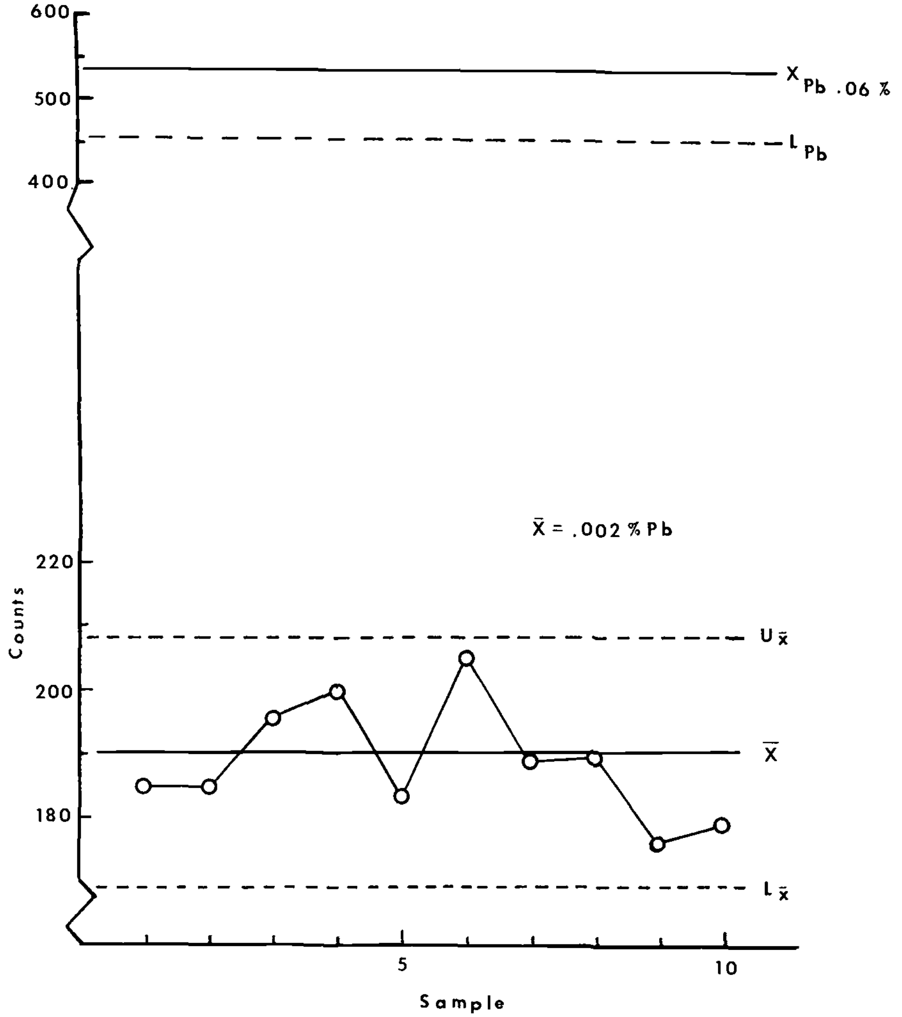


FIG. 11—*A plot of the intensity of the lead signal for consecutive batches of latex paint as measured by a dedicated X-ray analyzer.*

fluorescence spectrometry for quantitative analysis include its suitability for all elements except a few with lowest atomic number, applicability over a broad concentration range, tolerance of chemically reactive specimens, and applicability to samples of diverse physical states. Both X-ray diffraction and X-ray spectrometry are suitable for applications including basic research, product and process development, quality control, and practical problem solving. The area of greatest potential growth is the use of dedicated X-ray fluorescence spectrometers in production plants for quality control, particularly for online monitoring.

Acknowledgments

I wish to thank J. C. Ratliff for providing X-ray diffraction patterns, pigment analysis results, and X-ray fluorescence spectra, R. Gagne for providing X-ray diffraction patterns, and M. Feeney for providing the energy-dispersive X-ray fluorescence spectra included in this account. I also thank D. E. Hayes, E. L. Evans, D. R. Camp, and K. Hollertz for preparing paint samples used to illustrate the instrumental techniques.

References

[*1*] Friedrich, W., Knipping, P., and Laue, M. V., *Annalum der Physik (Leipzig)*, Vol. 41, 1912, pp. 971–988.
[*2*] Moseley, H. G. J., *Philosophical Magazine*, Vol. 26, 1913, pp. 1024–1034.
[*3*] Moseley, H. G. J., *Philosophical Magazine*, Vol. 27, 1914, pp. 703–713.
[*4*] Bragg, W. L., *Proceedings of the Cambridge Philosphical Society*, Vol. 17, 1912, pp. 43–57.
[*5*] Bragg, W. H. and Bragg, W. L., *Proceedings of the Physical Society (London)*, Vol. A88, 1913, pp. 428–438.
[*6*] Bertin, E. P., *Principles and Practices of X-ray Spectrometric Analysis*, Plenum Press, New York, 1970.
[*7*] Bertin, E. P., *Introduction to X-ray Spectrophotometric Analysis*, Plenum Press, New York, 1978.
[*8*] Jenkins, R. and De Vries, J. L., *Practical X-ray Spectrometry*, MacMillan, London, 1975.
[*9*] Liebhafsky, H. A., Peiffer, H. G., Winslow, E. H., and Zemany, P. D., *X-rays, Electrons and Analytical Chemistry*, Wiley, New York, 1972.
[*10*] De Vries, J. L., *X-ray Fluorescence Spectrometry—Review of the Literature*, 7th ed., Philips, Eindhoven, Netherlands, 1976.
[*11*] Carr-Brion, K. G. and Payne, K. W., *Analyst*, Vol. 95, 1970, pp. 977–991.
[*12*] Russ, J. C., *X-ray Spectrometry*, Vol. 1, 1972, p. 119.
[*13*] Porter, D. E. and Woldseth, R., *Analytical Chemistry*, Vol. 45, 1973, pp. 604A–614A.
[*14*] Scott, R. W., *Journal of Paint Technology*, Vol. 41, No. 534, 1969, pp. 422–430.
[*15*] Scott, R. W., *Treatise on Coatings*, Vol. 2, Part II, Marcel Dekker, New York, 1976, pp. 591–624.
[*16*] Kamarchik, P. and Cunningham, G. P., *Progress in Organic Coatings*, Vol. 8, 1980, pp. 81–107.
[*17*] Carter, J. R., Cody, C. A., DiCarlo, L., and Hacher, M. T., *Research and Development*, February 1984, pp. 124–128.
[*18*] JCPDS Powder Diffraction File, International Centre for Diffraction Data, Swarthmore, PA.
[*19*] Jenkins, J. and Holomany, M., *Powder Diffraction*, Vol. 2, No. 4, December 1987, pp. 215–219.
[*20*] Klug, H. P. and Alexander, L. E., *X-ray Diffraction Procedures*, John Wiley & Sons, New York, 1974.
[*21*] Chung, F. H., *Journal of Applied Crystallography*, Vol. 7, 1974, pp. 519–525.
[*22*] Chung, F. H., *Journal of Applied Crystallography*, Vol. 7, 1974, pp. 526–531.
[*23*] Goehner, R. P., *Advances in X-ray Analysis*, Vol. 25, Plenum Press, 1981, pp. 309–313.
[*24*] Karlak, R. F. and Burnett, D. S., *Analytical Chemistry*, Vol. 38, 1966, pp. 1741–1745.
[*25*] Davis, L. D., Smith, D. K., and Holomany, M. A., *Powder Diffraction*, Vol. 4, No. 4, 1989, pp. 201–205.
[*26*] Smith, D. K., Johnson, Jr., G. G., Scheible, A., Whims, A. M., Johnson, J. L., and Ullmann, G., *Methods and Practices in X-ray Diffraction*, 11.1.1, International Centre for Diffraction Data, Swarthmore, Pennsylvania.
[*27*] Johnson, J. E., *Journal of Applied Polymer Science*, Vol. 2, No. 5, 1959, pp. 205–209.
[*28*] Chung, F. H. and Scott, R. W., *Journal of Applied Crystallography*, Vol. 6, 1973, pp. 225–230.
[*29*] Ganesan, P., Kuo, H. K., Saavedra, A., and De Angelis, R. J., *Journal of Catalysis*, Vol. 52, 1978, pp. 310–320.
[*30*] Campbell, W. C., *Analyst*, Vol. 104, 1979, pp. 177–195.
[*31*] Leyden, D. E., "Fundamentals of X-ray Spectrometry as Applied to Energy Dispersive Techniques," Tracor X-ray, Inc., Mountain View, CA, 1984, pp. 39–45.
[*32*] Rasberry, S. D., *Applied Spectroscopy*, Vol. 27, No. 2, pp. 102–108.

Francis X. Young[1]

Practical Applications of Gas Chromatography in the Paint and Coatings Industry

---

REFERENCE: Young, F. X., "**Practical Applications of Gas Chromatography in the Paint and Coatings Industry,**" *Analysis of Paints and Related Materials: Current Techniques for Solving Coatings Problems, ASTM STP 1119,* American Society for Testing and Materials, Philadelphia, 1992, pp. 105–124.

ABSTRACT: Gas chromatography (GC) is an established analytical technique which is useful for the characterization of coatings and related materials. With the introduction of chemically inert and thermally stable fused silica capillary columns, many volatile and semivolatile polar compounds can now be chromatographed easily. Nonvolatile polymers used in coatings can be routinely characterized by pyrolysis-gas chromatography-mass spectrometry (pyrolysis-GC-MS).

Practical examples are presented showing how GC and pyrolysis-GC-MS can be used to monitor the quality of raw materials, resolve manufacturing problems and field complaints, and aid in the reverse engineering of various products. Routine quantitative GC methods, such as the analysis of coalescent agents in latex paint and residual monomers in latex emulsions, are illustrated. Examples are given showing how GC is used for the analysis of raw materials like mineral spirits and fatty acids. GC is also used to characterize and quantitate additives like low molecular weight nonionic surfactants, waxes and oils, and mildewcides. Headspace sampling is used for identifying odor problems and analyzing samples for which solvent dilution is not appropriate. The usefulness of pyrolysis-GC-MS in the characterization of several different types of polymers is demonstrated.

KEY WORDS: gas chromatography, pyrolysis, coatings, paints, solvents, mineral spirits, monomers, polymers, additives

Gas chromatography (GC) plays a key role in the analyses of coatings and related materials. GC is a versatile technique with applications ranging from the analysis of solvents to the identification of resins in coatings. As an analytical tool, GC can be used for the direct separation and analysis of gaseous samples, liquid solutions, and volatile solids. For known systems, compounds can be identified by their retention time and quantitated using an internal standard. Unknowns can be analyzed through the use of a benchtop mass spectrometer such as the mass-selective detector (MSD) or the ion-trap detector (ITD).

The column is the heart of the chromatograph and provides versatility in the type of analyses that can be obtained with a single instrument. Many technological advancements have been made in developing inert and reproducible fused silica capillary columns. The stationary phases are cross-linked and bonded to the silica surface, rendering the stationary phase insoluble and inert for the analysis of polar compounds such as acids, amines, and glycols. Most separations can be accomplished on either a nonpolar stationary phase like 5% phenyl-95% methylpolysiloxane or a polar phase like polyethylene glycol. The inner

---

[1] Research scientist, Sherwin-Williams Co., Cleveland, OH 44113.

diameters of these capillary columns range from 50 μm for supercritical fluid chromatography (SFC) up to 0.53 mm for wide bore columns. Packed columns (1/8 in. O.D.) have given way to 0.53 mm I.D. fused silica capillary columns. Wide bore capillary columns with an I.D. of 0.53 mm have a high capacity and are commonly used with high flow rates similar to conventional packed columns. The upper temperature limit in GC is restricted not only by the stationary phase coated inside the column, but by the polyimide protective coating on the outside of the column. The introduction of aluminum-clad fused silica capillary columns has raised the upper temperature limit of GC to 440°C.

GC is also an attractive analytical tool because of the variety of excellent detectors available. The flame ionization detector (FID) is by far the most widely used detector. The FID is very sensitive, has a large dynamic range, and is nearly a universal detector [*1*]. Also available today are benchtop mass spectrometers which greatly expand the power of GC. These detectors are relatively inexpensive, reliable, and easy to use and maintain. GC-MS is now affordable by most laboratories.

Nonvolatile polymeric material can be indirectly identified by the use of pyrolysis-gas chromatography. This is a modification wherein a nonvolatile sample is pyrolyzed (i.e., physically decomposed by heat) prior to its entering the column. Decomposition products are separated in the gas chromatographic column and then identified by mass spectroscopy (MS). Some polymers yield more information than others when pyrolyzed. It is desirable in most cases to have the polymer decompose to its monomers so the identity of the original polymer can be determined. If the component to be pyrolyzed is very complex, complete identification of all the fragments may not be possible. In this case the resulting pyrogram (a chromatogram resulting from the detection of pyrolysis products) may be used as a set of "fingerprints" for subsequent study. Pyrolysis-GC-MS can be used to qualitatively characterize polymers while quantitative information can be obtained from infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy.

Applications

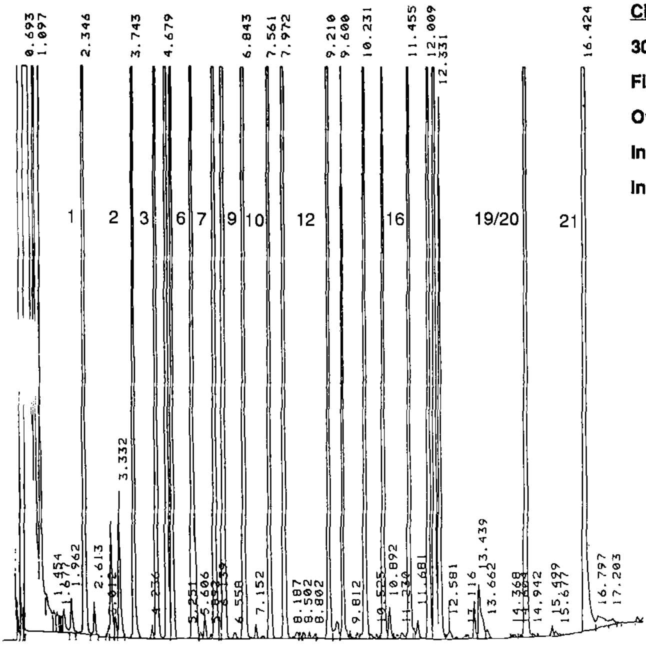
GC has a wide range of applications in the coatings industry. GC is used to monitor the quality of raw materials, characterize and quantitate additives in coatings, and resolve manufacturing and customer complaints.

Coalescent Agents in Latex Paint

GC is an excellent technique for quantitating coalescent agents in latex paint. The proper levels of coalescent agents are necessary to form a polymeric film. An unknown paint is analyzed by adding an internal standard (Cellosolve acetate) and dispersing it in acetone (1:9), then centrifuging out the solids. The supernatant solution is injected on-column into a 0.53-mm I.D. polyethylene glycol column. Figure 1 shows a standard chromatogram containing most of the common coalescent agents. Coalescent agents found in a paint sample are identified by their relative retention time. Figure 2 shows a chromatogram of coalescent agents found in a latex paint. The source of mineral spirits found in the paint is the alkyd modification of the formula. The presence of an alkyd is confirmed by analyzing the acetone extract by pyrolysis-GC-MS.

Residual Monomers in Latex Emulsions

Gas chromatography is routinely used for the analysis of residual monomers in latex emulsions. Monomers are lachrymators, and it is important that they be minimized in latex



CHROMATOGRAPHIC CONDITIONS:

30 meter X 0.53 mm DB-WAX Column

Film thickness: 1.0 micron

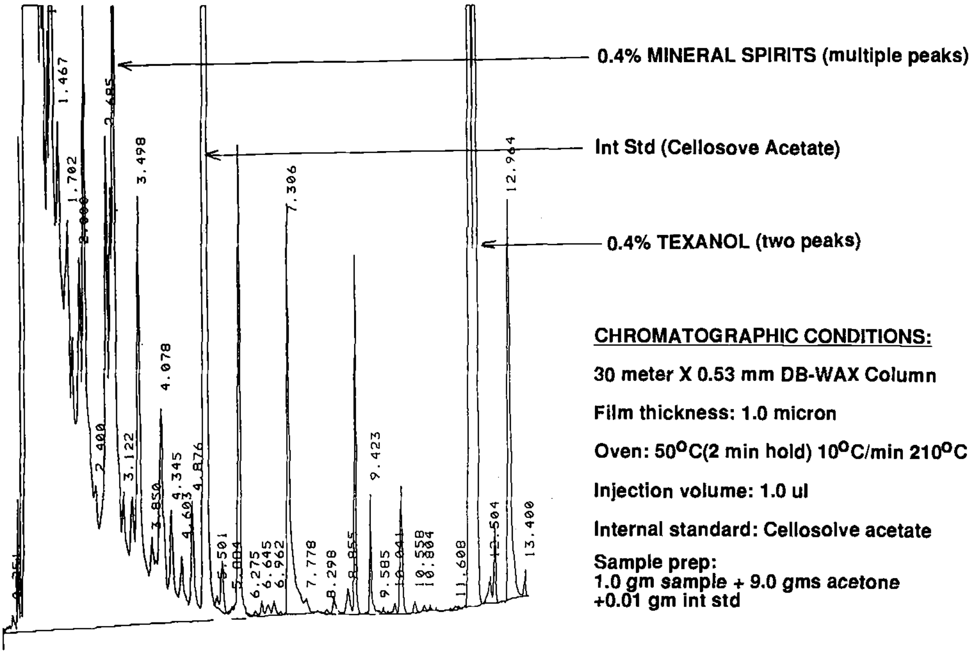
Oven: 50°C(2 min hold) 10°C/min 210°C

Injection volume: 1.0 ul

Internal standard: Cellosolve acetate

1. Butyl Acetate
2. Methyl Cellosolve
3. Methyl Cellosolve Acetate
4. Cellosolve
5. 2-Propanol,1 Propoxy
6. Cellosolve Acetate
7. 2-propanol,1-Butoxy
8. Diacetone Alcohol
9. Butyl Cellosolve
10. Butyl Cellosolve Acetate
11. 2-Ethyl Hexanol
12. Propylene Glycol
13. Ethylene Glycol
14. Carbitol Acetate
15. Trietylene Glycol Dimetyl Ether
16. Butyl Carbitol
17. Butyl Carbitol Acetate
18. Texanol (two peaks)
19. Tributyl Phosphate
20. Ethylene Glycol Phenyl Ether
21. Glycerine

FIG. 1—*Gas chromatogram of common coalescent agents found in latex paints.*



CHROMATOGRAPHIC CONDITIONS:

30 meter X 0.53 mm DB-WAX Column

Film thickness: 1.0 micron

Oven: 50°C(2 min hold) 10°C/min 210°C

Injection volume: 1.0 ul

Internal standard: Cellosolve acetate

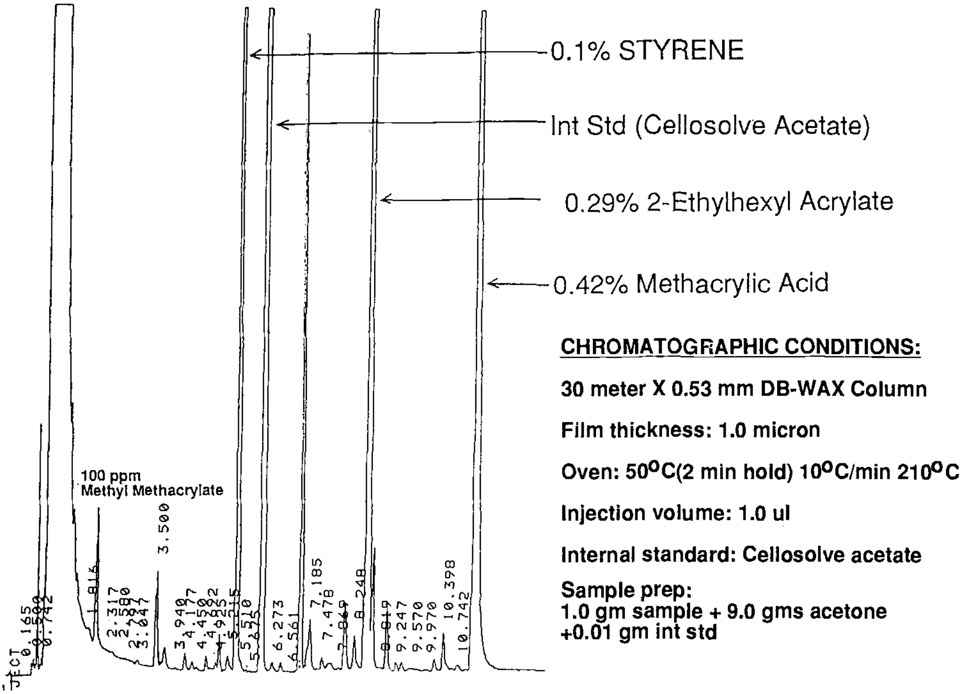
Sample prep:
1.0 gm sample + 9.0 gms acetone
+0.01 gm int std

FIG. 2—*Gas chromatogram of coalescent agents extracted from a latex paint.*

emulsions for health and esthetic reasons. GC has the low detection limits necessary to quantitate these monomers. The analysis of residual monomers in a latex emulsion is very similar to that used to determine coalescent agents in a paint. A 10% solution is made up in acetone or methanol to extract the residual monomers. The sample is then centrifuged to precipitate the polymer, and the supernatant solution is injected into the GC. Some polymers such as vinyl-acrylic copolymers dissolve in the solvent and form a thick syrup. Although headspace analysis might be a cleaner way to analyze this type of sample, quantitation is simplified by injecting the viscous solution directly into a split/splitless capillary injector [*2*,*3*]. Figure 3 shows a chromatogram of residual monomers in a latex emulsion containing several monomers. The methacrylic acid peak shows very little tailing, indicating that there is minimum interaction with residual silanol groups on the silica surface. The analysis of residual vinyl acetate and acrylonitrile are done on a 14% cyanopropylphenyl-86% methylpolysiloxane capillary column using a split/splitless injection. Figure 4 shows a chromatogram resulting from the injection of a vinyl acetate-butyl acrylate copolymer dissolved in acetone. This column has the proper selectivity to resolve these low boiling monomers from the solvent peak. The detection limit of monomers in a latex using these methods is approximately 10 ppm.

Aromatics in Mineral Spirits

Quantitating the amount of aromatics in mineral spirits is very important in the paint industry. Many properties of alkyd paint, such as viscosity, are affected by the aromatic content of the mineral spirits used. Two commonly used mineral spirits are the VM&P 50 flash naphtha and 140 flash naphtha. The determination of the aromatic content of VM&P



CHROMATOGRAPHIC CONDITIONS:

30 meter X 0.53 mm DB-WAX Column

Film thickness: 1.0 micron

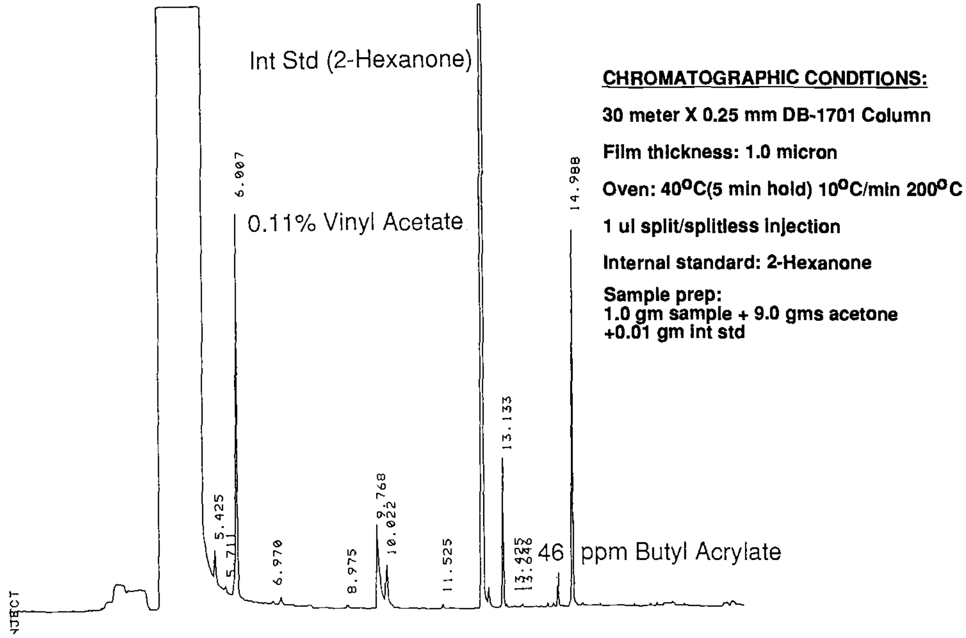
Oven: 50°C(2 min hold) 10°C/min 210°C

Injection volume: 1.0 ul

Internal standard: Cellosolve acetate

Sample prep:
1.0 gm sample + 9.0 gms acetone
+0.01 gm int std

FIG. 3—*Gas chromatogram of residual monomers in a latex emulsion.*



CHROMATOGRAPHIC CONDITIONS:

30 meter X 0.25 mm DB-1701 Column

Film thickness: 1.0 micron

Oven: 40°C(5 min hold) 10°C/min 200°C

1 ul split/splitless injection

Internal standard: 2-Hexanone

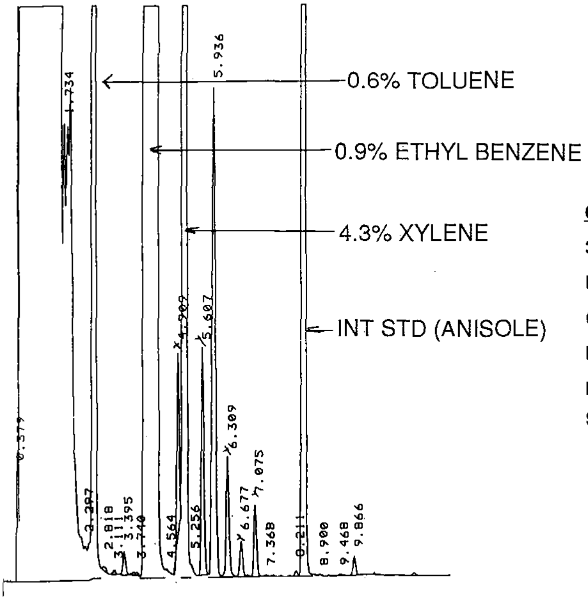
Sample prep:
1.0 gm sample + 9.0 gms acetone
+0.01 gm int std

FIG. 4—*Gas chromatogram of residual monomers in a latex emulsion.*

50 flash naphtha is straightforward because the light aliphatics can easily be separated from the higher boiling aromatics (Fig. 5).

The analysis of aromatics in 140 flash mineral spirits is more difficult because the boiling range of the aromatics overlap with that of the aliphatics. The 140 flash mineral spirits are composed mostly of straight and branched aliphatic hydrocarbons ranging from C_9 to C_{12}. Interdispersed in the envelope of aliphatic peaks are the aromatics. The analysis of 140 flash naphtha is traditionally done on a packed column containing a high loading of a very polar stationary phase such as n,n-bis(2-cyanoethyl) formamide, which will selectively retain the aromatics over the aliphatic hydrocarbons [ASTM Test Method for Aromatics in Mineral Spirits by Gas Chromatography (D 3257)—Fig. 6]. The total aromatic content is determined by summing the areas of all the aromatic compounds from toluene to the added internal standard, cyclohexanone. The chromatographic conditions used are optimized for the class separation of aliphatics and aromatics. Because this is an isothermal analysis, the run time is long, peaks are broad, and the aromatic compounds are not totally resolved from each other.

It is desirable to be able to characterize the aromatic portion of mineral spirits in more detail whereby the individual aromatics can be resolved and quantitated. Paint performance can then be correlated not only with the total aromatic content, but also with the concentration of individual aromatic compounds. The individual aromatics can be separated from the aliphatics by multidimensional GC [*4*]. Alternatively, quantitation of the aromatics can be accomplished in a two-step process using existing equipment. The aromatics are first separated from the aliphatics on a high performance liquid chromatographic (HPLC) silica column [*5,6*]. The aromatic fraction from the HPLC column is then injected into the GC for a detailed aromatic analysis. An internal standard, hexamethylbenzene, is first added to the mineral spirits. The mineral spirits is then injected into an HPLC silica column using hexane as the mobile phase to separate the aromatics from the aliphatics. Elution of the



CHROMATOGRAPHIC CONDITIONS:

30 meter X 0.53 mm DB-WAX Column

Film thickness: 1.0 micron

Oven: 40°C(2 min hold) 6°C/min 210°C

Injection volume: 0.05 ul

Internal standard: Anisole

Sample prep: 14 gm sample + 0.1 gm int std

FIG. 5—*Aromatic analysis of 50 flash VM&P naptha by gas chromatography.*

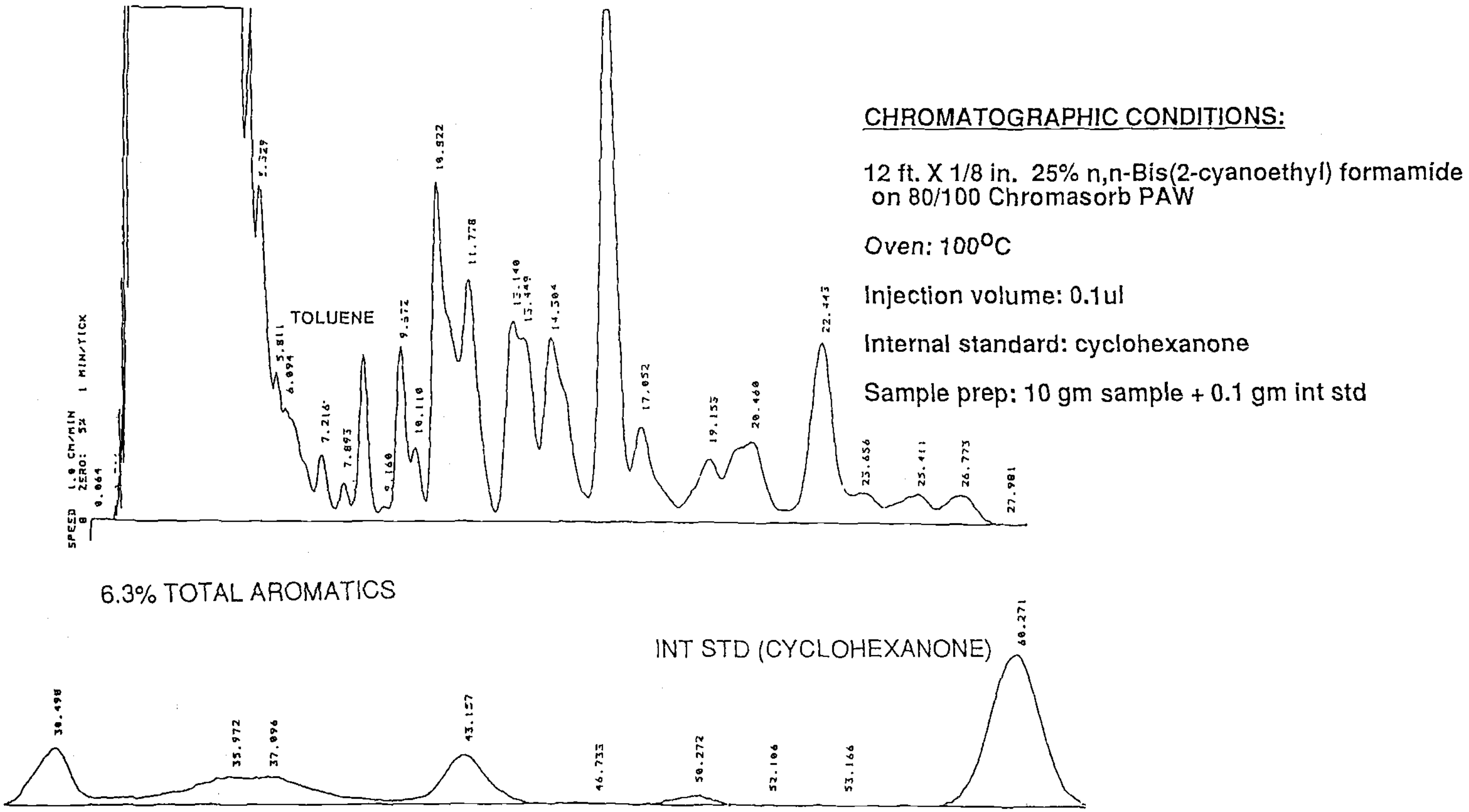
aromatics is monitored with a UV detector set at 254 nm. The aromatic fraction collected from the HPLC column is injected into the GC, which is optimized for the analysis of the aromatics (Fig. 7). This method is not only able to determine a total aromatic content, but it can also quantitate individual aromatic components [7].

Raw Material Characterization

GC is commonly used to characterize raw materials. ASTM methods exist for the analysis of fatty acids [ASTM Test Method for Fatty Acid Composition by Gas-Liquid Chromatography of Methyl Esters (D 1983)], polyhydric alcohols [ASTM Test Method for Monopentaerythritol in Commercial Pentaerythritol (D 2999)], oils [ASTM Method for Preparation of Methyl Esters from Oils for Determination of Fatty Acid Composition by Gas Chromatography (D 2800)] and the characterization of alkyd resins [ASTM Method for Identification of Carboxylic Acids in Alkyd Resins (D 2455) and ASTM Method for Identification Polyhydric Alcohols in Alkyd Resins (D 2456)]. Many of these methods involve making the methyl ester or trimethyl silyl (TMS) ether of the acid or alcohol prior to GC analysis. Figure 8 shows a gas chromatogram of a soya fatty acid chromatographed directly without making the methyl ester of the fatty acid. Because no derivatization procedure is involved, the analysis is much faster. The fatty acid is simply diluted in acetone and heptadecanoic acid added as the internal standard. A 30-m by 0.53-mm I.D. polyethylene glycol capillary column is used with an oven temperature at 200°C isothermal. All of the C_{16} and saturated and unsaturated C_{18} free fatty acids are resolved in about 30 min with good gaussian-shaped peaks.

Surfactant Characterization

Surfactants play a major role in the coatings industry. Surfactants are used in latex polymerization, in dispersing pigments and colorants, and in paint formulations. Although the



CHROMATOGRAPHIC CONDITIONS:

12 ft. X 1/8 in. 25% n,n-Bis(2-cyanoethyl) formamide on 80/100 Chromasorb PAW

Oven: 100°C

Injection volume: 0.1ul

Internal standard: cyclohexanone

Sample prep: 10 gm sample + 0.1 gm int std

FIG. 6—*Aromatic analysis of 140 flash mineral spirits using ASTM D 3257 GC method.*

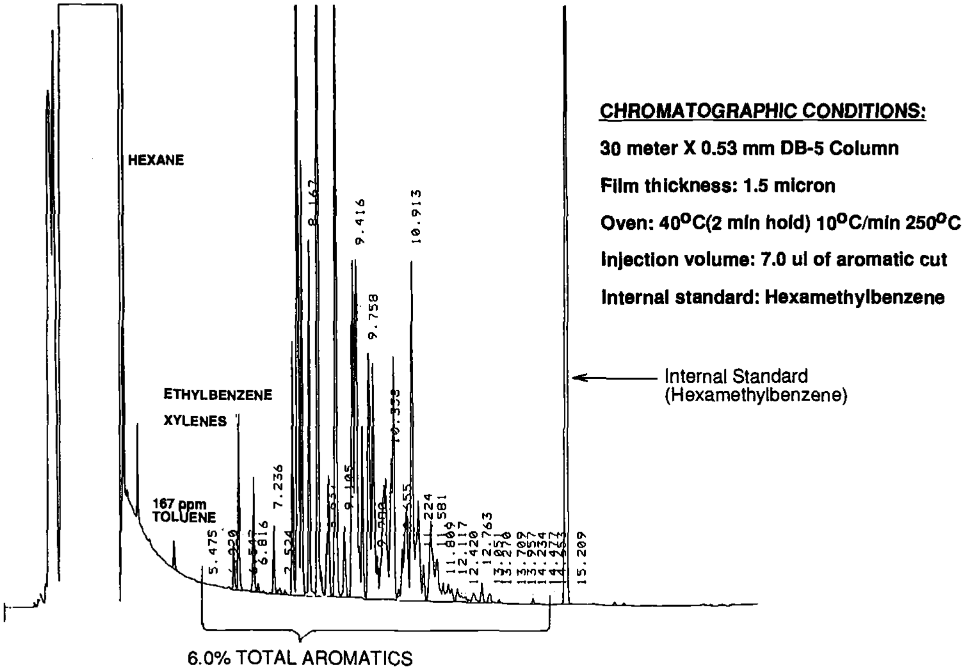


FIG. 7—*Gas chromatogram of aromatic cut taken from HPLC silica column.*

whole spectrum of surfactants is better characterized by HPLC and thin layer chromatography (TLC) [*8–11*], GC can be used for analysis of low molecular weight nonionic surfactants without derivatization [*12*]. GC has been used to specifically identify which surfactant was present in a colorant after an infrared analysis of the acetone extract indicated that an ethoxylated alkyl phenol was present. Gas chromatograms of a low molecular weight ethox-

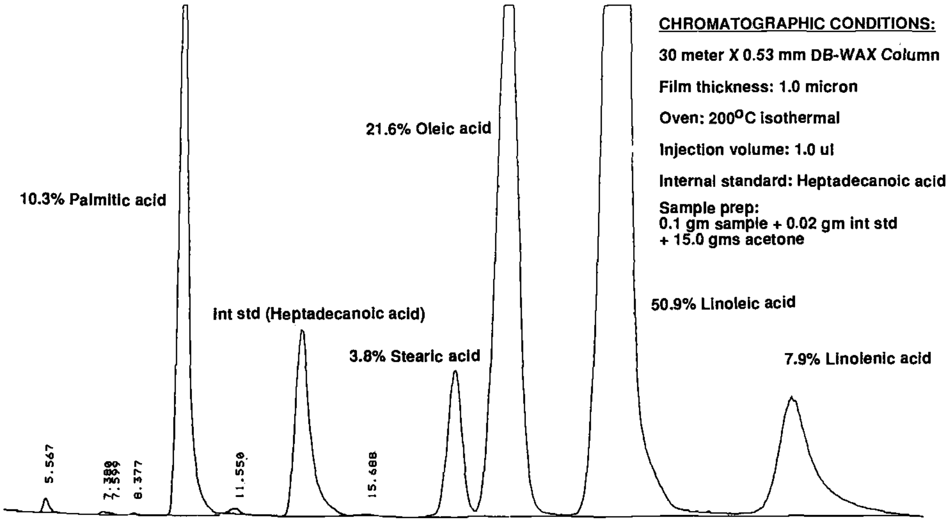


FIG. 8—*Compositional analysis of fatty acids by gas chromatography.*

ylated octylphenol and nonylphenol are shown in Fig. 9. The chromatogram of the ethoxylated octylphenol shows one peak for each additional ethylene oxide unit in the molecule, while the ethoxylated nonylphenol shows several peaks for each additional ethylene oxide unit. The multiple peaks found in the chromatogram of the ethoxylated nonylphenol are attributed to the branched isomers of the C_9 alkyl chain [*13*]. The gas chromatographic analysis of the colorant was able to identify if an ethoxylated octylphenol or nonylphenol was used and the degree of ethoxylation.

Characterization of Waxes

GC works well for the quantitation and characterization of waxes used in hardboard and waterproofing products. Figure 10 shows the chromatograms of two waxes which were Soxhlet extracted from two different brands of hardboard. Waxes in hardboard have the tendency to migrate through the factory-primed surface and top-coated paint to form a stained surface. Infrared analysis of the stain indicated that it is an aliphatic hydrocarbon. GC analysis indicated that the material is composed of low molecular weight aliphatic hydrocarbons. Figure 10 shows a high bleed wax with a very broad molecular weight distribution. This wax has a higher concentration of low and high molecular weight hydrocarbons. The hardboard manufactured with this broad molecular weight wax was more prone to wax bleed. This was attributed to the higher concentration of low molecular weight hydrocarbons, which tend to migrate easily. The chromatogram shows that the high molecular weight hydrocarbons are still eluting from the GC column after holding the temperature for 15 min at the upper temperature limit of the column of 310°C. A shorter and narrower column with a low film thickness would have reduced the analysis time and sharpened the late eluting hydrocarbon peaks.

Identification of Odor Problems

GC-MS of head-space samples is most appropriate for the identification of odor problems. The solid or liquid sample in question is placed in a 30-mL serum vial; then the vial is

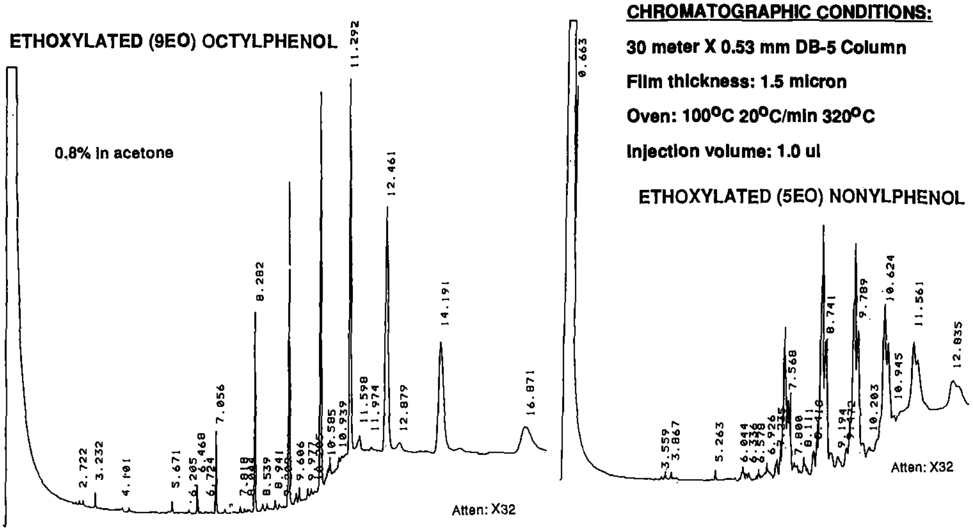
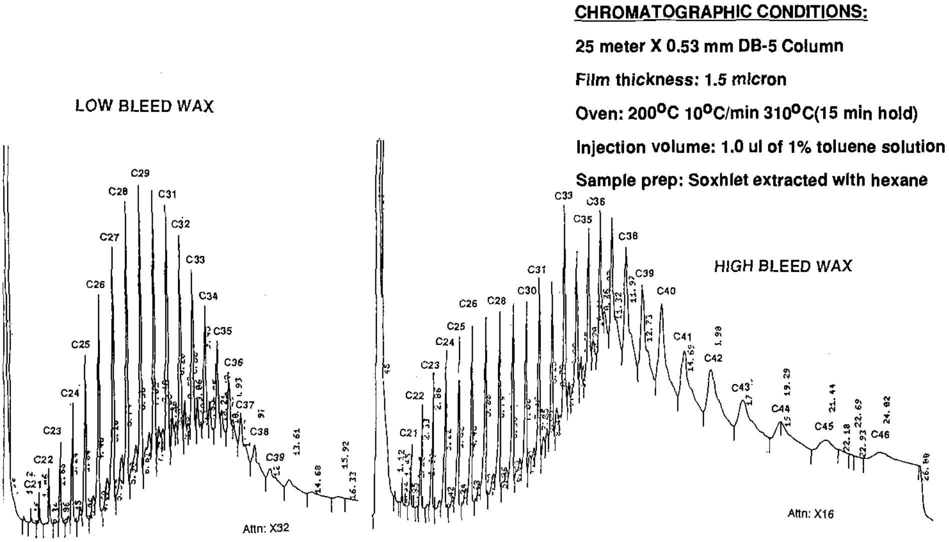


FIG. 9—*Characterization of nonionic surfactants by gas chromatography.*



CHROMATOGRAPHIC CONDITIONS:

25 meter X 0.53 mm DB-5 Column

Film thickness: 1.5 micron

Oven: 200°C 10°C/min 310°C(15 min hold)

Injection volume: 1.0 ul of 1% toluene solution

Sample prep: Soxhlet extracted with hexane

FIG. 10—*Gas chromatograms of waxes Soxhlet extracted from hardboard.*

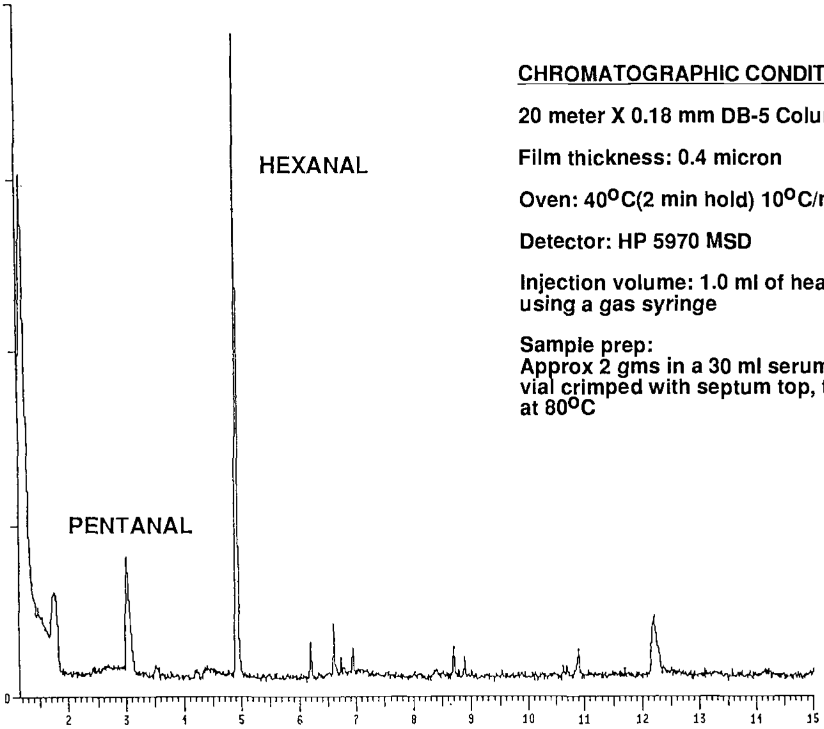
crimped with a septum top and thermostated at 80°C in order to enrich the volatiles into the headspace. A sample of the headspace is then injected into the GC-MS using a gas syringe. This technique was used when a customer complained about odors persisting several weeks after application of an alkyd paint. A sample of the cured paint was taken from the wall and placed in a crimped serum vial and thermostated at 80°C. The volatiles in the headspace consisted mostly of hexaldehyde and other aldehydes (Fig. 11). Aldehydes are natural degradation products from the autoxidation and subsequent chain scission of the fatty acids in the alkyd resin [*14*]. In this instance the surface had to be primed and topcoated with a latex paint to seal in the vapors.

Identification of Solvent Contamination via Headspace Analysis

Headspace analysis is not only used for odor complaints. Headspace analysis can be used in cases were the sample cannot be diluted with a solvent. A headspace analysis was performed on an alkyd stain which was suspected to have been adulterated with a lacquer thinner. The headspace from the field sample along with a retain of the alkyd stain was analyzed by GC-MS (Fig. 12). The total ion chromatogram (TIC) of the headspace from the field sample clearly shows the presence of acetone and toluene, which are not found in the retain. In this case the sample could not be diluted for liquid injection because the solvent used to dilute the sample would have masked the solvents being detected.

Quantitation of Mildewcides

Mildewcides are commonly added to coatings in order to prevent mildew growth in humid environments. Many of the mildewcides can be volatilized in a gas chromatograph and quantitated. Figure 13 shows the chromatographic analysis of a mildewcide in a wood preservative stain. Several months after application of this product, mildew growth started. A retain sample of the wood stain was analyzed by GC and found to contain a third of the required mildewcide. The wet sample was analyzed by dispersing it in methanol, adding



CHROMATOGRAPHIC CONDITIONS:

20 meter X 0.18 mm DB-5 Column

Film thickness: 0.4 micron

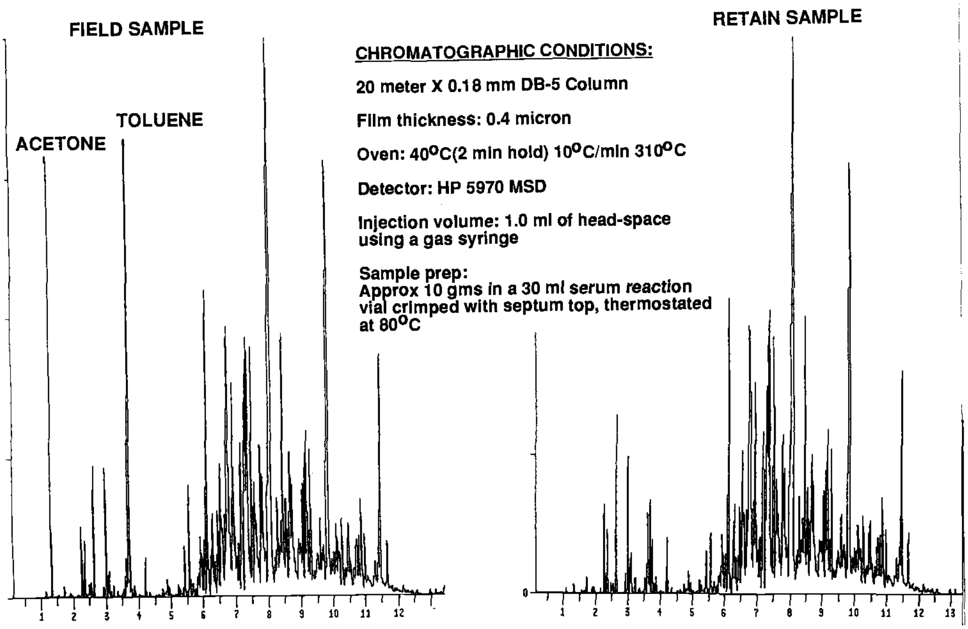
Oven: 40°C(2 min hold) 10°C/min 310°C

Detector: HP 5970 MSD

Injection volume: 1.0 ml of head-space using a gas syringe

Sample prep:
Approx 2 gms in a 30 ml serum reaction vial crimped with septum top, thermostated at 80°C

FIG. 11—*Total ion chromatogram of volatiles evolved from a cured alkyd paint.*



CHROMATOGRAPHIC CONDITIONS:

20 meter X 0.18 mm DB-5 Column

Film thickness: 0.4 micron

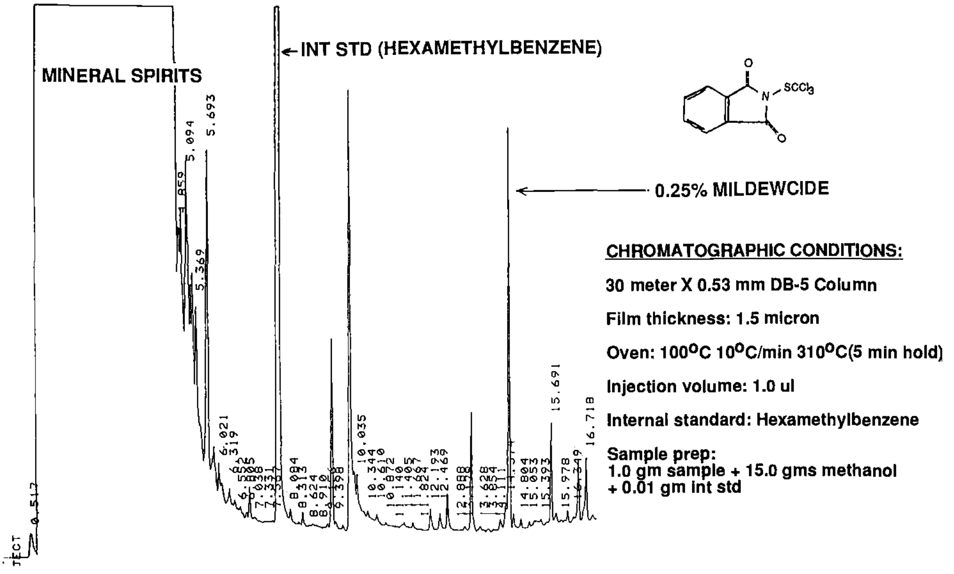
Oven: 40°C(2 min hold) 10°C/min 310°C

Detector: HP 5970 MSD

Injection volume: 1.0 ml of head-space using a gas syringe

Sample prep:
Approx 10 gms in a 30 ml serum reaction vial crimped with septum top, thermostated at 80°C

FIG. 12—*Total ion chromatogram of the headspace from an alkyd stain.*



CHROMATOGRAPHIC CONDITIONS:

30 meter X 0.53 mm DB-5 Column

Film thickness: 1.5 micron

Oven: 100°C 10°C/min 310°C(5 min hold)

Injection volume: 1.0 ul

Internal standard: Hexamethylbenzene

Sample prep:
1.0 gm sample + 15.0 gms methanol
+ 0.01 gm int std

FIG. 13—*Mildewcide analysis of a wood preservative stain by gas chromatography.*

hexamethylbenzene as the internal standard, centrifuging to precipitate the alkyd resin, and injecting the supernatant solution into the GC. The relatively nonvolatile mildewcide is well resolved from any interference from the mineral spirits.

Characterization of Polymers and Other Material Using Pyrolysis-GC-MS

Pyrolysis-GC-MS plays a key role in resolving customer complaints and characterizing polymeric material. The technique yields a wealth of information quickly and easily. Much work has been published using pyrolysis-GC for the determination of monomer ratios in acrylic and vinyl-acrylic copolymers [*15–21*]. Pyrolysis is very dependent on sample size, flow rates, and temperatures. The monomer yield found in a pyrogram of a polymer is dependent on the type and concentration of other monomers present. Obtaining quantitative information from pyrolysis-GC is extremely difficult. Quantitative information obtained from IR and NMR can be used to complement the qualitative information obtained through pyrolysis-GC-MS. Pyrolysis-GC-MS can be used for the analysis of wet or dry samples. Wet paint samples can be tetrahydrofuran (THF) extracted and a few microlitres of the supernatant solution applied to the platinum ribbon probe. The THF is evaporated by elevating the probe temperature to 150°C for 2 min. The probe is then inserted into the interface box at the head of GC injector and pyrolyzed instantaneously at 700°C for 10 s. Solid paint chips can be pyrolyzed by placing a few tenths of a milligram in a quartz tube in a coiled platinum probe and pyrolyzing instantaneously at 800°C for 10 s.

Pyrolysis is also a very sensitive technique. Many times very small quantities of sample have to be carefully abstracted from multilayer paint chips under an optical microscope. Pyrolysis-GC-MS and microinfrared spectroscopy are excellent complementary techniques for microanalysis.

It is important to understand the mechanism of thermal degradation during pyrolysis in order to properly interpret a pyrogram. The mechanism of pyrolysis follows generally three distinct paths: (*a*) depolymerization known as unzipping; (*b*) random chain rupture; and (*c*) nonchain scission [*20,21*]. The unzipping process (Fig. 14) involves a free radical chain reaction which results in the production of monomers. Alpha substituted vinyl polymers degrade during pyrolysis mostly through this process. Poly(methyl methacrylate), on pyrolysis, is converted to its monomer almost completely. The steric hindrance of the methyl group in the alpha position prevents the adjacent hydrogen from quenching the free radical and therefore stopping the depolymerization process. A copolymer of methyl methacrylate and butyl acrylate will not give the same monomer yields as a blend of poly(methyl methacrylate) and poly(butyl acrylate) in the same ratio as the copolymer. Since the rupture of the bonds is favorable to the sites of tertiary carbon atoms along the chain, the amount of methyl methacrylate produced on pyrolysis is an inverse function of the number of butyl acrylate-methyl methacrylate junctions.

Unsubstituted vinyl polymers having no quaternary carbon atoms degrade by random chain rupture (Fig. 15). The monomer yield is poor in such cases. The degradation products are a complex mixture of fragments.

When polar groups are present as the pendant group in the polymer, the nonchain scission process becomes predominant. This is due to an elimination reaction leading to unsaturation in the chain. Thus poly(vinyl chloride) can easily dehydrochlorinate to give a highly unsaturated structure. Decomposition of simple side chain esters occurs by way of a six-member ring transition state (Fig. 15). Poly(vinyl acetate) will yield acetic acid in a pyrogram.

Figure 16 shows a pyrogram of an acrylic polymer. The pyrogram clearly shows that the polymer is composed of methyl methacrylate, butyl acrylate, and vinyl toluene. Positive identification of all fragments are made by comparing their mass spectra to those in an in-house mass spectral library. The set of four peaks near the end of the pyrogram are unidentified, yet these peaks can be used as "fingerprint" peaks. These high molecular weight fragments are very unique to methyl methacrylate-butyl acrylate copolymers. The chromatographic conditions are always kept the same from one pyrolysis-GC-MS analysis to another in order that pyrograms can be easily compared.

Nonacrylic resins do not thermally decompose to their starting materials very well. Figure 17 shows a pyrogram of a urethane thickener. This thickener was made by reacting a

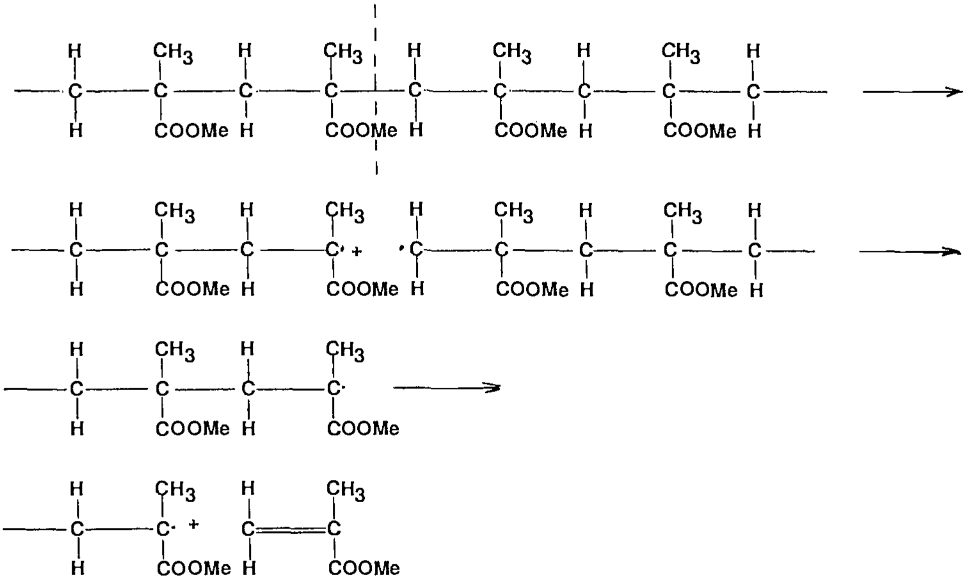


FIG. 14—*Degradation of poly(methyl methacrylate) via unzipping.*

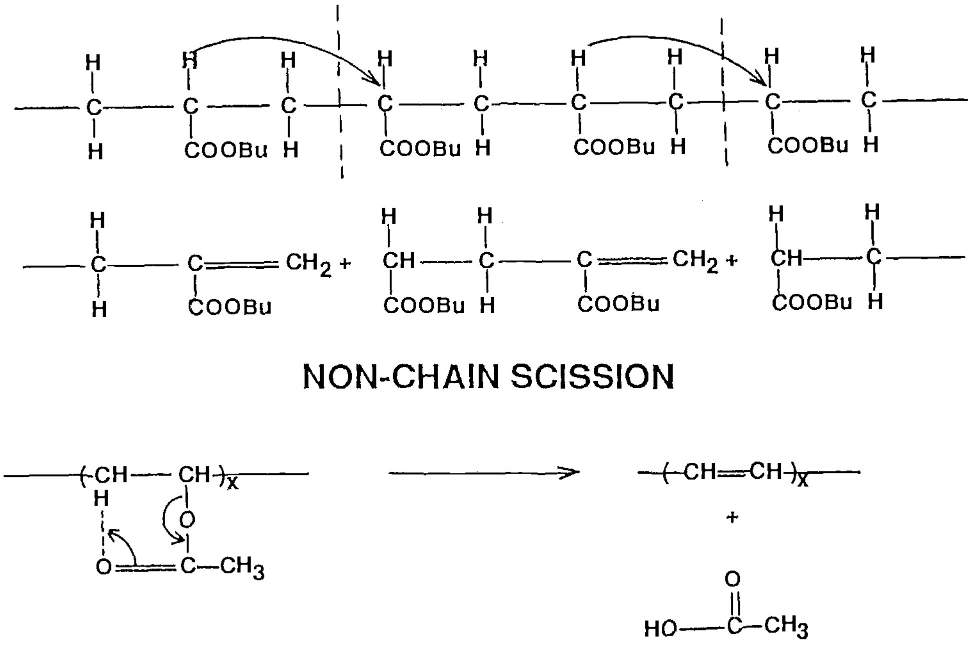
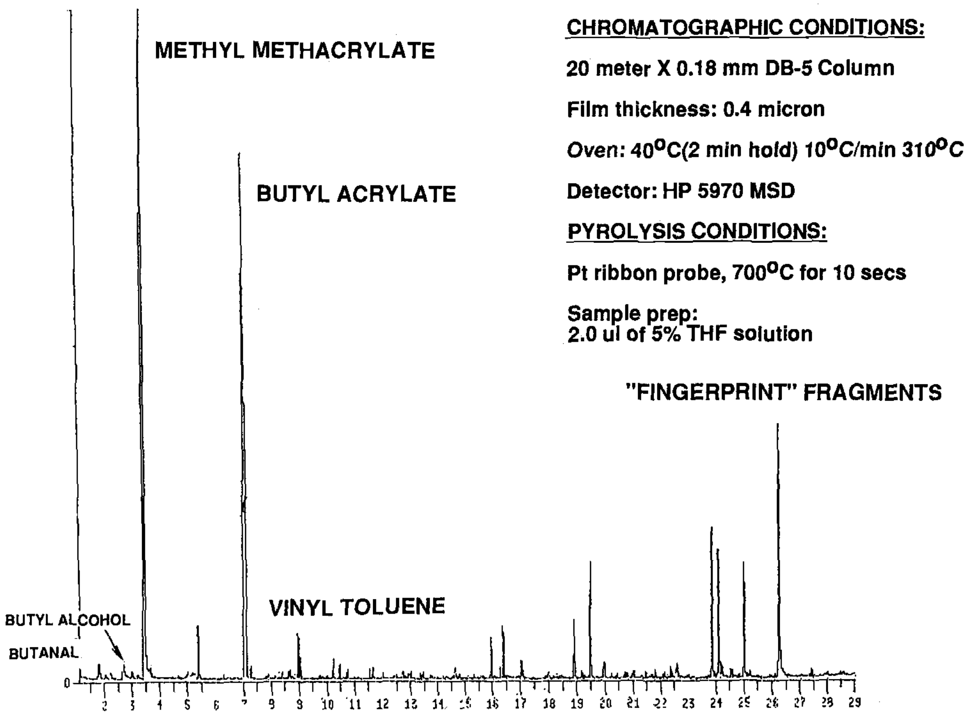


FIG. 15—*Degradation of poly(butyl acrylate) via random chain scission.*



CHROMATOGRAPHIC CONDITIONS:

20 meter X 0.18 mm DB-5 Column

Film thickness: 0.4 micron

Oven: 40°C(2 min hold) 10°C/min 310°C

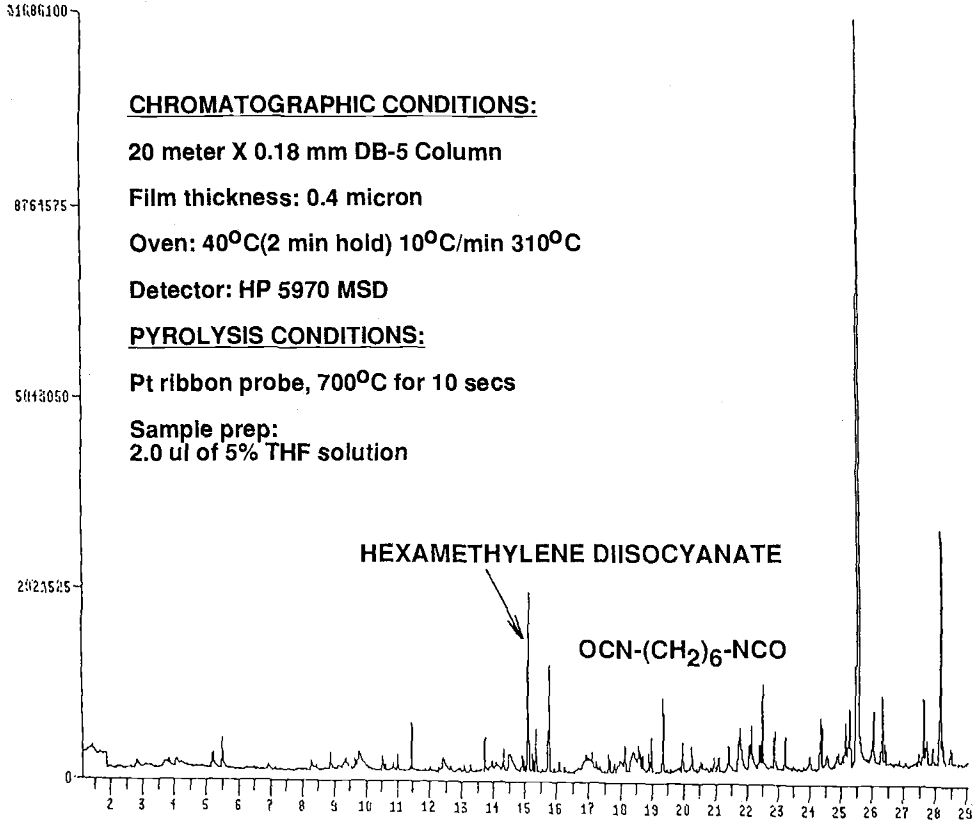
Detector: HP 5970 MSD

PYROLYSIS CONDITIONS:

Pt ribbon probe, 700°C for 10 secs

Sample prep:
2.0 ul of 5% THF solution

FIG. 16—*Pyrogram of an acrylic polymer.*



CHROMATOGRAPHIC CONDITIONS:

20 meter X 0.18 mm DB-5 Column

Film thickness: 0.4 micron

Oven: 40°C(2 min hold) 10°C/min 310°C

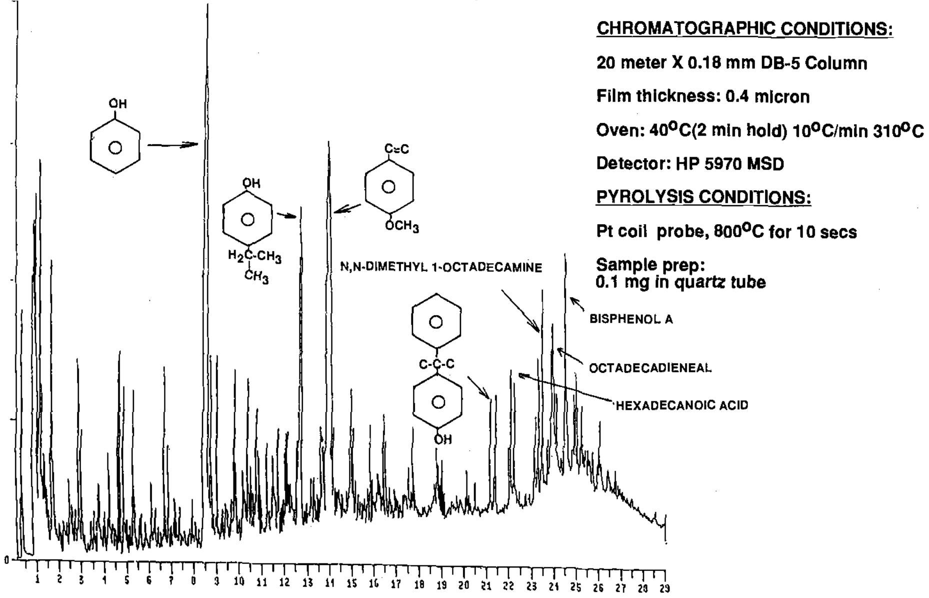
Detector: HP 5970 MSD

PYROLYSIS CONDITIONS:

Pt ribbon probe, 700°C for 10 secs

Sample prep:
2.0 ul of 5% THF solution

FIG. 17—*Pyrogram of a urethane thickener.*



CHROMATOGRAPHIC CONDITIONS:

20 meter X 0.18 mm DB-5 Column

Film thickness: 0.4 micron

Oven: 40°C(2 min hold) 10°C/min 310°C

Detector: HP 5970 MSD

PYROLYSIS CONDITIONS:

Pt coil probe, 800°C for 10 secs

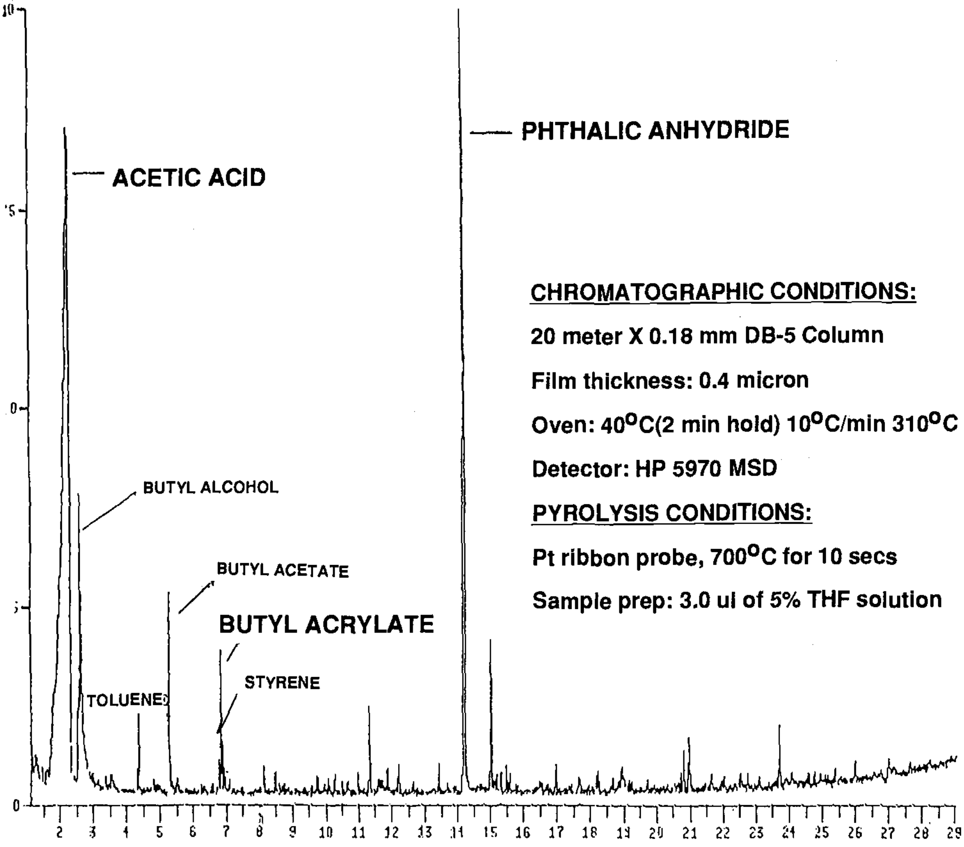
Sample prep:
0.1 mg in quartz tube

FIG. 18—*Pyrogram of a cured epoxy resin.*

diisocyanate with a high molecular weight polyethylene glycol (PEG). As can be seen from the pyrograms, the diisocyanate yield is very low. Many of the other fragments found in the pyrogram are PEG related. Figure 18 shows a pyrogram of a dried epoxy paint chip. The pyrogram consists mostly of fragments due to the decomposition of the epoxy diglycidyl ether resin made from epichlorohydrin and bisphenol A.

Figure 19 shows a pyrogram of a THF extract of a latex paint. The pyrogram clearly indicates that the paint is a vinyl acetate-butyl acrylate copolymer. The acetic acid in the pyrogram is due to the presence of the vinyl acetate. Butyl alcohol and butyl acetate are commonly detected when butyl acrylate is present. The presence of phthalic anhydride in the pyrogram indicates that the paint is alkyd modified. If a solvent analysis was performed on this latex paint, mineral spirits would also be detected, corroborating the presence of the alkyd.

Figure 20 shows a pyrogram of a paint chip. The major fragment in the pyrogram is phthalic anhydride. Also found are C_{16} and C_{18} saturated and unsaturated acids, benzoic acid, and low molecular weight acids and aldehydes. All these fragments are indicative of an alkyd resin. Also found in the pyrogram is the mildewcide used in the paint. Very often compounds found in the pyrogram are not thermal decomposition fragments. Often compounds with a low vapor pressure remain on the probe after drying. These compounds are vaporized faster than they thermally decompose when instantaneously heated to 700 or 800°C.



CHROMATOGRAPHIC CONDITIONS:

20 meter X 0.18 mm DB-5 Column

Film thickness: 0.4 micron

Oven: 40°C(2 min hold) 10°C/min 310°C

Detector: HP 5970 MSD

PYROLYSIS CONDITIONS:

Pt ribbon probe, 700°C for 10 secs

Sample prep: 3.0 ul of 5% THF solution

FIG. 19—*Pyrogram of a THF extract of a latex paint.*

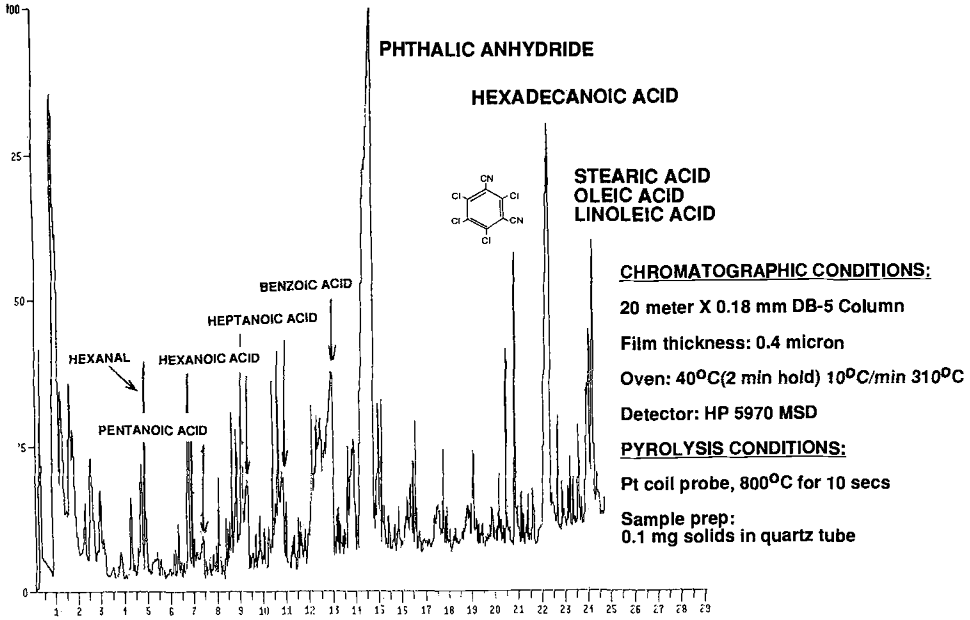


FIG. 20—*Pyrogram of a dried paint chip.*

Figure 21 shows the pyrogram of the nonvolatile material from an exterior waterproofing coating. Some mineral spirits are present because the sample was not completely dried. Also found in the pyrogram is paraffin wax. The wax peaks are not fragments due to pyrolysis. The paraffin wax was later quantitated on a 0.53 mm I.D. 5% phenyl-95% methylpolysiloxane capillary column using eicosane ($C_{20}H_{42}$) as an internal standard. Also found in the

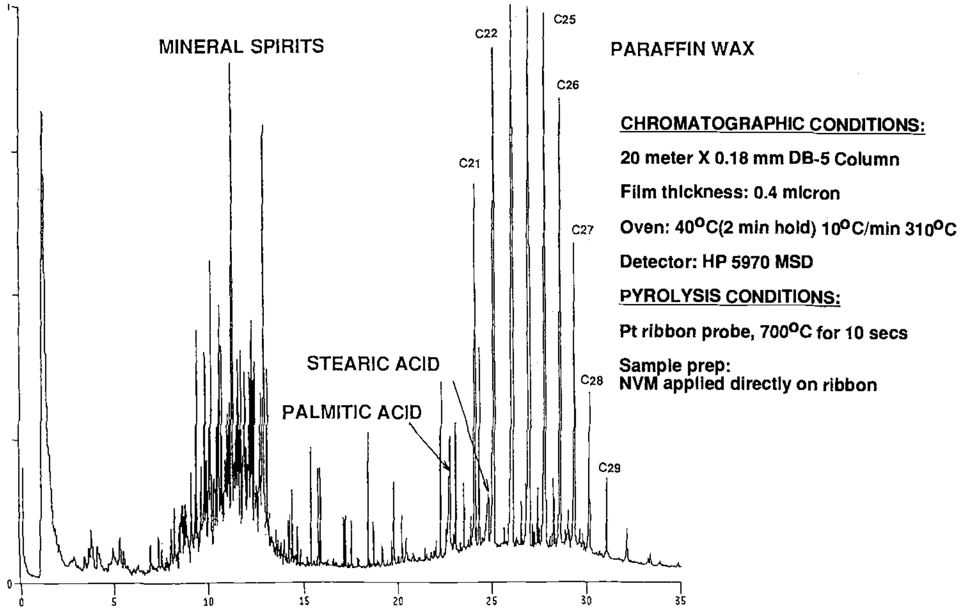


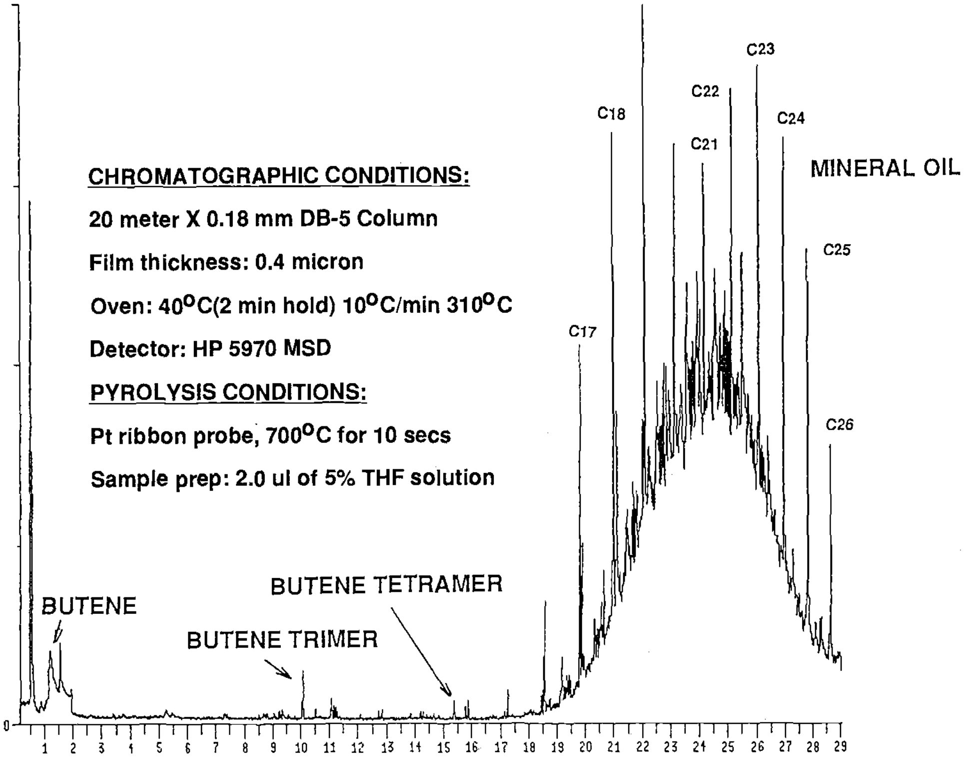
FIG. 21—*Pyrogram of nonvolatile material (NVM) from an exterior waterproofing coating.*

pyrogram are palmitic and stearic acids. These compounds were not attributed to the presence of an alkyd resin because no unsaturated C_{18} acids or phthalic anhydride were present. An EDXRS analysis of the ash of this material indicated the presence of aluminum. The infrared spectrum of the hexane-washed nonvolatile material was that of aluminum stearate. This is an example where elemental analysis, IR, and pyrolysis-GC-MS were all used to confirm the composition of a product.

Figure 22 shows a pyrogram of another waterproofing product. This product contained a mineral oil instead of a wax. Also found in the pyrogram are butene, butene trimer, and tetramer. These fragments are characteristic of polybutene. The exact molecular weight polybutene used in this product was later determined by gel permeation chromatography (GPC). Figure 23 shows the pyrogram of polybutene (butene-isobutene copolymer). The pyrogram shows a large amount of butene, butene trimer, tetramer, etc. The oligomers illustrated in this pyrogram are very characteristic of polyolefins [22]. This series is due to the random chain scission mechanism.

Summary

Gas chromatography is a versatile technique for the quantitative and qualitative analysis of coatings. It can be used to monitor the quality of raw materials as well as resolve factory and field complaints. GC method development is relatively rapid, especially when compared to HPLC. Pyrolysis-GC-MS is a quick and powerful tool for the characterization of polymers.



CHROMATOGRAPHIC CONDITIONS:

20 meter X 0.18 mm DB-5 Column

Film thickness: 0.4 micron

Oven: 40°C(2 min hold) 10°C/min 310°C

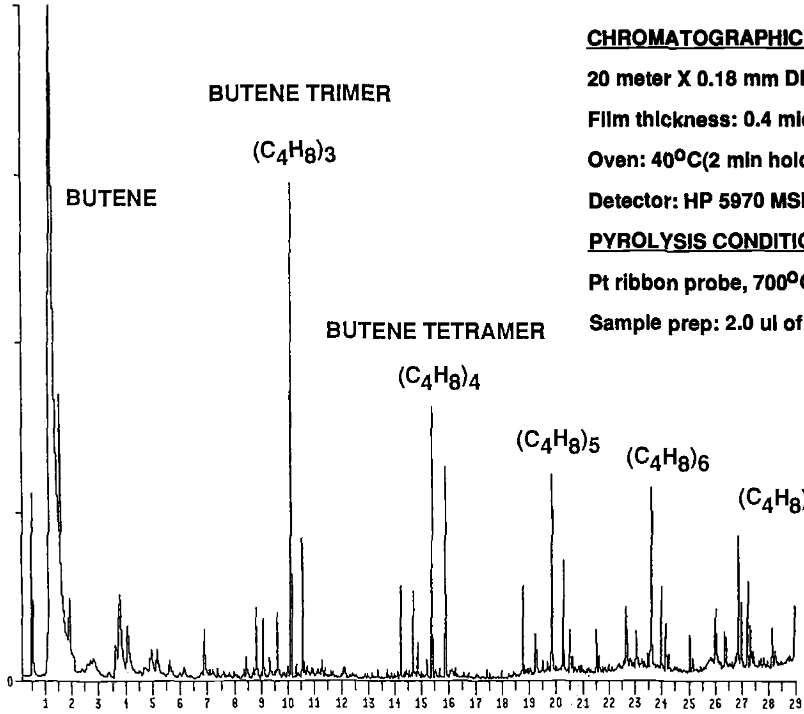
Detector: HP 5970 MSD

PYROLYSIS CONDITIONS:

Pt ribbon probe, 700°C for 10 secs

Sample prep: 2.0 ul of 5% THF solution

FIG. 22—*Pyrogram of NVM from an exterior waterproofing coating.*



CHROMATOGRAPHIC CONDITIONS:

20 meter X 0.18 mm DB-5 Column

Film thickness: 0.4 micron

Oven: 40°C(2 min hold) 10°C/min 310°C

Detector: HP 5970 MSD

PYROLYSIS CONDITIONS:

Pt ribbon probe, 700°C for 10 secs

Sample prep: 2.0 ul of 5% THF solution

FIG. 23—*Pyrogram of polybutene.*

References

[*1*] Hinshaw, J. V., *LC-GC,* Vol. 8, No. 2, October 1989, pp. 104–114.

[*2*] Lattimer, R. P. and Pausch, J. B., *American Laboratory,* August 1980, pp. 80–88.

[*3*] Jones, E., Davis, M., Gibson, R., Todd, B., Wallen, R., *American Laboratory,* August 1984, pp. 74–81.

[*4*] Slack, R. W., Heim, A. C., and Goekeler, U. K., "Multidimensional High Resolution Gas Chromatography For Individual Component PNA Analysis in a Double Oven GC," Application Note 708, ES Industries, Marlton, NJ.

[*5*] Suatoni, J. C. and Swab, R. E., *Journal of Chromatographic Science,* Vol. 13, 1975, pp. 361–366.

[*6*] "Determination of Aromatics in Hydrocarbon Solvents by Gas Chromatograpy," Unocal Science and Technology Test Method No. 576–82, Unocal Chemical Research, Clark, NJ, January 1982.

[*7*] Young, F. X., "Determination of Aromatics in Hydrocarbon Solvents," Sherwin-Williams Internal Test Method No. 744.030, Sherwin-Williams Co., Cleveland, OH, March 1987.

[*8*] Jandera, P., *Liq. Chromatogr. Environ. Anal.,* 1984, pp. 115–167.

[*9*] Garti, N., Kaufman, V. R., and Aserin, A., *Surfactant Science Series (Nonionic Surfactants: Chemical Analysis),* Vol. 19, Marcel Dekker, New York, 1987, pp. 225–283.

[*10*] Rabel, F. M., *Surfactant Science Series (Nonionic Surfactants: Chemical Analysis),* Vol. 19, Marcel Dekker, New York, 1987, pp. 285–293.

[*11*] Gabriel, D. M. and Mulley, V. J., *Surfactant Science Series (Anionic Surfactants: Chemical Analysis),* Vol. 8, Marcel Dekker, New York, 1977, pp. 47–57.

[*12*] Cross, J., *Surfactant Science Series (Nonionic Surfactants: Chemical Analysis),* Vol. 19, Marcel Dekker, New York, 1987, pp. 169–172.

[*13*] Marcomini, A. and Walter, G., *Analytical Chemistry,* Vol. 59, No. 13, July 1987, pp. 1709–1715.

[*14*] J. M. Waldie, Ed., *Surface Coatings,* Vol. 1, Chapman and Hall, London, 1983, pp. 27–30.

[*15*] Haken, J. K. and McKay, T. R., *Analytical Chemistry,* Vol. 45, No. 7, June 1973, pp. 1251–1257.

[*16*] Evans, D. L., Weaver, J. L., Mukherji, A. K., and Beatty, C. L., *Analytical Chemistry,* Vol. 50, No. 7, June 1978, pp. 857–860.

[*17*] Strassburger, J., Brauer, G. M., Tryon, M., and Forziati, A. F, *Analytical Chemistry,* Vol. 32, No. 4, April 1960, pp. 454–457.
[*18*] Haken, J. K. and McKay, T. R., *Journal of Chromatography,* Vol. 80, 1973, pp. 75–79.
[*19*] Brauer, G. M., *Tech. Methods Polym. Eval.,* Vol. 2, 1970, pp. 75–86.
[*20*] Maiti, S., *Chromatogr. Polym., Pet. Petrochem.,* Pap. Symp. Workshop, 1978 (meeting date), 1979, pp. 221–253.
[*21*] McCormik, H., *Journal of Chromatography,* Vol. 40, 1969, pp. 1–15.
[*22*] Kiran, E. and Gillham, J. K., *Dev. Polym. Degradation,* Vol. 2, 1979, pp. 9–15.

Cure Characterization, Durability, and Coating Problems

Jack H. Hartshorn[1]

Applications of FTIR to Paint Analysis

REFERENCE: Hartshorn, J. H., "**Applications of FTIR to Paint Analysis,**" *Analysis of Paints and Related Materials: Current Techniques for Solving Coatings Problems, ASTM STP 1119,* American Society for Testing and Materials, Philadelphia, 1992, pp. 127–147.

ABSTRACT: The value of infrared spectroscopy to the coatings industry has long been recognized. Now Fourier transform infrared (FTIR) equipment is replacing dispersive instruments because it is much faster, more accurate, and more sensitive. Of even greater impact is its data processing capabilities. Together, these advances enable the paint analyst to generate information which would have been impossible a few years ago. Applications of this technique to problem solving, cure and weathering studies, and quality control will be reported.

The extraction and identification of minor components and contaminants is one of the most difficult and time-consuming problems for the coatings analyst. The computational power of the FTIR spectrometer permits the point-by-point subtraction of one spectrum from another. The differential spectrum reveals minor differences, which are the other components in the system. This spectral stripping detects constituents which would be difficult, if not impossible, to isolate by chemical means. If the samples are skillfully prepared and subtractions carefully performed, even the concentration can be estimated. Further, the differential spectrum can be identified via computer searching of spectral libraries. This makes problem solving, such as contaminant detection and identification, rapid and effective.

Another difficult task for the coatings chemist is determining the chemical mechanisms of cure, weathering, and degradation. FTIR is providing new, valuable information about these processes. By taking and storing high-precision spectra at frequent, regular intervals, a moving picture of the process can be recorded. We call this technique "Time Lapse IR spectroscopy." Changes in band intensity are an indication of the chemical reactions taking place within the film. These spectral shifts can be measured quantitatively so that not only the path but also the rate can be determined. Weathering studies are now being carried out after the development of a durable substrate. This provides a useful chemical picture of what is taking place during cure, weathering, or degradation.

FTIR will likely make its greatest contribution to the coatings industry as a quality assurance tool. Du Pont's Finishes Division has developed and deployed a unique instrumental package, called CATS© (Compositional Assurance Testing System). By combining a horizontal attenuated total reflectance (ATR) sampling attachment with a FTIR spectrometer and proprietary software, we have a most effective test for raw materials, intermediates, and finished products. An operator with minimum training can run the spectrum of an incoming material and decide on its acceptability within minutes. If the material is mislabeled or contaminated, it can further be identified and dealt with before a serious problem develops. This eliminates much wasted manufacturing time and material.

KEY WORDS: spectroscopy, infrared—Fourier transform, chemical analysis, coatings, cure measurement, durability measurement, quality assurance

Whenever one sets out to survey a topic as broad as the contributions of Fourier transform infrared (FTIR) to the analysis of paints and coatings, they are faced with a dilemma. Time and space do not permit a comprehensive treatise, so one must decide which topics to

---

[1] Research associate, E. I. du Pont de Nemours & Co., Marshall R & D Laboratory, P.O. Box 3886, Philadelphia, PA 19146.

address and which to ignore. Since there are several excellent comprehensive resources, another would add little to the subject. The best compendium on infrared's application to the coatings field is "An Infrared Spectroscopy Atlas For The Coatings Industry," published by the Federation of Societies for Coatings Technology, Philadelphia [*1*]. I understand this basic volume may be updated soon. In the interim, the field is abstracted regularly by biannual reviews published in *Analytical Chemistry*. A novice coatings spectroscopist can consult these resources for a complete literature review. When one limits their topic, they should then have some criterion for selection. I have chosen to draw upon my own experience and describe some applications developed within our own laboratory. I beg your indulgence if your favorite technique or application has not been included in this discussion since the following are the areas in which we have found Fourier transform infrared spectroscopy most useful at DuPont's Marshall Laboratory.

Historical Perspective

Infrared spectroscopy has had a very long history of contributions to the coatings industry. Its application at DuPont's Marshall R&D laboratory dates back some 40 years [*2*]. This was shortly after the introduction of the double beam dispersive infrared spectrometer. Many early investigators recognized that an infrared spectrum reveals much significant information about the nature and composition of solvents, binders, resins, polymers, cross-linkers, and additives used in paint systems. It is easy to simply spread a vehicle onto a rock salt plate, run the spectrum, and examine the bands. These bands are then indicative of the materials present and show what may be different about that material. These are the kind of questions paint formulators need their analytical laboratories to answer. So powerful and useful was this approach that within a few years no respectable coatings laboratory could be without this technique. In the early sixties some of us from leading coatings laboratories formed a committee to devise an ASTM method for infrared testing. That procedure, Test Method For Infrared Identification of Vehicle Solids From Solvent-Reduced Paints (D 2621-87), is still in use, essentially unchanged.

The technique at that time was not without its shortcomings. Dispersive infrared spectroscopy requires an appreciable amount of sample, and a complete spectrum takes 20 to 30 min to record. The amount of energy available in these instruments is limited so that attachments such as spectral reflectance and attenuated total reflectance are rather ineffective. Quantitation is difficult at best and requires very careful sample and standard preparation. Finally, spectral interpretation requires a great deal of experience and practice. Most paint spectroscopists eventually develop the ability to do pattern recognition rather than trying to rely on band assignments. Spectral libraries, such as the "Infrared Atlas for the Coatings Industry" [*1*], are extremely valuable for comparing peak position and intensity. However, the spectral contributions of minor components and contaminants are very difficult to detect and even more difficult to identify. These usually are the materials of greatest concern.

At the same time the analysis of paints was changing very rapidly. Paint formulations were becoming much more complex. New materials were being developed and used alone and in novel combinations so that traditional methods of separation and analysis were no longer effective. Infrared spectroscopy has contributed to our knowledge by evaluating how well these methods were working. However, these newer materials made interpretation more difficult since they were not included in standard spectral libraries. Meanwhile, the minor components have become much more important to the formulating chemists and much more difficult to detect. Other analytical techniques, such as gas chromatography, nuclear magnetic resonance, and mass spectrometry, were also becoming popular, so that infrared lost much of its glamour to these recent additions to the laboratory. However, its utility remained in spite of heightened expectations and the competition from newer instrumental methods.

Emergence of FTIR

In the mid-seventies a radically different approach to producing infrared spectra became commercially available. Interferometry, or Fourier transform spectrometry as it is popularly known, is much faster and more sensitive than the standard dispersive instrumentation. These advantages and their sources have been well documented [*3*]. This technique also produces a spectrum with much greater precision and reproducibility. These superior attributes are extremely useful to the coatings spectroscopist. Not only can spectra be produced faster with greater precision, but the instrument's capabilities can be readily expanded. Attachments, samples, and techniques which were too inefficient for use with the older instruments can now be employed routinely.

A digital computer is a necessary part of the spectrometer system and can perform tasks for the coatings analyst which were previously impossible. The sample is measured as an interferogram, digitized, and the spectrum calculated by the computer using the Fourier transform. This leaves the spectrum in digital form so that a variety of data processing operations can be employed. The spectrum can be readily stored and retrieved without a loss in precision or integrity. The computer executes a number of mathematical operations, such as smoothing, base line correction, scale expansion, peak height, and area quantitation. The most valuable is the ability to subtract one spectrum from another. This can be used to perform separations which can not be done chemically. The computer can also rapidly compare a spectrum with a whole library of reference spectra and display the most likely choices. This can be a great blessing to the fledgling spectroscopist. Finally, the computer can be preprogrammed to carry out nearly all the instrumental operations automatically. This allows the technician to concentrate on sample preparation and spectral interpretation. It also allows essentially "black box" operations by operators with minimum training. Applications of these computer-derived benefits will be the thrust of this paper.

Applications of FTIR to Routine Paint Problems

Every paint laboratory is confronted by crises. The analytical section is usually called upon to contribute to its resolution by answering questions like "What is this stuff?" and "Where did it come from?", "What's the matter with this batch?", and "Why is this different from what we expected?" These questions originate from throughout the organization—the formulators and polymer chemists, the plant support people, and customer service representatives. All these requests are important and require immediate attention. Infrared is usually the first step in planning the analytical attack since it provides the most qualitative information in the shortest amount of time with the least sample preparation. Fourier transform spectroscopy makes this process considerably easier because it allows the spectroscopist to obtain a useful spectrum from almost any material. We believe that we can get a spectrum from any amount of material which we can see and isolate. If the amount is too small to see with the unaided eye we cannot be sure we have it within the beam. Once a spectrum is acquired we know a lot about the material and can formulate a scheme to identify it, isolate it, determine its properties, and trace the problem to its source.

For example, a common problem results when a component separates while standing in the shipping container. Figure 1 shows the spectrum of such a "float" we found on the surface of a paint can. Using a micropipette, the material was drawn off and spread onto a

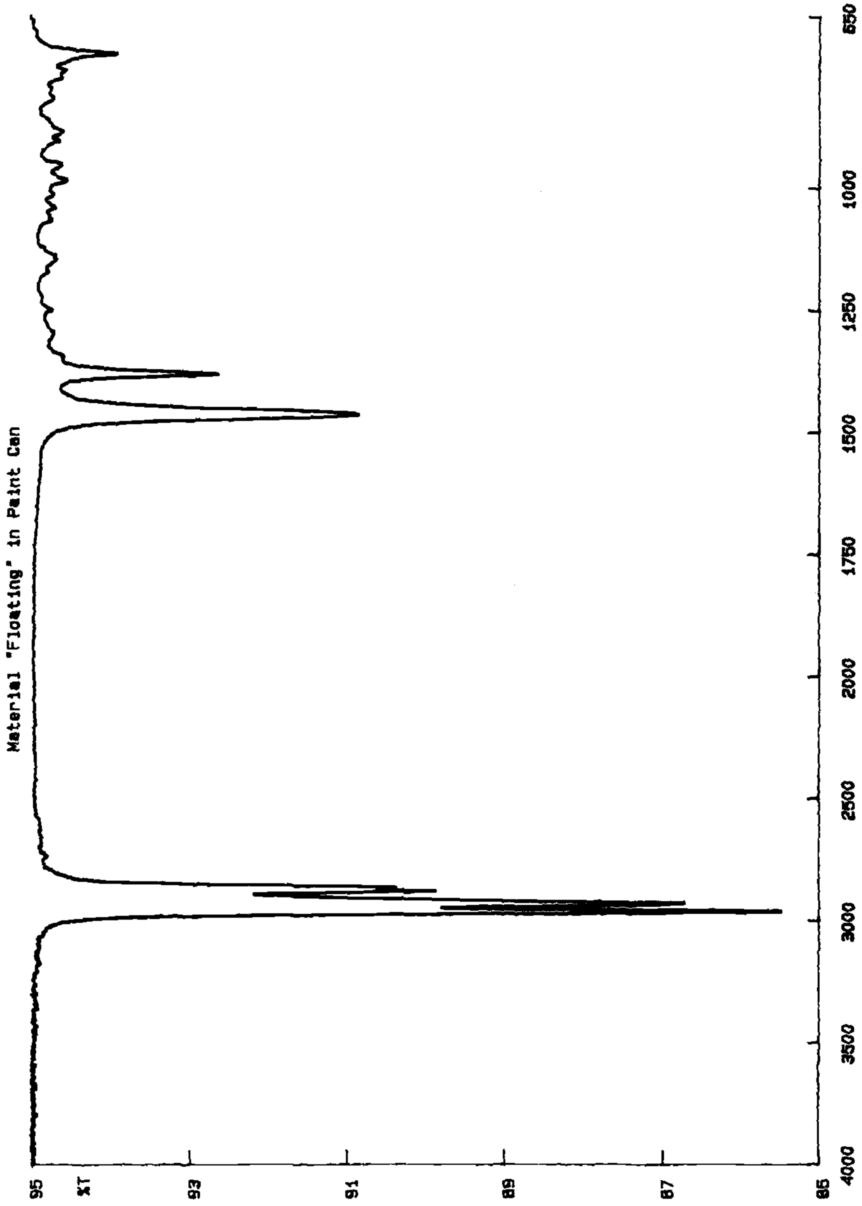


FIG. 1—*"Float" skimmed from paint can.*

potassium bromide (KBr) plate. Even though there was only a tiny amount of material, it was sufficient to produce a spectrum with about 10% absorption. Using scale expansion, it can be identified as mineral oil. This clue led to the discovery that a shipment of cans had not been adequately degreased.

Another common problem is the "scum" which develops on the surface of panels during exposure. It may be caused by an exudate from within the film or it might be deposited from the environment. The amount of material is very small and can easily be lost. By simply rinsing the panel with a solvent and evaporating the extract onto a plate the material can be transferred, examined, and identified. Figure 2 shows the spectrum of such an exudate. For those not familiar with infrared spectra, it is a polyester which was not supposed to be in that formula and represented a contaminant.

Difference Spectroscopy

Probably the most useful contribution of Fourier transform spectroscopy, as far as the coatings analyst is concerned, is its ability to remove known or unwanted components so as to reveal hidden or masked materials [*4*]. Spectral subtraction allows the analyst to perform separations which would be difficult and time consuming or even impossible by chemical means. Oldtimers may remember trying to place a matched film in the reference beam of a dispersive instrument in order to cancel out unwanted bands. I certainly was never able to make that technique work. Anyone who ever tried that procedure will readily appreciate modern FTIR instruments equipped with interactive subtracting programs. They allow the spectroscopist to dial in subtraction factors while watching their effects. The bands resulting from a component can be magically eliminated right before your eyes. Thus one can literally strip away portions of a complex mixture to reveal the components of interest. These can be the minor additives or contaminants or even subtle chemical variations. These are almost always the components of greatest interest.

A typical resin problem illustrates this subtraction approach. Occasionally a resin batch will not perform as expected. The assumption is that it is contaminated and if so with what. Figure 3 shows such a contaminated acrylic resin. When compared with a good lot of the resin we can see there is a spurious band at 700 cm^{-1} and a doublet near 1600 cm^{-1}. However, the source of that band is unknown, and it could be difficult to isolate that component for identification since we have no idea where it might originate. If we subtract the spectrum of a known "good" resin (3b) from that of the "bad" one (3a), we will reveal the spectrum of the contaminant (3c). The isolated spectrum is now recognizable as a phthalate plasticizer and matches the butyl benzyl phthalate reference. Total time required for this analysis is only a few minutes and is much less than if chemical separations were performed.

Spectral Searching

Fourier transform instruments usually offer spectral search algorithms as a part of their software package, either included or as an additional option. Several third party packages are also available. These can be very helpful to the coatings spectroscopist, particularly the novice. They provide a quick way to eliminate a great body of possibilities so that one can concentrate on the best fits in their quest to discover what an unknown spectrum is chemically. Several approaches, such as peak matching and vector analysis, have been employed; however, the objective is the same. They all endeavor to pick the best matches to an unknown spectrum from a spectral reference library database [*5*]. These libraries can be commercial collections from a third party or they may be generated internally. One deficiency in this

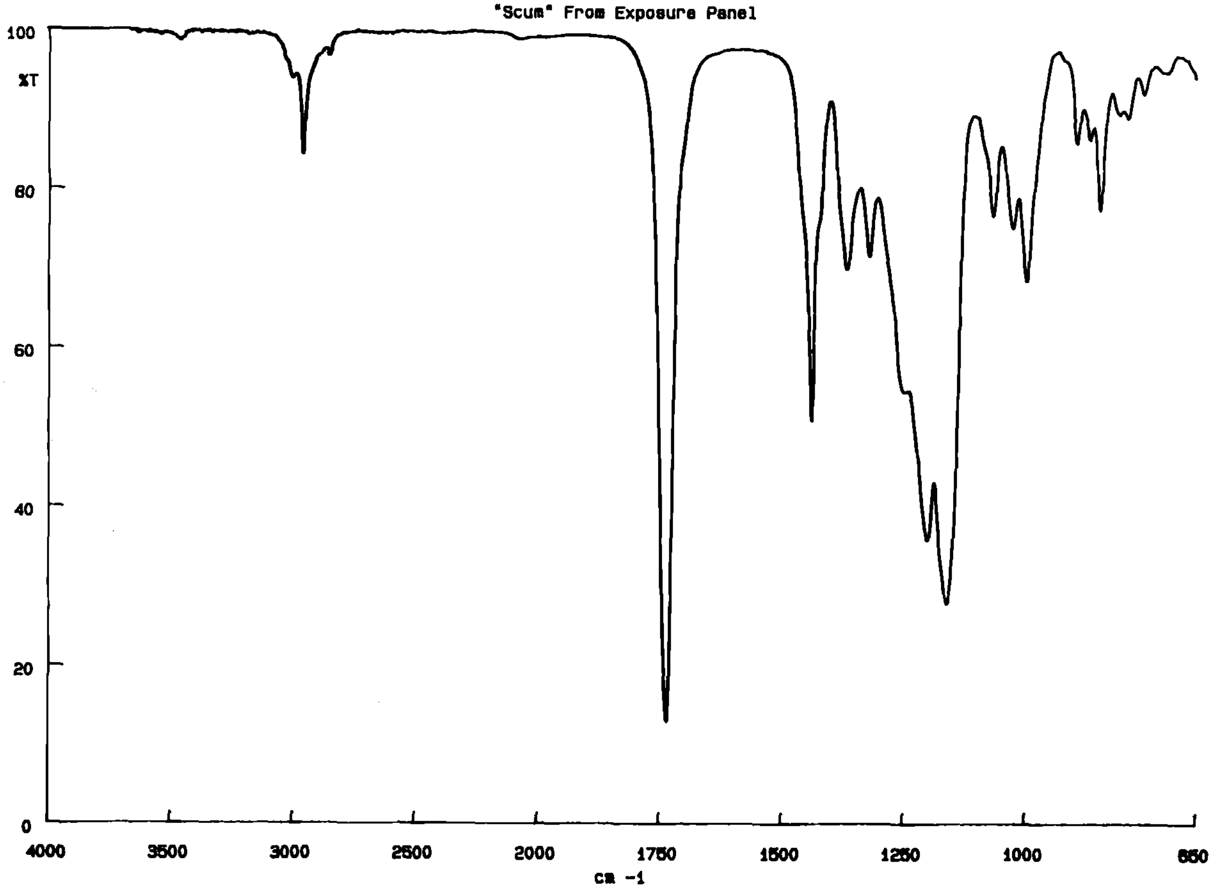


FIG. 2—*"Scum" rinsed from exposure panel.*

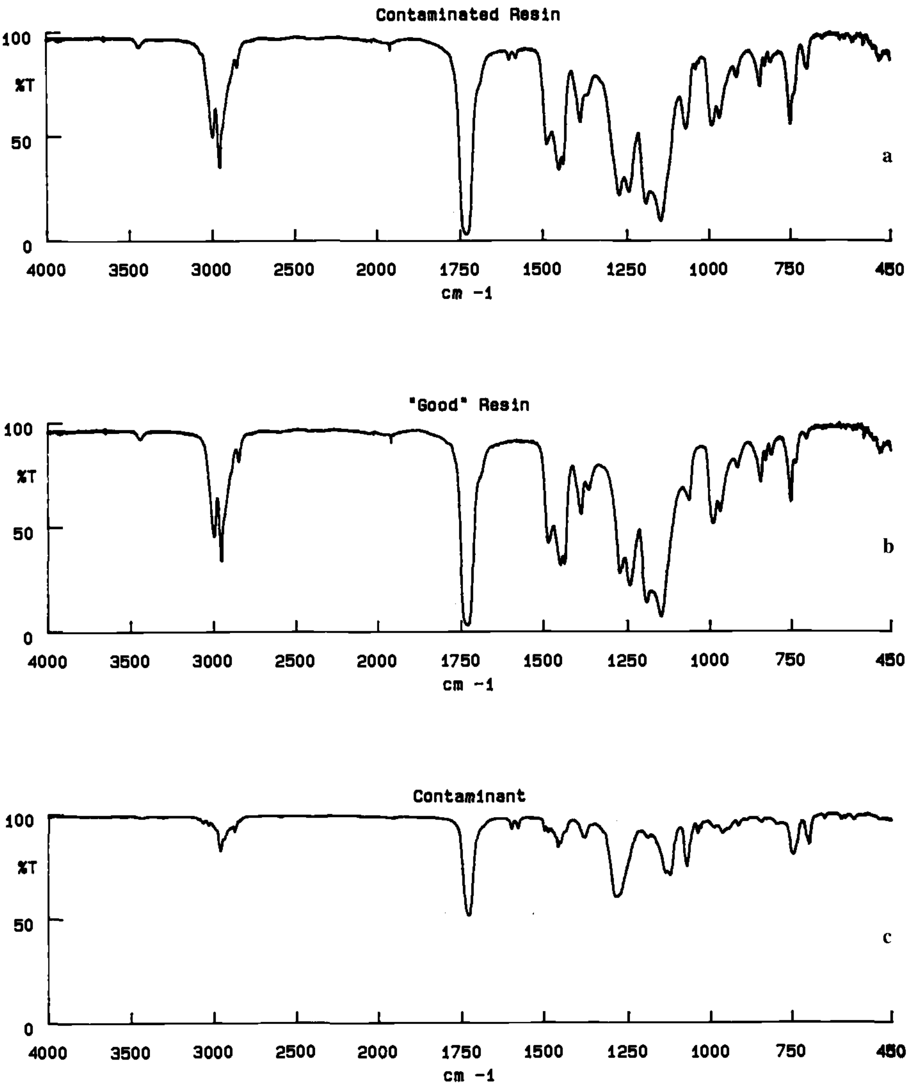


FIG. 3—*Separation of resin contaminant by spectral subtraction.*

approach is that no search system can find a match for a material which is not in the library. However, closely allied matches may suggest possibilities which are helpful in identifying an unknown. One must always compare the actual spectrum with the library reference since even apparently good scores can be very misleading. Most laboratories eventually like to develop their own libraries using their own products. This makes searching much faster since the database is smaller and the "hits" more accurate because both the samples and references are run in the same manner.

Another plant-type crisis shows how ingenuity, subtraction, and searching can be used to solve a difficult problem. Sometimes a batch of resin is not as clear as expected. This is often referred to as "cloud" or "haze." The "cloud" can be concentrated by centrifuging the resin. Hopefully the contaminant will either raise to the top or sink to the bottom. Figure 4 is a hazy resin which was centrifuged and the concentrated material from the bottom of the tube spread onto a KBr plate for examination (4a). Most of the spectrum is the resin and only a hint of the "cloud" can be detected. By subtracting the spectrum of the centrificate (4b), the pure spectrum of the haze can be isolated (4c). A search of several libraries indicated the best match would be a silica. A silica flock is very often used as a filter aid. Apparently a small hole had developed in one of the process filters and allowed the filter aid to leak through.

In the hands of a skilled spectroscopist subtraction can be both a qualitative and quantitative tool. If the sample and reference films are carefully prepared and well matched for spectral intensity, several components can be sequentially stripped from the spectrum so as

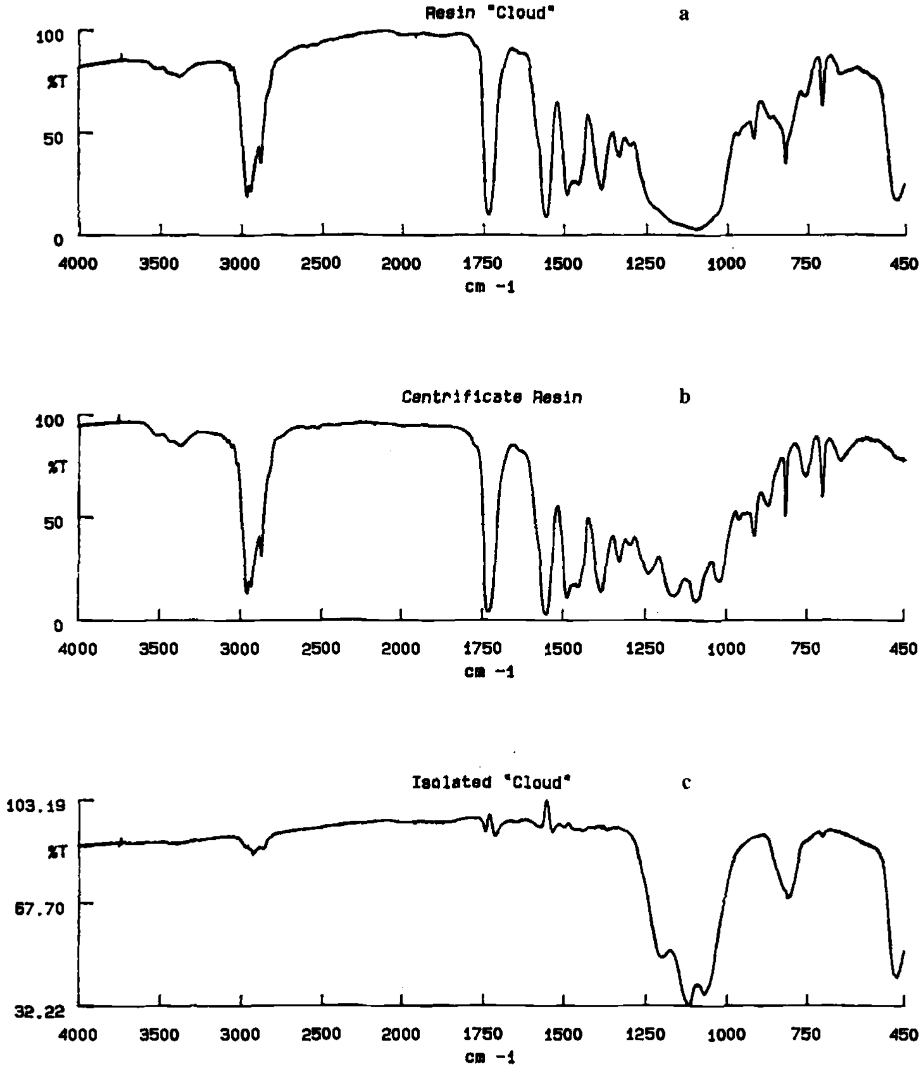


FIG. 4—*Isolation of resin "cloud" by spectral subtraction.*

to reveal very minor constituents. This must be done very carefully with considerable knowledge of the system, otherwise a noninterpretable mess of both positive and negative peaks will result. Alternatively, one can spectrally add the individual components together mathematically and then perform the subtraction. The safest method of difference spectroscopy is a comparison between the unknown and a control where the control is blended from ingredients chemically. With care, the subtraction factors can be used to estimate the concentration of components. That may be accurate enough for some applications. With sufficient calibration samples, multicomponent analysis can be employed to determine the constituents. Usually it is desirable at this point to shift to other analytical techniques which are more easily quantified, such as nuclear magnetic resonance, rather than pressing infrared further.

Time Lapse Spectroscopy

Digitized Fourier transform spectra are readily stored on magnetic disk media and then retrieved at some later time without any loss of accuracy or integrity. This allows spectra to be accumulated over a period of time and compared. Thus, studies may be carried out over hours, days, or even years. By examining the same point within a film, very subtle chemical changes can be detected. This is used to determine the reactions taking place during curing and has even been used to assess the degradation which occurs during exposure to the elements, i.e., coating durability. If spectra are taken and stored at frequent, regular intervals, the course of these reactions can be followed. The spectra may be likened to the single frames of "Time Lapse" photography [6]. Since the spectral bands are a result of the composition within the film, the chemical changes taking place can be assessed by carefully examining the spectral shifts occurring during that time. In this manner not only overall conversions, but sequential reactions can be detected. If the intensity of the disappearing bands are measured and correlated with time, reaction rates can be determined.

Cure Studies

The mechanism of cure is among the most important pieces of information to the coatings chemist. It is vital that it be understood since the reactions which take place during that time will dictate how the coating will perform. The coating analyst is frequently asked to contribute to that understanding. Fourier transform infrared has proven to be a valuable technique for obtaining that information. We developed the Time Lapse procedure for that purpose some years ago and have used it successfully to examine the air drying of a soya alkyd and linseed oil [7]. Figure 5 shows 29 sequential Time Lapse spectra of that alkyd taken approximately every 2 h over a 66-h period during its cure. The overall reaction can be seen by subtracting the initial spectrum from the final one (Fig. 6). By examining the same spot in the film, no difference factor needs to be applied. The subtraction is simply a one-to-one point-by-point difference. By viewing these incremental differences developed during the first 2 h, the initiation process can be assessed (Fig. 7). The oxidative cross-linking can be differentiated and determined independently (Fig. 8). This technique provides a unique insight into the air-curing process in nearly real time.

Later, we installed a commercial heated cell holder in our spectrometer and conducted thermal curing experiments in the infrared beam. Using a temperature controller, the heater could be rapidly ramped and then held at the baking temperature. Melamine cross-linking of a hydroxyl functional acrylic polymer was studied using this technique [8]. Figure 9 shows the loss of methoxyl group from the melamine and the disappearance of hydroxyl functionality from the acrylic during a nominal 250°F (121°C) bake. From this data, rates of reaction could be determined and the extent of cross-linking estimated.

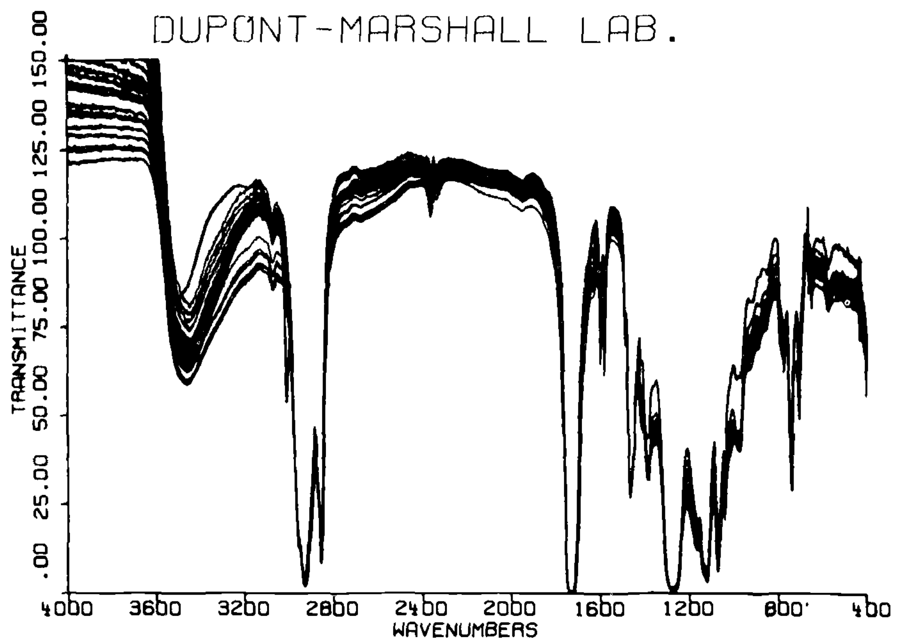


FIG. 5—*Twenty-nine Time Lapse spectra taken during alkyd cure* [6].

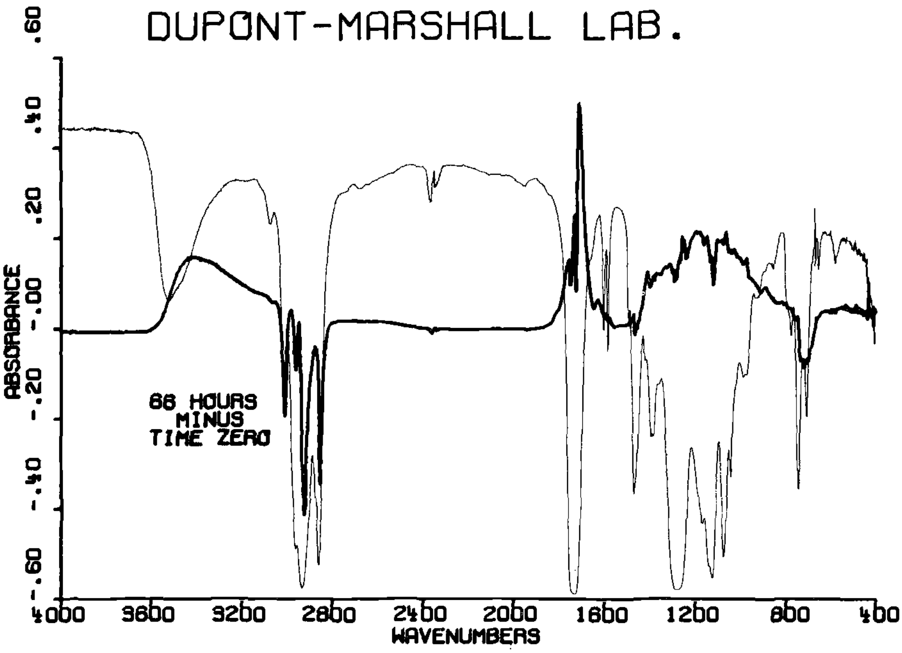


FIG. 6—*Differential spectrum before and after cure* [6].

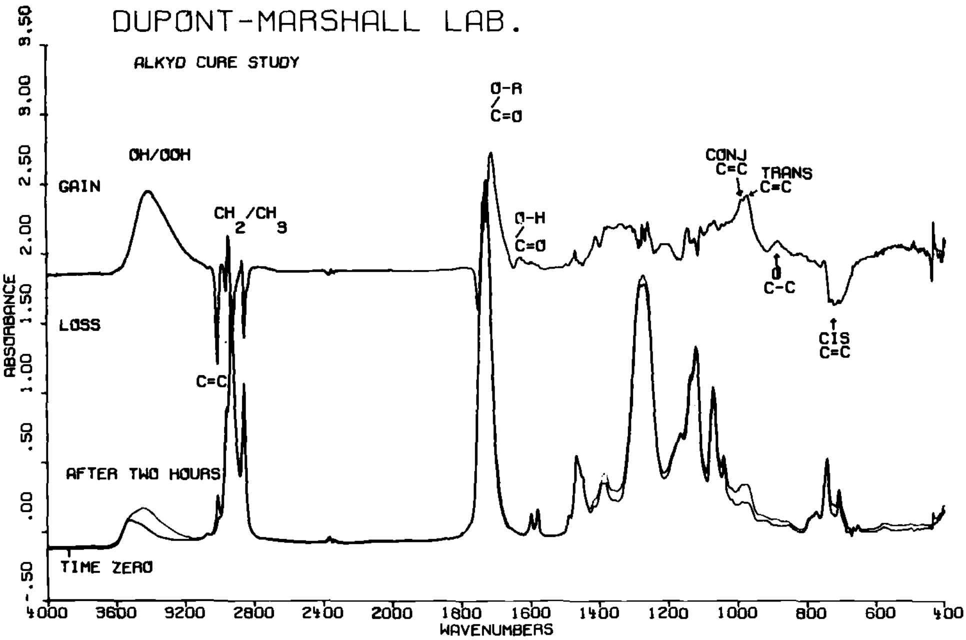


FIG. 7—*Initiation phase of alkyd cure* [7].

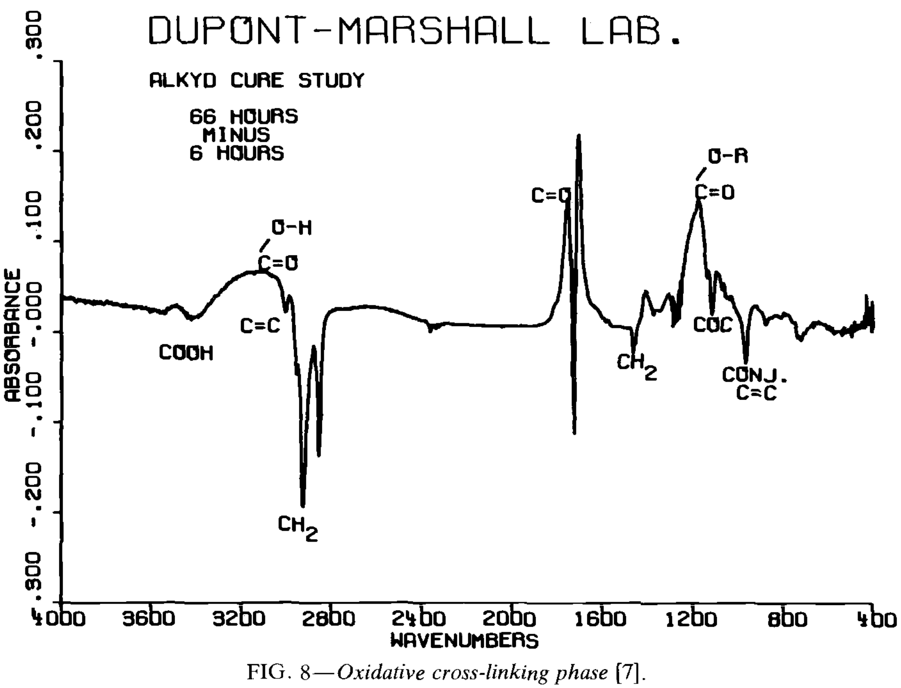


FIG. 8—*Oxidative cross-linking phase* [7].

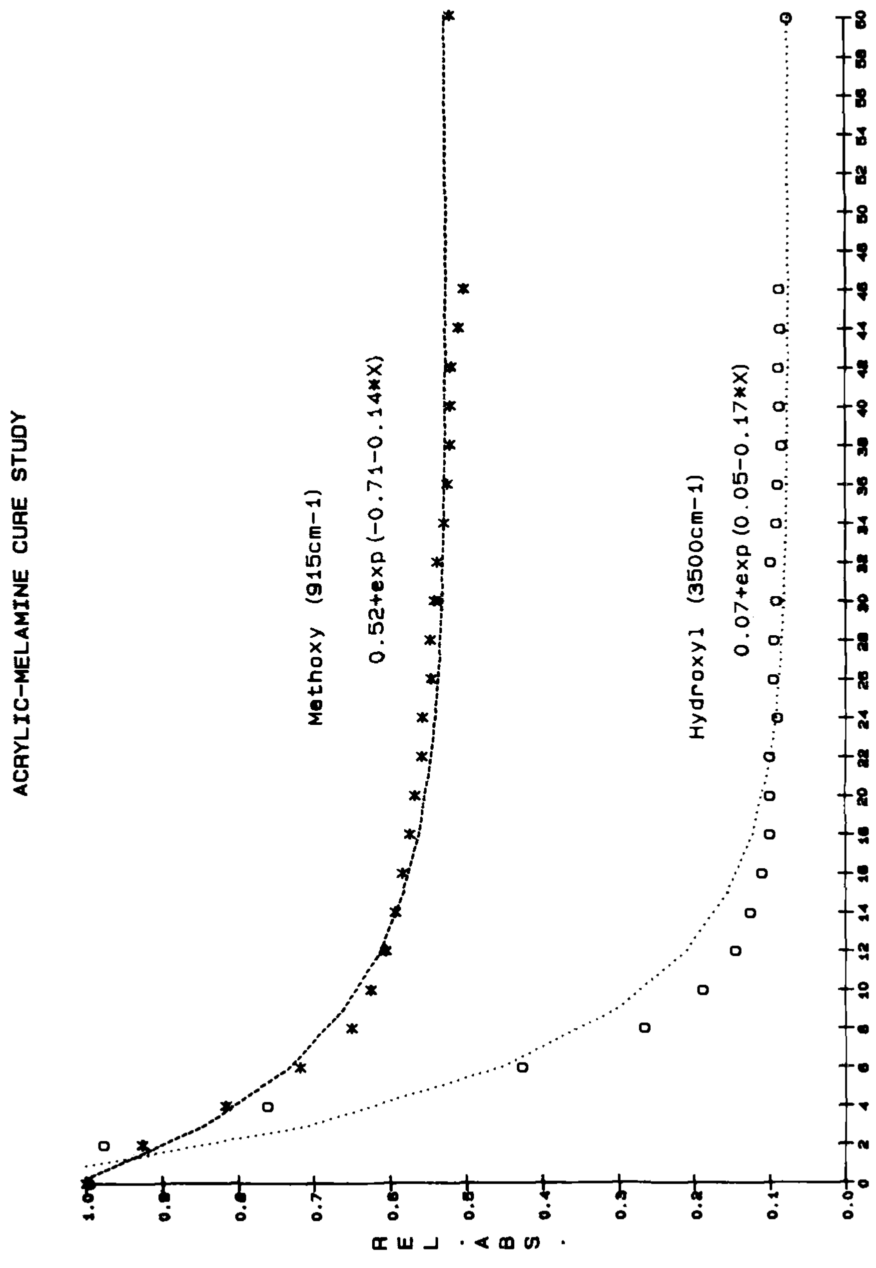


FIG. 9—*Acrylic-melamine enamel cure rates at 250°F (121°C)* [8].

Durability Studies

Even more important to the coatings chemist is an understanding of the chemistry which occurs when a coating is exposed to the elements. Moisture and ultraviolet radiation, individually and synergistically, cause failures that are normally not amenable to analytical measurements. Fourier transform infrared would be an ideal technique for examining the chemical changes if a suitable support were available. The common infrared plates are either moisture sensitive [potassium bromide (KBr), sodium chloride (NaCl), etc.] or are affected by light [silver chloride (AgCl), silver bromide (AgBr), etc.]. We discovered that amorphous elemental silicon is not only translucent in the mid-infrared but is essentially unaffected by exposure to the elements under ordinary conditions. Thus our Time Lapse technique could be applied to humidity, accelerated weathering (QUV), and Florida exposures [9]. Figure 10 shows the spectral changes taking place in a melamine acrylic enamel during 30 months of Florida exposure. Most of the degradation is believed to result from hydrolysis of the melamine cross-links. Since we can follow the loss of individual bands, those associated with the melamine disappear first on humidity exposure alone (Fig. 11). Ultraviolet seems to catalyze that reaction since QUV exposure is far more rapid than moisture alone (Fig. 12). The useful life of the film can be projected from the rates of degradation. This can significantly reduce the length of exposure necessary to reach a decision as to a formulation's durability.

Quality Assurance

Fourier transform spectroscopy's greatest contribution to the coatings industry is only now being written. The recent increased emphasis on product quality makes automated

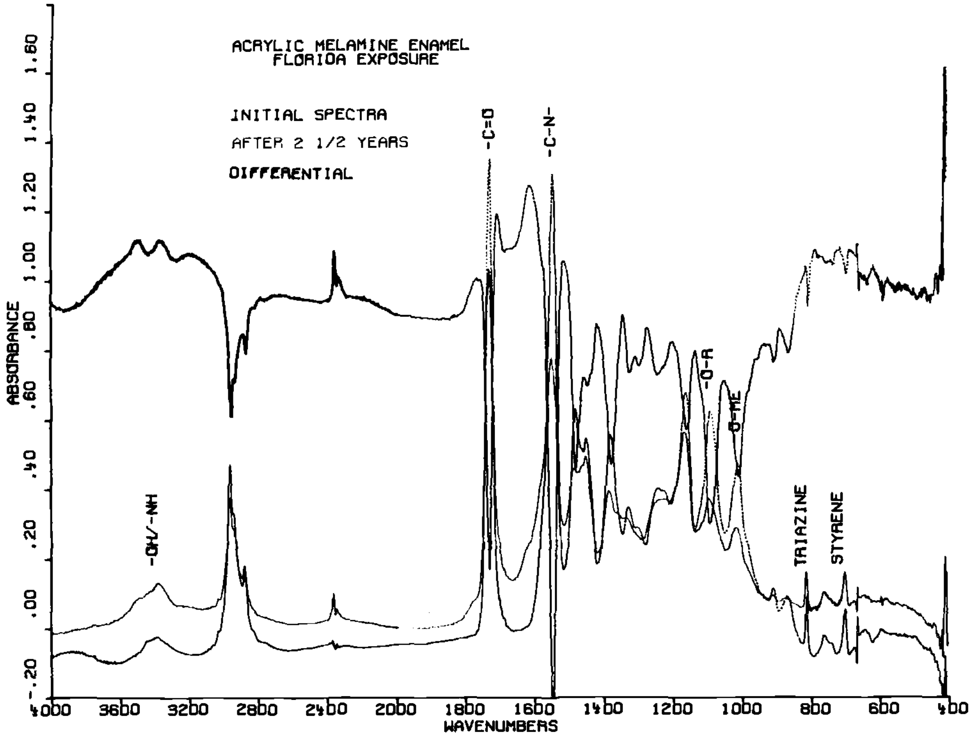


FIG. 10—*Acrylic-melamine enamel—30 months Florida exposure* [9].

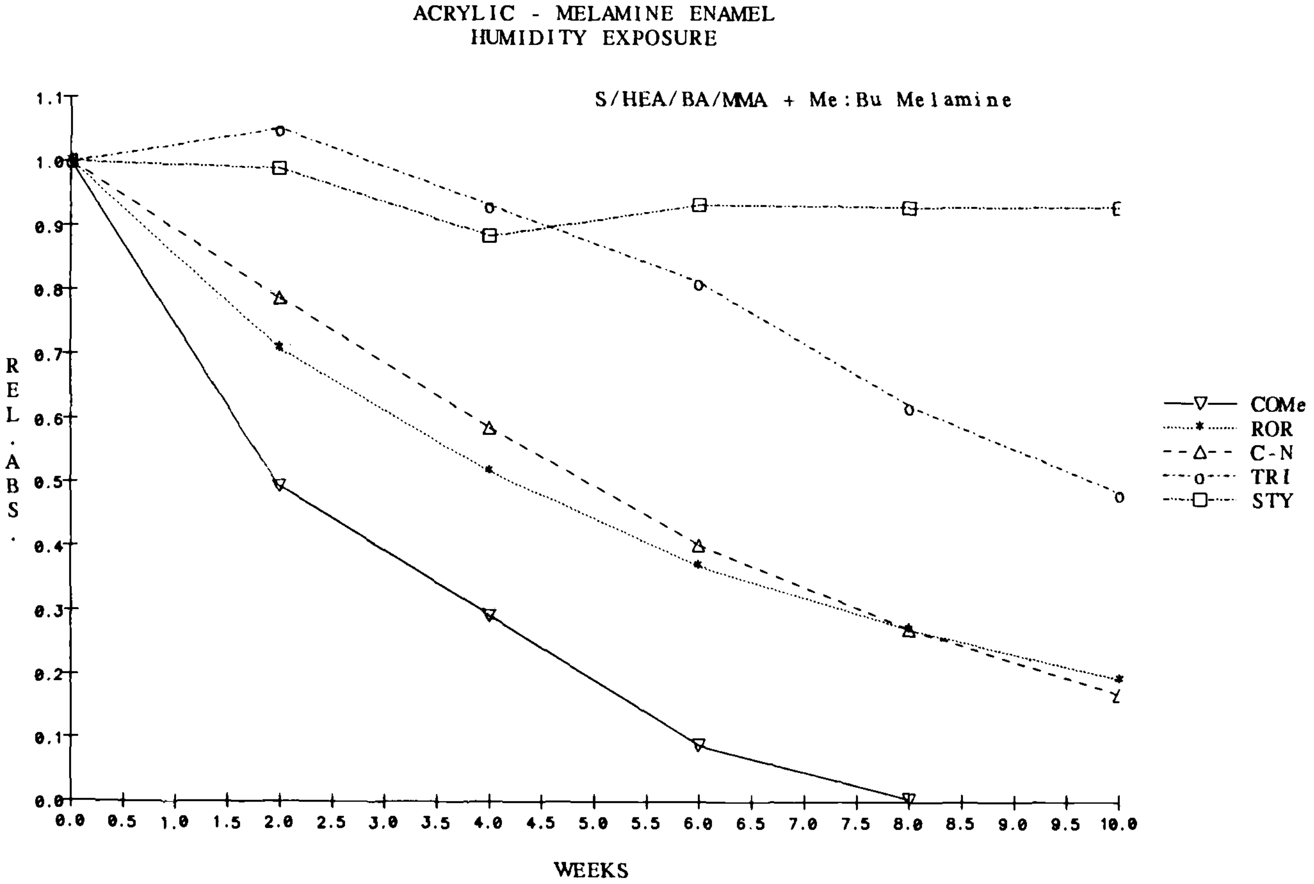


FIG. 11—*Degradation of various bands during humidity exposure* [9].

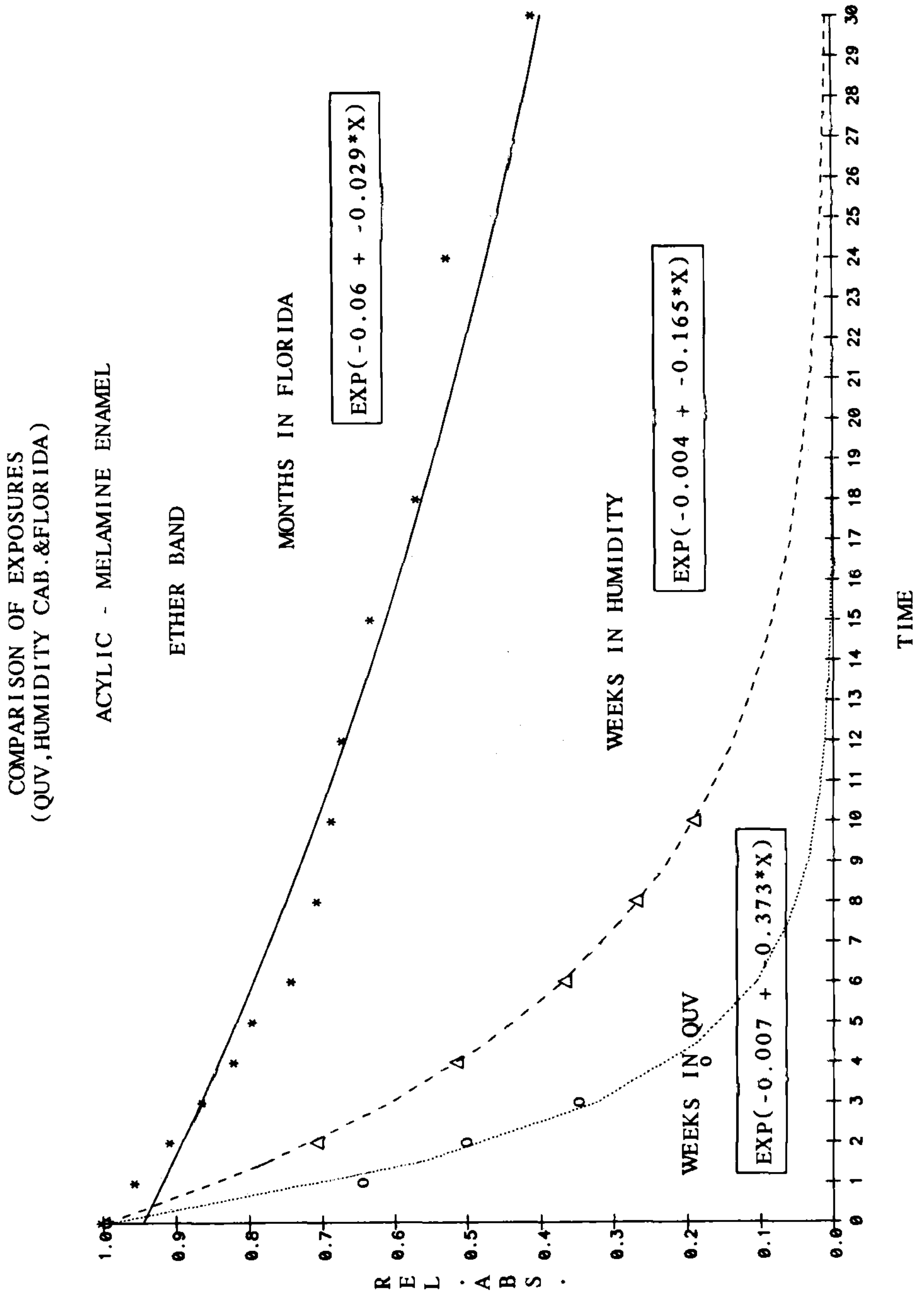


FIG. 12—*Comparison of degradation rate at different exposures* [9].

analytical techniques not only practical but necessary in order to remain competitive. Some suppliers have in the past advertised that they checked every batch by infrared. To the uninitiated that may seem impressive, but the spectroscopist realizes that they are simply overlaying the spectral "fingerprint" of that lot with a known. With dispersive instrumentation 5 to 10% or more of another material can be hidden and go undetected. Using computerized spectral subtraction, a fraction of a percent of a foreign material can be found and identified. By preprogramming the spectrometer computer, the spectroscopic functions can be relegated to the background so that it becomes in effect a "black box." An operator with minimum training can then perform very sophisticated analyses by just pressing a few buttons. Applying these principles, we have developed a system for testing incoming raw materials, manufactured intermediates, and finished products. These programs allow a control laboratory operator to call up a stored standard spectrum, run the current sample, and make the comparison—all automatically—in less than 5 min. We called the proprietary software our "Compositional Assurance Testing System" or CATS© for short [*10*]. A significant achievement has been the ability to examine each lot reproducibly. This is not a trivial matter when dealing with thick, viscous resins and highly volatile solvents. Working jointly with an accessory supplier, SpectraTech Inc., Stamford, CT, we developed a unique horizontal attenuated total reflectance boat. The "Contact Sampler™" is shown in Fig. 13. This attachment allows the operator to simply pour the sample into the boat and tell the computer what reference to compare it against. The computer and the CATS program does the rest. The operator does not need to worry about the amount of sample since the intensity of the spectrum is fixed by the area of the crystal and the depth of penetration which results from the angle of beam incidence. These are functions of the boat's construction and are set by the manufacturer. Thus, the testing is very reproducible. Figure 14 shows the results from a mislabeled raw material, while Fig. 15 is the output from a mischarged batch. Figure 16 is the product of a good match showing only expected lot-to-lot variation. The result of

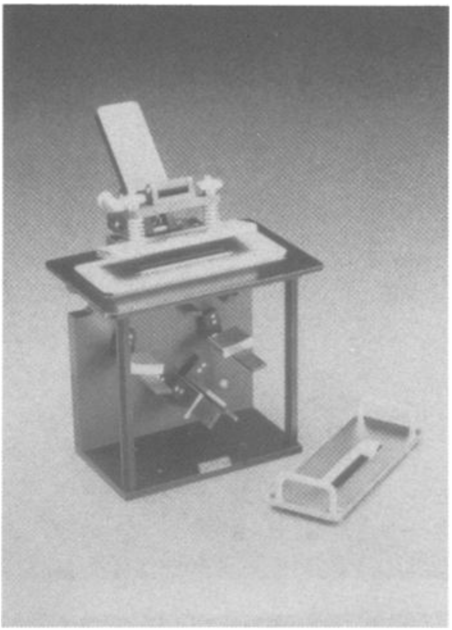


FIG. 13—*Horizontal ATR boat (courtesy of SpectraTech, Inc.).*

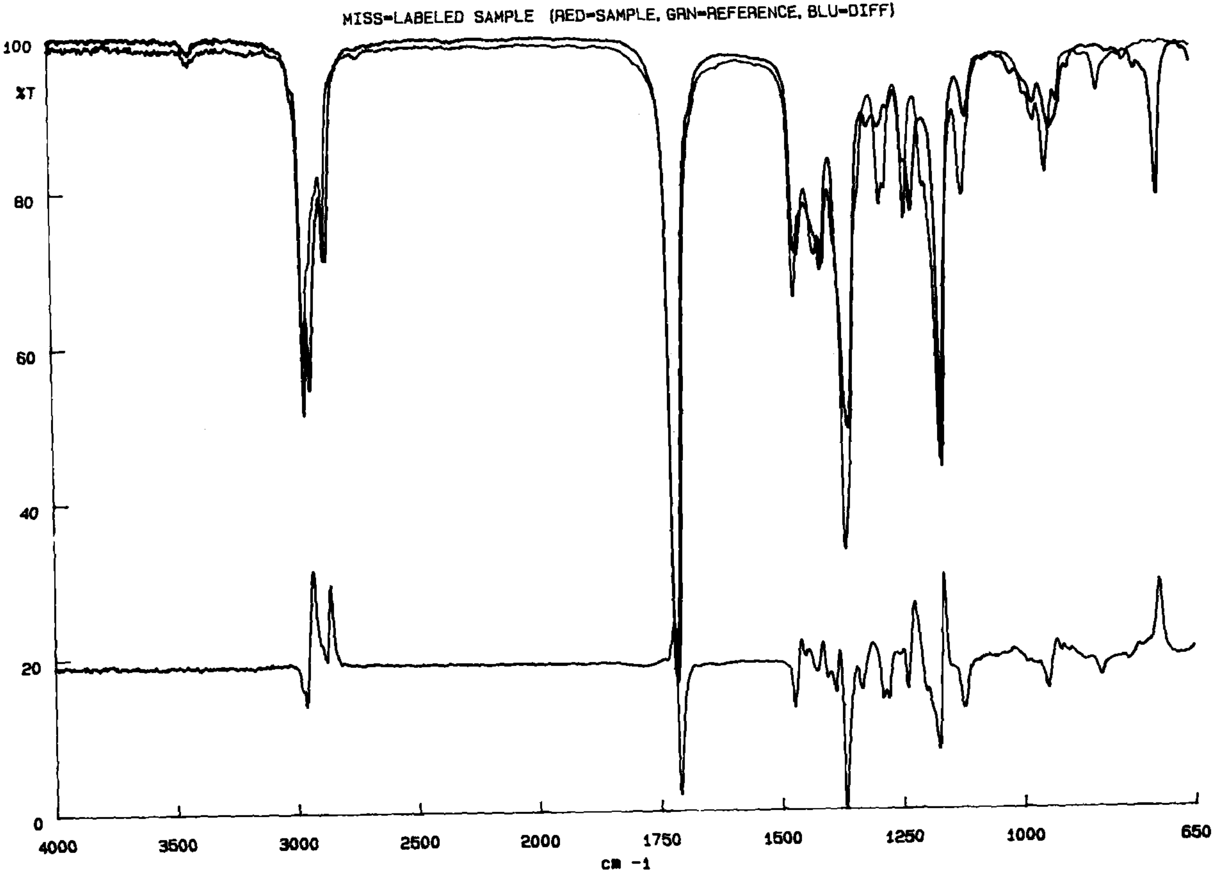


FIG. 14—*Mislabeled raw material* [10].

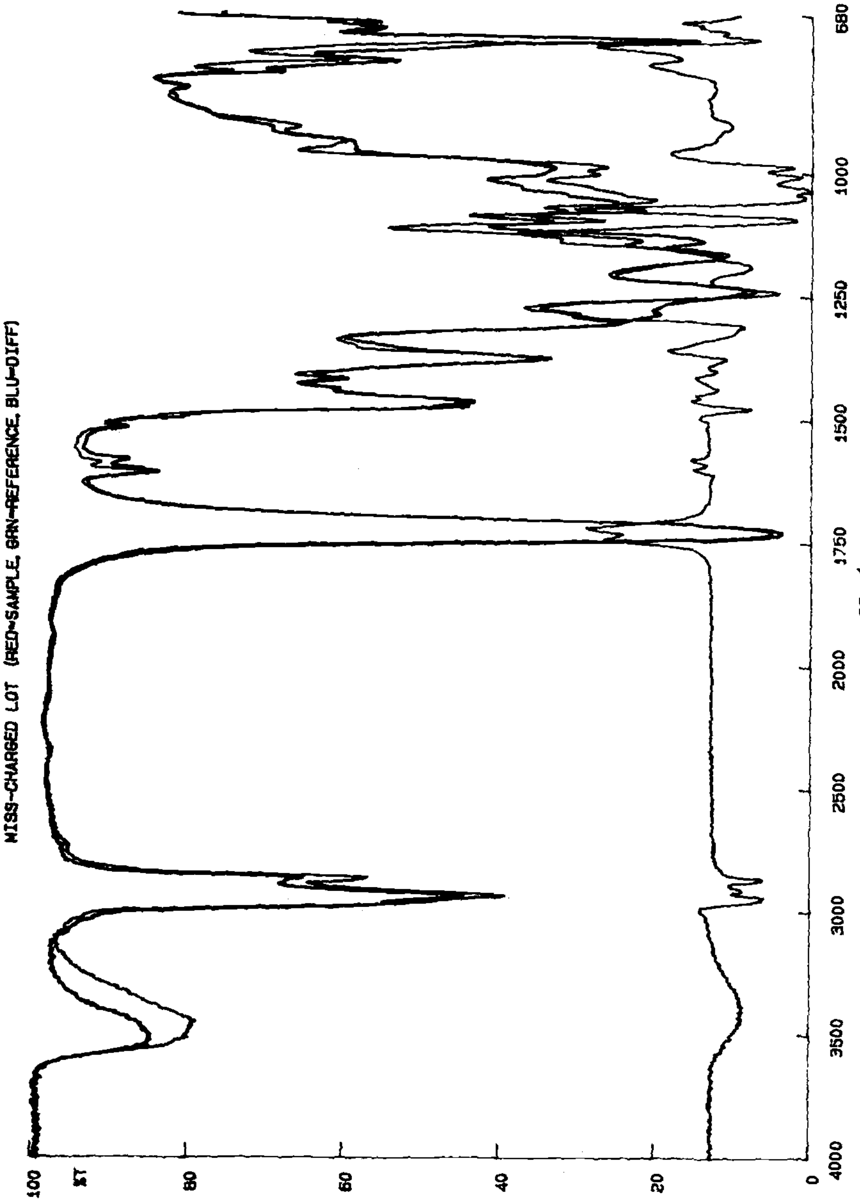


FIG. 15—*Mischarged batch* [10].

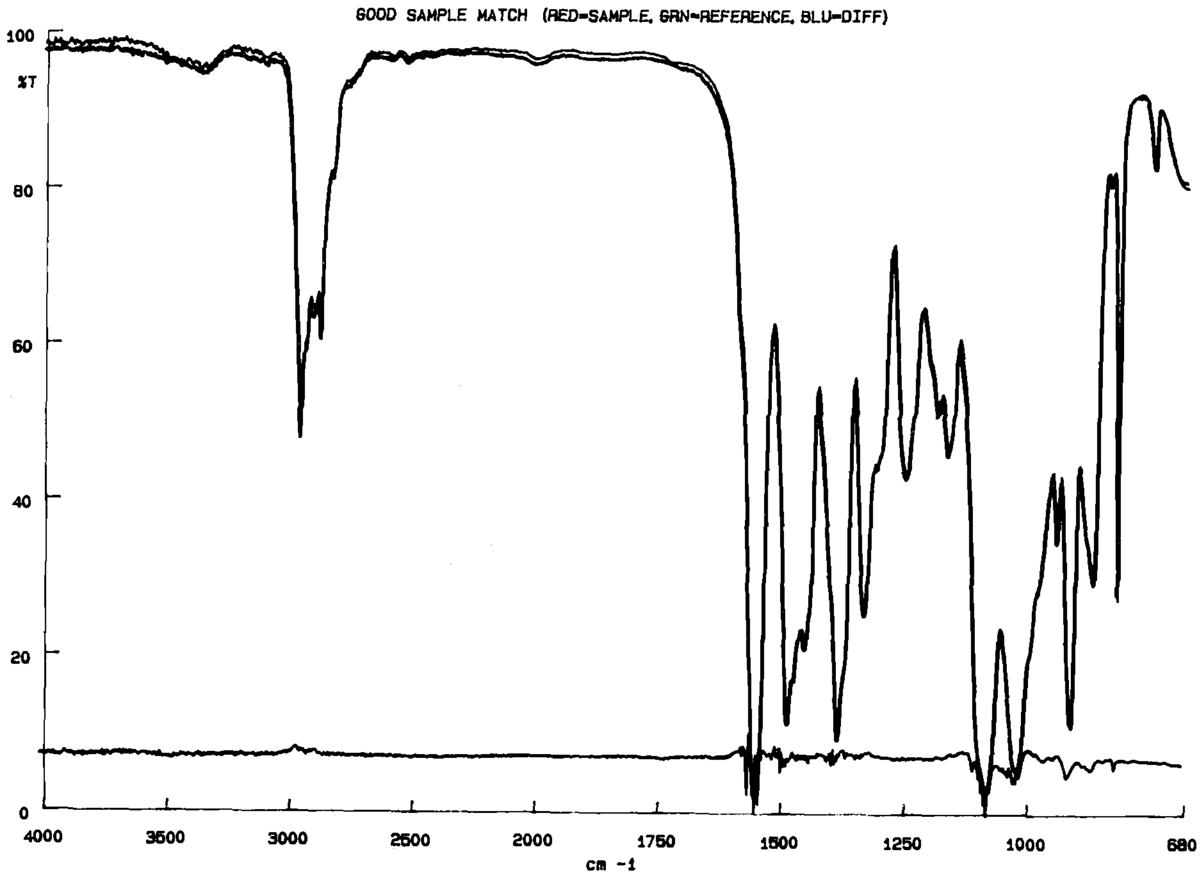


FIG. 16—*Good spectral match of good material* [10].

the CATS program is a goodness of fit number, which allows the operator to decide on whether the lot is acceptable or not. That number can be used for statistical process control.

With the advent of high-speed satellite communications it is possible to link plant control units together in a network. That way, reference standards run in one location can be accessed by any other site in the network. Du Pont is now in the process of developing such a network and divisionwide standards. Universal standards will lead to more consistent and reproducible products since materials made at any one of our plants will be compared with the same references. This is particularly important to a multi-national company where products can be manufactured at many sites worldwide.

Conclusions

Infrared has proven over the years to be one of the most valuable problem-solving tools available to the coatings analyst. It is usually the first technique applied to a difficult analytical problem because it provides unique qualitative information on samples in almost any physical state. The extent of the problem can then be assessed and a plan of attack can be formulated. The advent of FTIR removed many restrictions as to sample size and form. Its computer allows the analyst to strip away known components to reveal minor additives and contaminants. Spectral subtraction can perform separations which would be difficult if not impossible by chemical means. Data-handling techniques are proving to be the most valuable contributions of this technology for the paint industry. Digital spectral storage and retrieval permits the comparison of films with time so that the chemistry taking place during cure and exposure can be determined. It also can deduce when and at what rate these reactions are taking place. The ability to preprogram the spectrometer allows relatively unskilled operators to perform very sophisticated analyses without being burdened by spectroscopic functions. Thus, we have created essentially an automated quality assurance tester, i.e., a "black box" analyzer.

Acknowledgments

I would like to express my appreciation to the organizing committee for the opportunity to discuss the work going on in our laboratory, especially before such a distinguished audience. I should also like to thank DuPont management for allowing me to have so much fun "playing with these expensive toys." But, most of all, I would like to recognize my associate, James W. Halpin, Jr., who performs most of the experimental work and is indeed a major share of the editorial "we."

References

[*1*] Chicago Society For Coatings Technology, "An Infrared Spectroscopy Atlas For The Coatings Industry," Federation of Society for Coatings Technology, Philadelphia, 1980.
[*2*] Shreve, O. D., *Analytical Chemistry*, Vol. 23, 1951, p. 441.
[*3*] Griffiths, P. R., *Chemical Infrared Fourier Transform Spectroscopy*, Wiley-Interscience, New York, 1975.
[*4*] Koenig, J. L., *Applied Spectroscopy*, Vol. 29, 1975, p. 293.
[*5*] Sprouse, J. F., "Spectral Searching," 1985 International Conference on Fourier and Computerized Infrared Spectroscopy, J. G. Grasselli and D. G. Cameron, Eds., *Proceedings*, SPIE 553, International Society for Optical Engineering, Bellingham, WA, 1985, p. 70.
[*6*] Hartshorn, J. H., *Applied Spectroscopy*, Vol. 33, 1979, p. 111.
[*7*] Hartshorn, J. H., *Journal of Coatings Technology*, Vol. 54, No. 687, 1982, p. 53.
[*8*] Zimmt, W., Lazzara, M., Senkler, C., and Collete, J., "Cross Linking Studies on Polyol-Melamine Resin Systems," IXth International Conference in Organic Coatings Science and Technology, Athens, Greece, 1983, p. 301.

[*9*] Hartshorn, J. H., "Time-Lapse Infrared Examination of Coating Durability," XIIIth International Conference in Organic Coatings Science and Technology, Athens, Greece, 1987, Institute for Material Science, State University of New York, New Paltz, NY, p. 159.

10] Hartshorn, J. H., "Compositional Assurance Testing—A Systems Approach To Chemical Quality," 7th International Conference on Fourier Transform Spectroscopy, D. G. Cameron, Ed., *Proceedings*, SPIE 1145, The International Society for Optical Engineering, Bellingham, WA, 1989, p. 126.

L. G. J. van der Ven,[1] *G. D. B. van Houwelingen,*[1] *and*
R. R. Lamping[1]

Chemical Characterization of Cross-Linked Polyurethane Films

REFERENCE: van der Ven, L. G. J., van Houwelingen, G. D. B., and Lamping, R. R., **"Chemical Characterization of Cross-Linked Polyurethane Films,"** *Analysis of Paints and Related Materials: Current Techniques for Solving Coatings Problems, ASTM STP 1119,* American Society for Testing and Materials, Philadelphia, 1992, pp. 148–156.

ABSTRACT: The chemical composition and the physical properties of two-component polyurethane coatings are influenced by the curing conditions, viz. relative humidity and temperature. Apart from the formation of urethane, carbon dioxide can be released by hydrolysis of the isocyanate groups, leading to the formation of urea groups.

Chemical-analytical methods have been developed to characterize cross-linked polyurethane coatings based on hydroxy-functional acrylic resins and trifunctional isocyanates. Spectroscopic and wet chemical methods as well as carbon dioxide measurements were applied. Quantitative data were obtained on the content of isocyanate, hydroxyl, and amino groups and on urethane and urea cross-links.

The influence of the curing temperature, relative humidity, and type of hydroxyl groups on the network structure has been investigated. The relative humidity influences the composition of the coating cured at ambient temperature. During curing at elevated temperatures, the relative humidity hardly affects the chemical structure of the film. However, during storage after baking, urea groups are formed.

KEY WORDS: coating, polyurethane, curing, infrared, titration

Polyurethane coatings are widely applied as clear coats in the automotive, the car refinish, and the aerospace fields. The properties, such as flexibility, durability, chemical resistance, etc., are outstanding.

The curing of two-component isocyanate coatings is found to be strongly dependent on catalysis, temperature, relative humidity, and the types of hydroxyl and isocyanate groups [*1–3*]. The film formation comprises two competitive reactions. Besides the formation of urethane groups, the isocyanate group can be hydrolyzed, leading to the formation of urea groups:

Urethane formation (Reaction 1)

$$\text{R-NCO} + \text{R}_1\text{-OH} \rightarrow \text{R-NH-CO-O-R}_1$$

Urea formation (Reaction 2)

$$\text{R-NCO} + \text{H}_2\text{O} \rightarrow \text{R-NH}_2 + \text{CO}_2$$

$$\text{R-NH}_2 + \text{R-NCO} \rightarrow \text{R-NH-C-O-NH-R}$$

---

[1] Akzo Research Laboratories Arnhem, Analytical and Environmental Chemistry Department, 6800 SB Arnhem, The Netherlands.

The chemical structure of cross-linked polyurethane films has been studied qualitatively by Mondt and Tsubota using infrared (IR) spectroscopy [4,5]. Both suggest the presence of residual amino groups in the paint film.

The content of urethane versus urea in the paint film may influence the properties of the coating. The purpose of this study is to explore the chemical structure of polyurethane clear coats as a function of temperature, relative humidity, and composition of the resins.

Experimental

Polyurethane clear coats were prepared using acrylic resins containing primary or secondary hydroxyl groups and the isocyanurate trimer of hexamethylene diisocyanate as crosslinker.

The molar ratio of hydroxyl/isocyanate was chosen 1/1.

The film originally contained 1.7 mmol/g (on solids) of these functional groups.

Three acrylic polyol resins were applied: Setalux 1152 and Setalux 1151 [molecular weight (Mw) 9000, hydroxyl (OH) value 140 to 150, acid number (AN) <10], containing primary and secondary hydroxyl groups, respectively, in the case of low-temperature curing and an experimental high solid resin (Mw 2500, OH-value 140–150, A.N. 17) used for curing at elevated temperatures.

The curing of the clear coat was investigated without catalysis and with catalysis using triethylenediamine (DABCO) or dibutyltin dilaurate (DBTDL) at concentrations of 0.1 and 0.06% weight/weight (w/w) on the binder, respectively.

After application of the clear coat, the flash-off and the curing were performed under conditions controlled in respect of temperature and relative humidity. The curing conditions are given in Table 1.

Paint films were prepared by spraying on glass panels or—for IR spectroscopic measurements—by brushing on a potassium bromide crystal or a silicon wafer.

The IR spectra were recorded on a Perkin Elmer 983 spectrometer. A closed heated cell, with potassium bromide windows, was used for the IR measurements at elevated temperatures. The cell was flushed with air having a defined relative humidity at 21°C. The isocyanate concentration during curing was quantified by tracing the infrared absorption of the isocyanate group (2272 cm^{-1}).

The formation of urea was traced by continuously measuring the carbon dioxide emission from paint films using the apparatus described in Ref *6*.

The amino concentration in the paint films was quantified by titration; 300 to 400 mg of the (in)soluble film was treated with 5 mL of 0.03 *M* perchloric acid in isopropanol. After 8 h, an aliquot of the isopropanol solution was titrated with tetrabutyl ammonium hydroxide in isopropanol. The decrease in acid concentration is a measure of the amount of amino

TABLE 1—*Curing conditions.*

LOW-TEMPERATURE CURING

Resin: Setalux 1152/Setalux 1151
Temperature: 21°C
Relative humidity (at 21°C): 30, 60, 90%

HIGH-TEMPERATURE CURING

Resin: Exp. high solids resin (code HSR)
Time: baking for 30 min followed by storage at 21°C
Temperature: 70, 80, 90, 120°C
Relative humidity (at 21°C): 30, 60, 90%

groups in the paint film. A film cured under dry conditions (to prevent the formation of amino groups) was used as a blank.

The sum of amino and hydroxyl groups has been determined by acetylation. A polyurethane film is treated with a solution of acetic anhydride in pyridine containing dimethylaminopyridine (DMAP) as catalyst. Though pyridine as such already catalyzes the acetylation reaction, DMAP is about 10^4 times more active [7].

After one night the film is removed from the solution and the excess of acetic anhydride has been hydrolyzed to acetic acid, which is subsequently titrated with lye. Urea groups do not react with acetic anhydride. The hydroxyl concentration can be calculated from the difference between the results of this analysis and the quantity of amino groups in the film.

The formation of urethane can be calculated from the decrease in concentration of the hydroxyl groups (Reaction 1) or can be determined directly from IR spectra using model compounds. For this method the acrylic polyol resin is derivatized with butyl isocyanate. The absorption of the urethane bands (1545 and 1248 cm^{-1}) in this derivatized resin corresponds to a total conversion of all the hydroxyl groups into urethane.

Results and Discussion

Isocyanate

The curing rates of Setalux 1152 and 1151 are depicted in Figs. 1 and 2. The relative humidity strongly affects the rate of isocyanate decrease. At lower relative humidities (RH) and during the first stage of the curing, differences in the curing rate are noticed: after curing for five days at 30% RH, the isocyanate concentrations in Setalux 1152 and 1151 amount to 35 and 45%, respectively, of the original quantity.

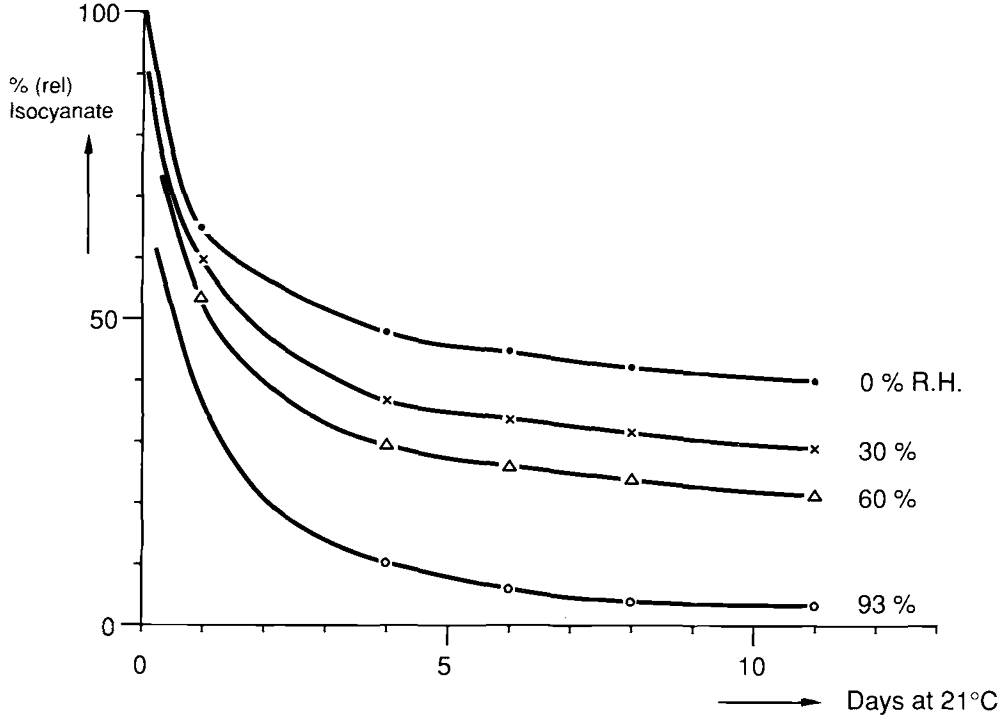


FIG. 1—*Curing rate of Setalux 1152 (primary hydroxyl groups) at 21°C; no catalyst.*

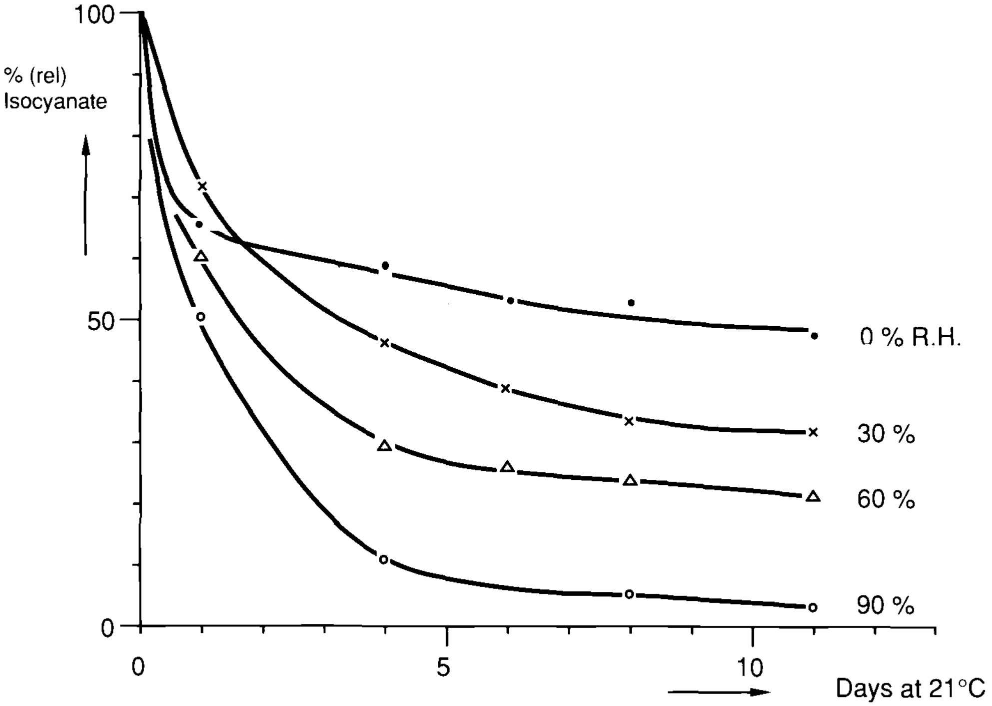


FIG. 2—*Curing rate of Setalux 1151 (secondary hydroxyl groups) at 21°C; no catalyst.*

Catalysis enhances the reaction of isocyanate groups only in the first stage of the curing, which is also the case using polyester resins [*6*]. Apparently the mobility of the matrix has —after some days—diminished to such an extent that the reaction rate becomes independent of the catalyst.

After storage for several weeks under conditions prevailing in practice, viz. 21°C and 30 to 60% RH, a considerable amount, 10 to 20%, of isocyanate is still present in the film.

Figure 3 shows the decrease of isocyanate during the curing of the HSR at elevated temperatures and subsequent storage at room temperature. After baking for 30 min at 70°C and five days of storage at 21°C, over 95% of the isocyanate groups have been reacted.

During curing at elevated temperatures, the relative humidity has no influence on the curing rate. Presumably, the water concentration in the film is very low under these conditions.

Urea

The influence of the RH on the hydrolysis of isocyanate in uncatalyzed films, as calculated from the carbon dioxide emission, is illustrated in Fig. 4. According to Reaction 2, two isocyanate groups are consumed for the formation of one urea linkage. As a consequence, approximately 20% of the isocyanate groups are converted into urea (60% RH), assuming no residual amino groups to be present in the paint.

The effect of the temperature on the urea formation is depicted in Fig. 5. Urea is formed only during storage at 21°C after baking.

The uptake of moisture by the film depends on the temperature, the relative humidity, and the hydrophilicity of the binder.

Polyester-based, two-component polyurethane films contain up to 1.8% water (w/w on solids) [*6*] and acrylic polyol films up to 0.4% water (w/w on solids).

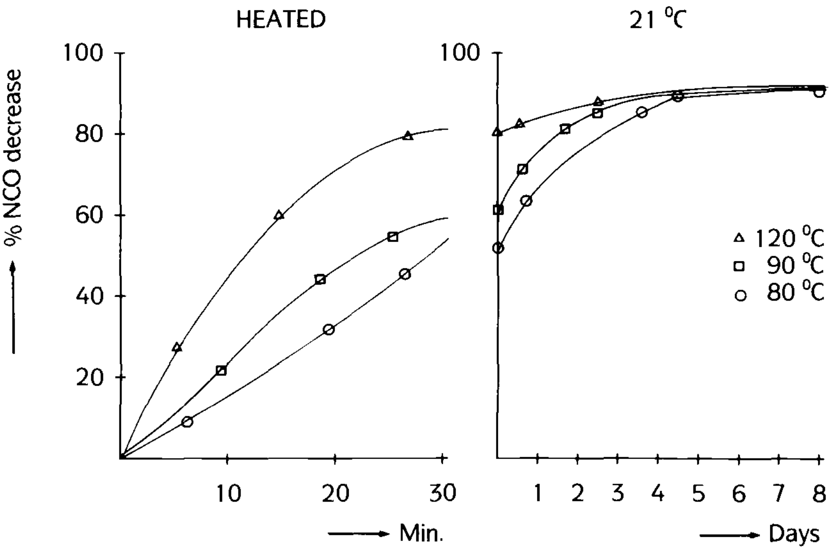


FIG. 3—*Curing rate of HSR at different temperatures at 30% RH; storage at 30% RH, 21°C; no catalyst.*

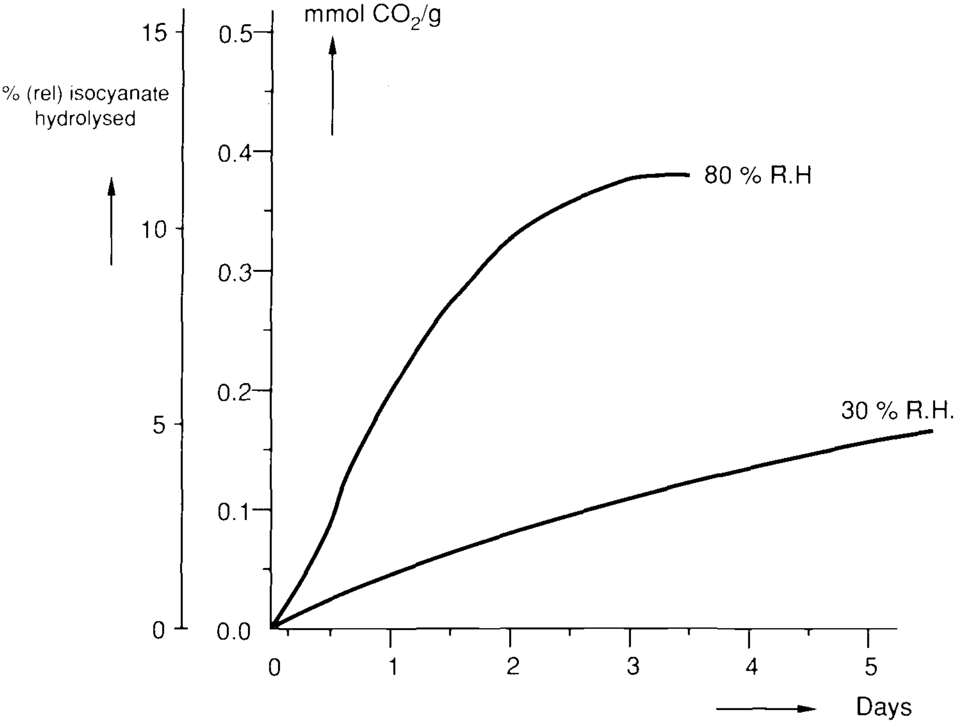


FIG. 4—*Rate of hydrolysis of isocyanate during curing of Setalux 1152 at 21°C; no catalyst.*

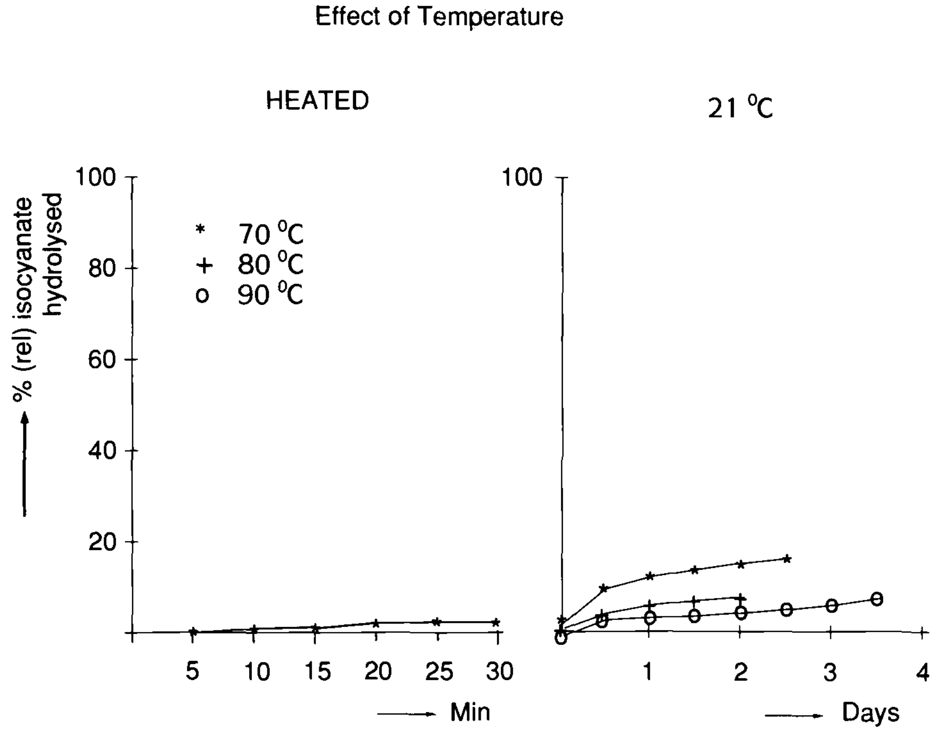


FIG. 5—*Rate of hydrolysis of isocyanate during curing of HSR at 60% RH.*

As can be derived from the literature [*3*] DABCO enhances the hydrolysis of the isocyanate group to a larger extent than DBTDL. However, after prolonged storage at room temperature, films with and without catalyst prove to contain equal quantities of urea.

Amino Groups

Figure 6 shows the amino content of a film traced with the perchloric acid solution as a function of the contact time. A contact time of at least 6 h is required to neutralize all the primary amino groups in the film. At high relative humidities, 2% of the isocyanate groups are hydrolyzed to give amino groups without consecutive reaction to urea.

The presence of these small quantities of amino groups can be explained from the hindered mobility of the polymer and the absence of neighboring isocyanate groups.

After curing at elevated temperatures, the amino content of the film was very low: less than 1% of the isocyanate groups originally present.

Amino Plus Hydroxyl Groups

A complete acetylation of the amino plus hydroxyl groups is achieved within 8 h (Fig. 7). The reproducibility of the method, expressed as coefficient of variation, is about 10%.

The films contain, after storage for 14 days at room temperature, high quantities of free hydroxyl groups, as shown in Table 2. Curing at elevated temperature decreases the residual hydroxyl content considerably (Table 3). As shown already, hydrolysis of the isocyanate groups does not occur at elevated temperature.

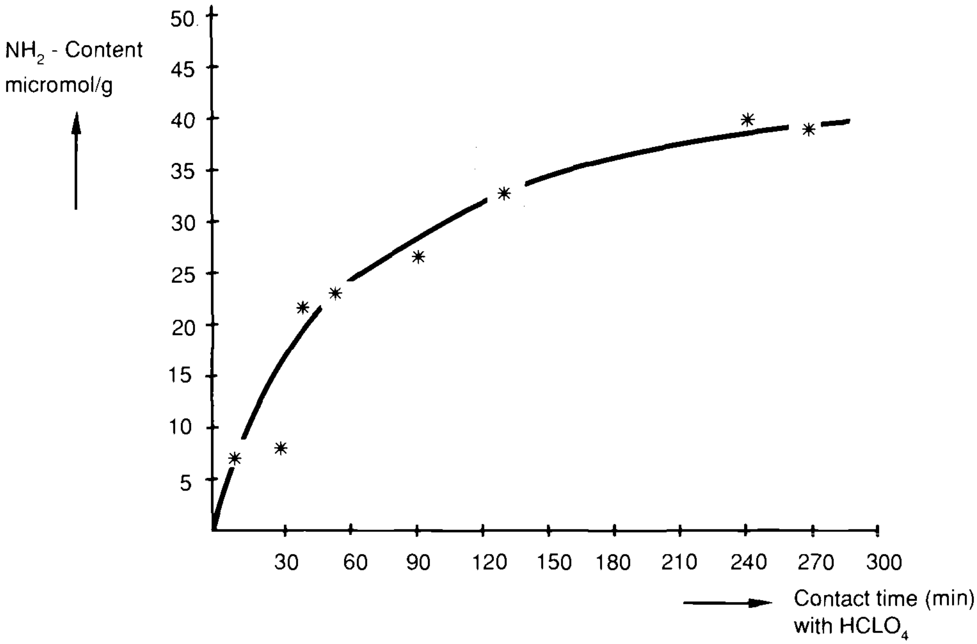


FIG. 6—*Amino content of a film traced in dependence on the contact time with a solution of perchloric acid in isopropanol.*

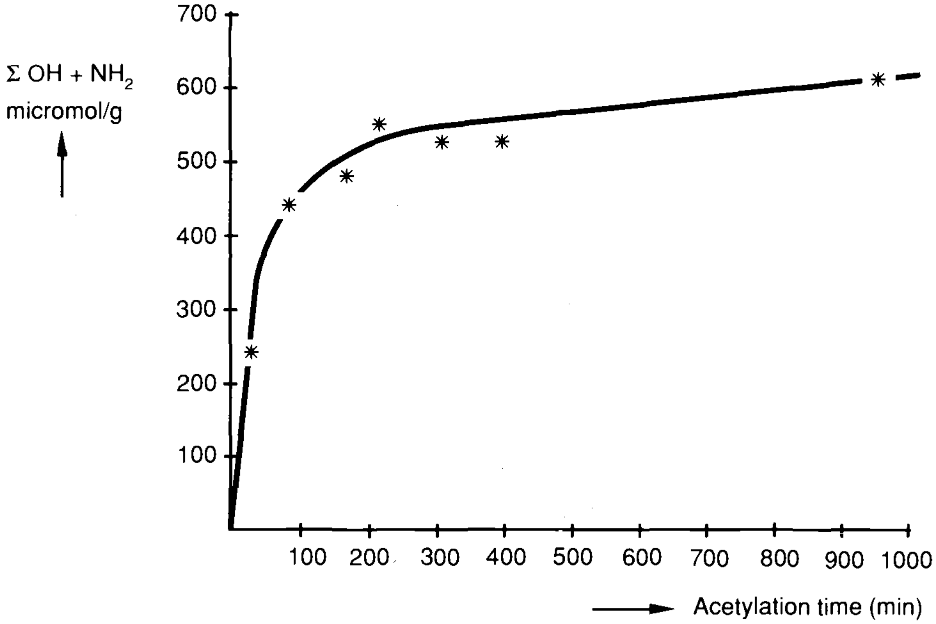


FIG. 7—*Content of hydroxyl plus amino groups as determined by acetylation using DMAP as catalyst.*

Urethane

In order to check the statement that the urethane concentration in the film is equal to the decrease of the hydroxyl concentration, IR measurements have been performed using model compounds. The hydroxyl groups in Setalux 1152 are derivatized with butyl isocyanate.

Figure 8 depicts the urethane concentration at 21°C and 60% RH, as determined by IR spectroscopy. The concentration after 14 days of curing corresponds well with the decrease of hydroxyl under the same conditions (Table 2).

Conclusions

The results of the chemical characterization of urethane films cured at room temperature or elevated temperature are summarized in Tables 2 and 3. The data in these tables are expressed as percentages of the initial isocyanate concentration. Since one urea group is formed from two isocyanate groups, the sum of the groups (isocyanate, amino, urethane, and urea) in the tables should theoretically be 100% if the urea content is multiplied by two.

Curing at room temperature makes the composition of the film strongly dependent on the relative humidity. Up to 40% of the isocyanate groups are converted into urea groups, resulting in a high residual content of hydroxyl groups. Only small quantities of amino groups are left in the coating, even after curing at 90% RH.

The relative humidity has no significant influence on the film composition during curing at elevated temperatures. During curing, only urethane linkages are formed, while storage at room temperature results in the formation of minor quantities of urea groups. Apparently, the water concentration in the film at elevated temperature is very low. It is noticed that even after baking for 30 min at 90°C a considerable amount of the isocyanate groups is still present in the film.

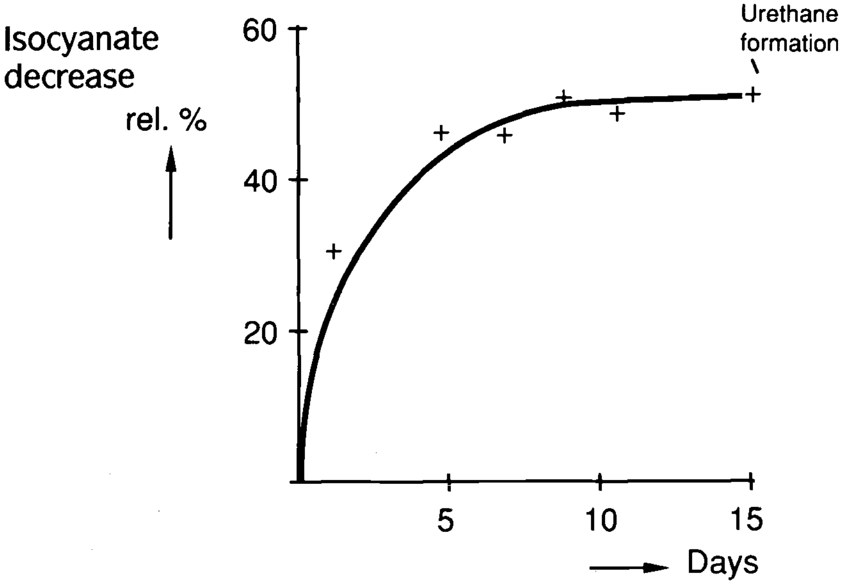


FIG. 8—*Urethane formation, plotted as isocyanate decrease, traced by IR at 60% RH, 21°C.*

TABLE 2—*Chemical composition of cross-linked Setalux 1152; curing: 21°C, no catalyst.*

RH, %	$-NCO$, %	$-OH$, %	$-NH_2$, %	Urethane, %	Urea, %
		AFTER 1 DAY			
30	53	48	1	52	2
60	47	53	2	47	6
90	35	60	2	40	13
		AFTER 2 WEEKS			
30	25	37	1	63	9
60	16	41	2	59	17
90	4	49	2	51	20

TABLE 3—*The influence of baking temperature and relative humidity on the chemical composition of cross-linked HSR. Baking time: 30 min.*

Temp., °C	$-NCO$, %	$-OH$, %	Urethane, %	Urea, %
		RELATIVE HUMIDITY 60%		
70	45	44	56	2
90	30	25	75	3
120	1	14	96	3
		TEMPERATURE 90°C		
30	32	29	71	2
60	30	25	75	3
90	29	24	76	4

The analytical methods developed give quantitative information about the chemical composition of polyurethane films. After minor modifications, application of these methods to other coating films will be possible.

Acknowledgment

The authors wish to express their gratitude to H. J. W. van den Haak, Akzo Coatings, Research Centre Sassenheim, and to T. Bartels, Akzo Coatings Wapenveld, for their support throughout this investigation.

References

[*1*] Thiele, L., *Acta Polymerica,* Vol. 30, No. 6, 1979, pp. 323–342.

[*2*] Usmani, A. M., *Journal of Coatings Technology,* Vol. 56, No. 716, 1984, pp. 99–103.

[*3*] Wong, S. and Frisch, K. C., "ACS Polymer Materials," *Science and Engineering,* Vol. 50, 1984, pp. 480–484.

[*4*] Mondt, J., *Kunstharz Nachrichten,* H. 21, Jg. 43, 1984, pp. 1–15.

[*5*] Tsubota, M., Tomita, H., and Honda, S., *Shikizai Kyokaishi,* Vol. 56, No. 3, 1986, pp. 135–142.

[*6*] van der Ven, L. G. J., van Dijk, J. H., and de Vries, O. T., *Proceedings*, XVIII Fatipec Congress, Venice, Italy, 1986, pp. 291–313.

[*7*] Hofle, G., Steglich, W., and Vorbruggen, H., *Angewandte Chemie,* Vol. 90, No. 8, 1978, pp. 602–615.

Joseph A. Gardella, Jr.[1]

Principles and Applications of Photoelectron and Ion Spectroscopy for the Analysis of Polymer Surfaces

REFERENCE: Gardella, J. A., Jr., "**Principles and Applications of Photoelectron and Ion Spectroscopy for the Analysis of Polymer Surfaces,**" *Analysis of Paints and Related Materials: Current Techniques for Solving Coatings Problems, ASTM STP 1119,* American Society for Testing and Materials, Philadelphia, 1992, pp. 157–170.

ABSTRACT: Advances in the development of techniques for the energy and mass analysis of ejected particles form the basis of their use as surface analytical spectroscopies. Methods such as X-ray photoelectron spectroscopy (XPS or ESCA), low-energy ion-scattering spectroscopy (ISS), and secondary ion mass spectrometry (SIMS) are becoming more widely applicable to problems in the chemical analysis of coatings surfaces and interfaces. In this paper a brief review of instrumentation and theory allows projection of new capabilities for the method. Recent progress in the analysis of homopolymer and multicomponent polymer interfaces is described.

KEY WORDS: surface analysis, polymer surface science, ESCA, XPS, low-energy ion scattering, SIMS, multicomponent polymers, functional polymers, polymer/metal interfaces

For the coatings industry, several key objectives are the result of surface and interfacial chemistry. Obviously, an understanding of the mechanisms of processing and aging at the air interface is of primary importance. Secondly, a full understanding of adhesion chemistry between a coating and a metal surface is of importance. This is not just limited to chemical coatings; applications are also found in the semiconductor packaging industry [*1*]. These are the result of the general objective in polymer materials science and engineering: structure property relationships. In this particular venue, for surface science, this means understanding the relationship between bulk structure and composition and the resulting surface structure and composition to develop surface structure property relationships.

Previous reviews from the polymer surface science perspective have stressed the potentials of broader application of ultra high vacuum (UHV) surface analytical methods [*2,3*]. Hercules [*4*] has discussed the challenges for surface science implicit in determining microphase heterogeneity near a multicomponent polymer surface. In response to these challenges, rapid development of new spectroscopic and microscopic probes and continuing evolution of more established methods [*5–8*] are advancing these problem areas. In particular, X-ray photoelectron spectroscopy (XPS) or electron spectroscopy for chemical analysis (ESCA) has been the technique most relied upon for applications to polymers. This is primarily because of the inherent analytical aspects of the method, e.g., chemical bonding information, high-surface sensitivity, low damage, and relative insensitivity to the insulating properties of the sample. The quantitative analysis of surface species and the detection of impurities

---

[1] Professor of chemistry, Department of Chemistry and Industry University Center for Biosurfaces, University at Buffalo, SUNY, Buffalo, NY 14214.

or modifications at the surface have been heavily traversed areas of ESCA application for polymer surfaces. It is now rather routine to use ESCA to obtain surface composition of polymers to follow processing steps and degradation chemistry. This means the method can be used to study systems of greater complexity.

Of great interest is information about surface structure with further sophistication at a higher level of precision. For example, detecting the presence and concentration of surface-active functional groups is desirable, indeed achievable routinely with ESCA (especially in concert with infrared or Raman vibrational spectroscopy). Yet, more desirable for applications in interfacial bonding important in coatings is the knowledge of orientation and subsequent reactive availability of these functional groups. Beyond functional group information, monomer arrangement along a chain in copolymers and intrachain interactions, again, as they are exemplified at the surface, would be important information not easily available. In addition, macromolecular chain arrangement, termination, branching, and micromorphological information (i.e., domain size and distribution) are important in determining sophisticated surface structure property relationships. Further, isotopic sensitivity for detection of labeling experiments and diffusion between interfaces is very desirable. Molecular weight distributions at or near the surface (in comparison with the average bulk distribution) would have major impact in many problems. Higher degrees of spatial resolution are required in all three dimensions so that buried interfaces may be precisely determined. Speed of data acquisition for kinetic studies is a general desirable characteristic of analytical methodology, which is very limited in UHV surface analysis of polymers.

Instrumental developments in the application of surface-sensitive electron and ion spectroscopies [6,7] have always led to broader application. To approach these types of structural and reactivity information at surfaces and interfaces, evolution in methodology of established methods and development of new methods must both be accomplished. It is unlikely that any single surface analytical method can answer all questions about any system, and this is especially true for the complexity of macromolecular materials. This review will emphasize results from electron spectroscopy for chemical analysis (ESCA), low-damage (macro)molecular secondary ion mass spectrometry (SIMS), and low-energy ion scattering spectrometry (LEIS or ISS). Of course, other non-UHV spectroscopic and analytical methods play a continuing and increasing role in determining surface structure-property relationships for polymers. Table 1 shows a comparison of the analytical characteristics of surface-sensitive spectroscopic measurements for polymer analysis.

The present paper is organized into four sections. A brief review of the instrumentation required to make the measurements will be given. Sample handling difficulties will be reviewed. Some analytical aspects will be presented to highlight the potential information content as it applies to polymer structure. Selected examples of application will hopefully illustrate the interrelationships with other methods and the limitations of current use.

Instrumentation

One common characteristic of the spectroscopies described below is that they all require a UHV environment. This is mandatory for the electron or ion beam used either to probe or analyze the surface and to keep the surface clean of any contamination from the environment. The level of vacuum necessary is extreme; typically, 10^{-7} to 10^{-10} millibar pressure must be maintained.

Electron Spectroscopy for Chemical Analysis (ESCA)

Recent reviews have stressed the basic instrumentation [6] and advances [7] which have allowed great strides in this technique. The basic ESCA experiment requires a source of X-

TABLE 1—*Characteristics of some analytical techniques suitable for studying polymeric materials.*

	XPS (ESCA)	IR and Raman	SIMS	ISS
Vacuum	High vacuum	Ambient	UHV	UHV
Resolution	0.6 eV	≈1 cm^{-1}	0.1 to 1 amu	Variable
Elemental/molecular information	No H detection Chemical shifts	??? Functional Group id	All + isotopes MW molecules Fragmentation	No H or He Resolution limited
Detection limit	% of monolayer	% in volume 0.01 monolayer	ppm/ppb element 0.01 monolayer Molecular	% monolayer
Lateral resolution	5 μm	≈10 μm	10 nm (atomic) ??? molecular (ions)	. . .
Depth sensitivity	>50 Å	μm range	10 Å?	3 to 5 Å
Sample damage	Small, sometimes with unmonochromatized X-rays	none	High (needs study)	High (needs study)
Major outcomes	Elemental and chemical analysis, electronic structure	Molecular vibrations Functional Groups Bulk	Low detection limits, molecular ions/fragmentation ions-bonding	Elemental atomic orientation

rays (c.f., Table 2), a lens system to collect and focus photoemitted electrons, an energy analyzer, and a detector. This equipment, within vacuum, is generally interfaced to data acquisition and analysis software on an operating computer. The desirable characteristics of the X-ray source involve narrow line width, high intensity, and minimal damage. The lens system serves to allow collection of electrons from a sample distanced away from the entrance of the analyzer. This means other techniques can be focused at the same surface position. Further, the lens system usually retards the energy of the incoming electrons to provide higher energy resolution. The energy analyzer operates as a filter to pass specific energies of electrons to the detector. The detector serves to amplify the electron signal and produce a counting rate. Data acquisition using common interfaces (e.g., RS-232) allows for signal averaging needed to provide acceptable signal/noise ratios. In addition, the scanning and control of other parameters is possible with the computer.

Experimentally, a sample is introduced into the vacuum chamber, illuminated by X-rays, and the electron energy analyzed. Commonly, it is thought that the vacuum will have some effect on the sample, making the relevance to a "real" environment questionable. Certainly, physically adsorbed gases or liquids (e.g., water) are desorbed under UHV. Thus, "wet" samples are difficult to analyze without special precautions. The use of freeze drying and low-temperature sample handling can mediate some of this problem. Nevertheless, the UHV can affect the sample in ways which prevent analysis of samples in the ambient environment. It is notable that both air and vacuum are very high-energy environments, encouraging low-energy species to segregate at the interface. Vacuum effects themselves are not always deleterious. In many older ESCA instruments, for instance, sample heating from secondary electron emission of the source causes sample damage sometimes ascribed to vacuum alone. It is in the best interest of the analyst to evaluate the range of damage under any type of UHV analysis.

Typically, a low-energy resolution survey scan allows for determination of detectable elements. These signals are then scanned at higher resolution conditions to provide information on binding energy and intensity. The binding energy of the electron gives chemical information; the intensity allows for quantitative analysis. Experimentally, it is desirable to vary the angle of the sample plane to allow different depths to be probed (angle-dependent ESCA). Further, the use of several X-ray energies also produces different sampling depths. The range of depths probed by the technique using the angle and energy-dependent experiments ranges from 10 to 200 Å in polymers [*6*].

The most recent advances have been in three areas [*6*]: (1) higher energy resolution for finer ability to distinguish chemical states, (2) higher spatial resolution for lateral analysis, and (3) speed of data acquisition for studies requiring low damage or kinetics. The latter characteristic has allowed for development of more dependable quantitative information

TABLE 2—*Characteristics of X-ray sources for ESCA.*

Anode Material	Energy, eV	Line Width, eV	Relative Intensity
Mg Kα	1253.6	0.7	1.0
Al Kα[a]	1486.6	0.85	0.5
Si Kα	1739.5	1.0	0.19
Zr Lα	2042.4	1.7	0.05
Au Mα	2122.9	2.4	0.03
Ag Lα[a]	2984.3	n.a.	0.02
Ti Kα	4510.9	2.0	0.05
Cr Kα	5417.0	2.1	n.a.

NOTE: n.a. = not available.

[a] Often used with monochromator.

from polymers. Damage [*8*] has been a major concern under the X-ray, making quantitative analysis less precise. Precision, accuracy, and speed are now such that polymer surfaces can be quantitatively analyzed in a few moments of exposure. This allows more signal-intensive experiments like shallow angles to be probed. Alternatively, more sensitive polymers like PVC can be probed and radiation damage can be limited [*8b*].

The lower damage rates, the higher speed, and the better signal/noise in modern ESCA machines have opened up a better understanding of the limitations of previous applications of ESCA toward polymers.

Secondary Ion Mass Spectrometry (SIMS)

The current status of SIMS instrumentation is one of rapid development [*9*], and it is not appropriate to review its complete status or its history in this article. SIMS is really a family of methods and has several component variables which are governed by the type of information desired. Experimentally, an ion/atom beam based SIMS experiment involves the generation of a keV ion (or atom) beam focused on the sample surface and the collection and mass analysis of secondary ions generated from desorption or sputtering. For polymers and organic materials in general, the static SIMS experiment requires low ion dosages and current densities. This minimizes damage and preserves the surface sensitivity. This contrasts with the use of higher current densities for SIMS depth profiling, the ion microprobe and ion microscope. These latter configurations are very powerful in the analysis of semiconductor materials and other inorganic species. Their application to polymers, as seen below, is a growing area.

For static SIMS, currently two sets of specific instrumental configurations are commonly used. These involve a combination of two types of primary ion (atom) beam sources and two types of mass analyzers. The ion (or atom) source either involves noble gas ion beams (subsequently neutralized if an atom source), which are at very low current densities via defocusing, or, alternatively, focused ion beams, which are produced from liquid metals (gallium) or desorption from a solid state source (cesium). The latter ion beams are also used at very low ion currents, although the current densities are quite high. After secondary ions are generated from the sample, they are collected by ion optics and focused for analysis into a mass spectrometer. Every type of MS detector has been used for SIMS types of experiments; for polymers, the two common approaches have been quadrupole or time of flight (TOF) detectors. The latter analyzer especially has been useful because of its multichannel capabilities, detecting all masses simultaneously. This provides for lower damage levels. Also, imaging capabilities are beginning to be developed for use in static SIMS, although this is a burgeoning area.

Low-Energy Ion Scattering Spectrometry (ISS)

Basic instrumentation for low-energy ion scattering involves components common to ESCA (charged particle energy analyzer) and SIMS (low current ion source). In fact, one problematical aspect of the instrumentation is that it exists usually as an afterthought to ESCA or Auger spectrometers; since most include an ion source for surface cleaning or depth profiling, simply a change in polarity of the energy analyzer is all that is needed for doing rudimentary ISS experiments. However, most often ISS is also the least utilized and therefore in a design disadvantage; component geometries and alignments are optimized usually for electron spectrometry to be done.

Instrumentation required for the ISS experiment involves the same type of noble gas ion sources discussed above for static SIMS and sector or mirror-type energy analyzers used commonly for ESCA or Auger spectroscopy. Because of the limited signal levels at low current densities and the low-energy resolution requirements, the cylindrical mirror analyzer (CMA) is preferable. This is due to a combination of the higher signal throughput at lower energy resolutions over the hemispherical sector and, when the ion source is coaxial with the CMA, the 360° solid acceptance angle of the analyzer. However, this desirable design is not currently realized in such combination instruments. More likely, the hemispherical analyzer of an ESCA or part of a CMA (with the ion gun off axis) is used. Besides the change of polarity of the analyzer, a change in ion optics is also generally required; retardation used in ESCA electron optics for increased energy resolution is generally not needed, and the intensity loss due to retardation mediates against its use also.

Sample Handling for Polymer Analysis

In comparison with metals, alloys, semiconductors, even glasses or catalysts, technical polymers present inherent analytical difficulties. As practical materials, they are rarely "clean" or "pure." Typical polymer formulations contain additives and stabilizers. Further, a polymer material usually involves a large distribution of molecular weights. In some cases amorphous and disordered phases are in contact with microcrystalline structure. Important for these methods is the fact that they are generally insulating materials. When photoelectrons are generated, or when low-energy ion beams (500 eV to keV) in SIMS or ISS impinge on polymers, the surface builds up an electrostatic charge that rapidly impedes the acquisition of spectral information. Finally, as alluded to above, polymeric materials are quite radiation and heat sensitive.

More particularly for SIMS and ISS, sputtering is an unavoidable aspect of the ion beam/solid interaction. Therefore, concerns about the sampling depth of each method are convoluted with the effects of ion beam based radiation damage. Even under mild ion beam conditions where material may not be consumed through sputtering, damage will still occur in terms of breaking and reforming molecular bonds, which impart the important structure and properties in polymers. Thus, description of the potentially powerful orientation and bonding information in ISS and SIMS must be tempered by a clear knowledge of the extent and mechanisms of damage. In turn, this complicates the determination of the actual depth of analysis. Each new technical advance in minimizing damage due to the ion beam has led to drastic new advances in the type of information available in SIMS and ISS.

Experimental Aspects

ESCA

Three aspects of ESCA make it a desirable surface analytical technique for polymers. Qualitative information from chemical shifts allows the identification of surface functionality in a polymer. Quantitative analysis of the surface allows the determination of elemental and functional group concentrations. Finally, angle and energy-dependent measurements allow this information to be determined for a depth profile, albeit with great difficultly due to the attenuation of signals from deeper depths. All of these aspects have been discussed in great detail for polymers previously [*2,3,5,7,8*]. However, the speed of newer instrumentation increases confidence in the measurement because of the lower amount of experimentally induced sample damage [*7*]. This allows extension to more complex samples. Further, this lower damage allows for higher accuracy in the measurement.

In particular, recent studies of homopolymer blends of PVC and PMMA [*8b*] have shown that composition can be determined within 5% absolute error, with and without sensitivity factors. In particular, sensitivity factors are used to calibrate elemental analysis with core level photoemission. However, with careful curve fitting, analysis without sensitivity factors can be accomplished using the areas under a single photoemission peak if distinctive shifts allowing unambiguous assignment of functional groups and chemical states is possible. Further, a series of homopolymer blends yielded surfaces with equivalent composition to the bulk over the sampling depth of ESCA. This unusual circumstance is due to the mixing producing compatible blends of materials with nearly equivalent surface-free energies. Thus, no thermodynamic driving forces exist for surface segregation. Of course, the more typical application of ESCA to multicomponent polymers yields results describing the extent of segregation of multicomponent polymers.

Figure 1 illustrates the limitations of this approach for unknown systems. Analysis of glow discharge surface treatments to fluoropolymers [*8c*] yields a variety of states which cannot be unambiguously resolved into components. In this case, the limitations of chemical shift/change in state of carbon 1s are clearly evident over a series of sample surfaces. The spectra show the effects of hydrolysis of expanded PTFE (Fig. 1*a*) using oxygen/water vapor (Fig. 1*b*), hydrogen/oxygen (Fig. 1*c*), hydrogen/water vapor (Fig. 1*d*), and hydrogen/methanol

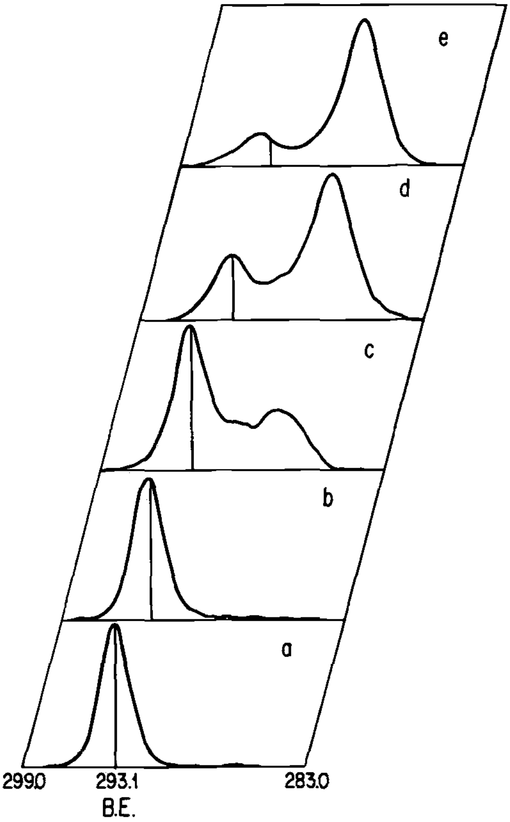


FIG. 1—*ESCA analysis of radio frequency glow discharge surface treatments on expanded PTFE. Carbon 1s spectra is referenced to fluorine 1s as an internal standard. For conditions see Ref* 8c (a) *unmodified ePTFE* (b) *ePTFE treated with O_2/H_2O vapor RFGD* (c) *ePTFE treated with H_2/O_2 RFGD* (d) *ePTFE treated with H_2/H_2O vapor RFGD* (e) *ePTFE treated with H_2/methanol vapor RFGD.*

vapor (Fig. 1*e*) on the carbon 1s spectrum. The changes to the surface oxygen concentration could be quantified using ESCA elemental analysis, but the identification of new functionality required FTIR confirmation. Subsequent chemical reactions were needed to confirm the incorporation of hydroxyl groups into the surface. However, given the difficulty of identifying hydroxyl groups in the presence of C-F groups, this is an especially challenging application. It is evident that ESCA was a necessary component of this analysis since infrared spectroscopy alone could not quantify changes to the surface of the materials.

SIMS and ISS

Both techniques are based on the interaction of low-energy ion beams with condensed phase surfaces. Secondary ion mass spectrometry (SIMS) involves the mass analysis of sputtered or desorbed secondary ions. Originally focusing on the atomic ions generated in this process, yielding high sensitivity and low detection limit elemental analysis for depth profiling, the basic principles have now been recognized as the same for molecular secondary ions. This allows the derivation of molecular structure information based on molecular ion and fragmentation information similar to that inherent in traditional mass spectrometry. These developments occurred [*9–12*] over the last 15 years and were based on minimizing sputtering rates produced by the primary ion beam and damage due to high current densities and energies to produce "static" or low damage conditions. Early work [*13*] pointed out the necessity of lowering ion beam damage conditions for both methods and compared the results from ISS and SIMS to ESCA. SIMS analysis of polymers was further refined [*14*] using low mass positive ion fragmentation patterns and negative ion analysis [*15*]. Most recently, Benninghoven and Hercules in collaboration [*16*] have shown the ability to generate high-mass ions; this leads to many other information possibilities, among them direct molecular weight distribution determination.

The SIMS experiment analyzes the results of low-energy ions which implant and transfer their momentum. The ion scattering experiment involves analysis of that fraction of primary ions which scatter as a billiard ball collision. ISS is both conceptually and theoretically simple. The experiment involves the two-body conservation of momentum and energy in a collision between (typically) a noble gas ion beam (at a few hundreds to thousands of electron volts at low current densities) and the sample surface and the subsequent energy analysis of the loss due to the "billiard ball" collision. The scattering can be described by an energy after collision (E) ratioed to the energy before collision (E_0) as related to the masses of the primary ion (M_1) and target atom (M_2) and the laboratory scattering angle by the following equation

$$\frac{E}{E_0} = \frac{M_1^2}{(M_1 + M_2)^2}\left(\cos\theta + \left\{\frac{M_2^2}{M_1^2} - \sin^2\theta\right\}^{1/2}\right)^2$$

ISS has found wide application in the field of catalysis [*17*], yet, because of damage concerns similar to SIMS, has only recently been extended to polymer surface structure and orientation analysis [*13,18,19*]. The primary attribute of the technique is the high-surface sensitivity; sampling depths involve detection of the topmost exposed atomic layer when using a noble gas ion beam. Neutralization of the scattered ion beam from lower layers limits contributions of the signal. ISS is especially sensitive, because of this attribute, to orientations of surface atoms. Thus, in combination with ESCA especially, sensitivity to the topmost surface layer complements ESCA in building depth profiles, and sensitivity to orientation of atoms (or functional groups) again complements ESCA, where most chemical shifts are not large enough to sense differences in orientation.

Current Progress

ESCA

Much of the current progress in ESCA is also discussed in the following sections on ISS, since ISS serves as a fine complement to the particular information from the ESCA depth profile. One recent development is the application of the higher energy titanium anode to the depth profiling of polymers [*20*]. In this work, we were able to show that, through the use of multichannel detectors, the signal to noise was now appropriate to allow use of this source. Sensitivity factors for quantitative elemental analysis were reported. This advance essentially is most useful for the higher energy of the source, yielding higher kinetic energies. This allows sampling to 200 Å depth, allowing the probing of deeper regions. Table 2 lists data for alternative X-ray sources used in the ESCA experiment. The application of these sources to polymer surface analysis is still under development.

Low-Energy Ion Scattering

Homopolymer Surface Structure—Work in the use of low-energy ISS as an analytical technique for polymers has gone on for about eight years and is built on initial work on methacrylates [*13*] to develop low damage conditions which preserve slight changes in surface conformation. This early work showed that for the glassy methacrylates, the surface composition was equivalent to the bulk composition even with ISS surface sensitivity, except for three polymers with bulky side chains which might have some sort of steric hindrance. However, no work was done to show why this was manifested in certain polymers and not in others until recent studies [*18*], which showed that ISS could distinguish between conformations of stereoregular poly(methyl methacrylate) (PMMA) and slight amounts of poly(methacrylic acid) (PMAA) copolymerized randomly with PMMA. Very different carbon/oxygen scattered ion intensity ratios were measured in the ISS experiments. Angular-dependent ESCA results were unable to distinguish between any of these polymers. Atactic, syndiotactic, and isotactic PMMA and PMMA/PMAA random copolymers all have the same atomic composition and no differences in monomer bonding. Molecular models were utilized to explain the differences in measured surface atomic concentrations as resulting from shielding and shadowing of functional groups in different conformations. Similar results were seen from methyl- and phenyl-substituted polysiloxanes, where the silicon/oxygen ratio showed significant differences. We have since extended this work [*19*] to probe differences in shielding of nitrogen functionalities in different isomers of vinyl pyridine polymers. In this study, rather than explain the results after the fact with models, polymers were chosen with well-known structures from molecular mechanics calculations, verifying NMR results. It was predicted that different nitrogen/carbon scattered ion intensity ratios would be measured for these polymers. In fact, since the nitrogen in poly(2-vinyl pyridine) (P2VP) is shielded by the backbone carbons, no initial nitrogen scattering signal should be measured, which is what occurred. It was observed that nitrogen/carbon ratio increases upon sputtering to the equivalent of poly(4-vinyl pyridine) (P4VP), which always shows nitrogen scattering. The quaternization of the nitrogen in P2VP via methyl, ethyl, or t-butyl groups causes the rotation of the nitrogen, because of steric considerations, out away from the backbone. This yields very different nitrogen-to-carbon signals, indicating the sensitivity to the orientation of this particular functional group.

Multiple Technique Depth Profiles of Multicomponent Polymers—Integrating the ISS method into the multitechnique analysis of multicomponent polymer materials has allowed the superior surface sensitivity to be used to complement ESCA and FT-IR sampling at different depths. This was illustrated by the analysis of random block copolymers of bisphenol-a-polycarbonate (BPAC) and dimethyl siloxane (DMS) [*21*]. Quantitative surface compositions determined from angle-dependent ESCA and ISS were combined with SEM to develop a morphological model of the domain segregation approaching the air-facing interface. The same approach was then used on polymer blends created from homopolymers of BPAC and DMS. This serves to compare the forces which drive segregation to the near surface region in a blend of the same components as in copolymer systems under study, to observe effects of both surface energy differences, and to blend component "compatibility" (i.e., interchain bonding interactions) in the overall free energy of mixing. We [*22*] were able to show that, in blends of less than 11% (by weight) DMS, the surface composition as measured by angular-dependent ESCA and ISS was always 85% (by weight) DMS. This would suggest that a "compatible" mixture exists at that concentration, yet this system is considered to be incompatible. It is important to note that at higher concentrations (25% DMS) visible phase separation occurred and the surface was 100% DMS. We are currently busy studying a variety of incompatible and compatible blends described above with the simplest goal of using ISS to complement angle-dependent ESCA.

Another application area is in the area of surface-modified polymers [*23–25*]. In a series of studies of different treatments to PMMA, we have used the higher surface sensitivity of ISS to develop specific models of orientation of modified functional groups. In particular, noting ISS results which showed a great increase in surface oxygen, ESCA showed a decrease in oxidized carbon concentrations [*23,24*]. These results were completely consistent with the adsorption of water vapor rather than permanent oxidation. Different treatments which promoted specific oxidation were then developed [*25*]. Contact angle methods were used to also differentiate functionality in the latter study. One outcome of that work has been attempts to determine the relationships between ISS conformational sensitivity and contact angle techniques.

Static SIMS

Homopolymer Structure Sensitivity—This discussion will progress by considering three different types of ions generated in the static SIMS experiment from polymers, roughly divided by mass range (i.e., low, high, and in between), but mostly divided by mechanism of formation (fragmentation and rearrangement, desorption and cationization of oligomers, and simple bond-breaking/charge stabilization). The most complex of the three are low-mass [i.e., less than 300 atomic mass units (amu)] fragment ions, the original focus of much static SIMS polymer characterization. The first applications of the static SIMS to the analysis of polymer-surface, low-mass (0 to 150 amu) fragment ions [*13,14*] were used to distinguish structure and isomerism (butyl methacrylates) in a series of methacrylate polymers with different side chain structures via fragmentation pattern from the side chain, within a common pattern characteristic of the backbone, primarily from positive ion spectra. A significant result from these early studies was the differentiation of isomeric structures of butyl methacrylate, which could not be distinguished by ESCA core level analysis and the analysis of slight reactive surface degradations of the t-butyl methacrylate [*26*]. Subsequent improvement in SIMS experimental conditions to lower surface damage induced by the primary ion bombardment has allowed for the analysis of higher mass fragments that are related to the original structure of the polymer [*14*]. Over these studies the "acceptable" description of static or low damage conditions evolved from the original current density (1 nA/cm^2) criterion based on sputter yields to preserve a surface for 1 h [*9*] to minimum ion dosages (e.g., 10^{-13} ions) [*14,19*]. In addition, other criteria for minimal damage have been proposed, for example, based on the thesis that chemical and structural disruption is the result of inefficient dissipation of the primary charge input due to the inherent low conductivity of the polymer sample [*15*]. The use of a primary atomic (neutral) beam was suggested in this case to remove the input of charge to the sample, with similar spectral results as derived from primary ion beam analysis and better negative ion spectra [*15*]. However, precise spatial and low current control of the atomic beam is much more difficult in comparison to ion beams [*15*].

It is instructive to compare results from the ISS work on nitrogen-containing polymers discussed above to the typical conditions for static SIMS. ESCA analysis was done before and after typical ion beam irradiation times for the ISS experiment. No ion beam induced changes in bonding or composition were detectable by ESCA analysis. Yet, damage to the native polymer structure, as assessed by changes in nitrogen/carbon signal intensities was apparent after 2 min of irradiation at 2 nA/cm^2 (i.e., 1.5×10^{-12} ions) 2 kV helium. This dosage is at or below static SIMS conditions, in part because of the lower sputter yield of helium than a typical static SIMS experiment using argon or xenon primary ions. *Clearly, very slight chemical modification and damage of the surface of the polymer is occurring without necessarily the sputter-induced consumption of the material.* It is now believed that polymers and organic materials are more sensitive to ion beam induced changes than inorganic materials. The problem of considering the higher damage cross sections in the determination of primary ion beam conditions for organic species, as opposed to sputter yields, has been recognized by Benninghoven's group [*16,27*] in the design of a TOF-SIMS, which incorporates a pulsed ion source of very low beam density (<1 pA/cm^2). Lower dosages are possible because of the simultaneous detection of all ions from a pulse of primary ions in the TOF experiment. As conditions and instrumentation have improved, more information has been gained. The low-damage/low-dosage studies have opened up homopolymer and multicomponent polymer analysis to much greater levels of information because of the simplicity of assignment for higher mass ions.

Applications of the TOF-SIMS experiment to nylons, polystyrenes, polydimethyl siloxanes, and surface-modified polymers [*16,27,28*] has presented information beyond characterization of the monomer identity. For instance, high-mass oligomeric ions generating an accurate molecular weight distribution have been demonstrated [*16*]. The potential here is great; a surface-sensitive molecular weight distribution would be extremely important for many polymer processing problems. High-mass fragmentation patterns have been postulated to be sensitive to intrachain bonding in nylons [*16*] and composition in complex polyurethanes [*28*]. Differentiation of isomeric differences is evident from high-mass ions also [*16*].

Recently, attention has focused on the ions generated from fragmentation along the chain into charged stabilized ions which we have been termed "n-mer ions" [*29*]. These potentially have a great deal of information about intrachain bonding and chemical reaction sites. N-mer ions have been observed from a variety of polymers: Teflon [*27*], homopolymer and copolymer nylons, and segmented poly(ether urethanes) [*30*]. Our most recent work discussed charge stability in ion formation from functional polymers (e.g., the vinyl pyridines and substituted polystyrenes) with emphasis on the effects of charge and reaction site and structure determination via analysis of the n-mer ions [*29*]; the potential impact in qualitative and quantitative surface analysis of a variety of multicomponent polymer applications where functional and nonfunctional polymers are combined is obviously great.

Focus on the mechanisms of formation of these three types of ions involves different considerations as the information content of the ion increases with mass. However, more attention to the simple ability of static SIMS to differentiate the surfaces of polymer materials with equivalent atomic compositions and difficult ESCA chemical shift information has meant even great excitement about fragmentation pattern analysis.

Recent work has allowed the definition of a means to provide quantitative molecular ion intensities [*31*]. We have examined the kinetics of polymerization of thin films cast by Langmuir Blodgett techniques [*32,33*]. This was accomplished by following the loss of monomer-related ion and the gain of polymer-related ions. In these studies, we have been able to show the sensitivity of SIMS to the initial stages of polymerization. The impact of this is potentially quite great. The use of the method to study the kinetics of cross linking at a polymer surface would be very exciting.

Multicomponent Polymers—A few studies of multicomponent polymers have successfully used model polymers to explore the effects of fragment ion formation [*30*,*34*,*35*]. Block and random copolymers were analyzed, and fragment ions unique to each structure were identified. Quantitative ion intensity ratios were correlated to composition, and sampling depths were estimated via comparison to ESCA data. However, many open questions still exist from this type of study: low-mass fragment ions originate from a variety of processes; in unknown multicomponent polymers, it would be impossible to unambiguously assign ions to particular structures or components. Dynamic SIMS depth profile work has studied diffusion between isotopically labeled polymers [*36*]. In addition, a series of very exciting papers using dynamic SIMS depth profiling on block copolymer thin films by Russell et al. was recently described in overview [*37*]. A regular series of domain structures was measured with highly controlled block length polymers. This work shows the power of focusing strictly on elemental ions in determining profiles; where unique isotopic tags can be used to identify one component, complex different ion formation mechanisms can be ignored. One nice aspect of the work by Russell is the correlation to ESCA and light and X-ray scattering. However, with these advances, much work remains to be done to identify exact conditions which describe sampling depth issues and instrumental advances to further enhance the probability of formation and detection of high-mass ions.

Future Directions

In the area of ion beam methods, specifically with low-energy ISS, two important areas of application to polymers should be opening with further developments in instrumentation. The so-called impact collision ISS experiment (ICISS) developed by Aono [*38*] to determine bond orientations from shadow cone formation considerations would allow the determination of exact bond angles in highly oriented regular surface structures. For some types of systems this information would be highly desirable. In addition, electronic structure-related effects on charge neutralization are completely unknown in ISS of polymers; these fundamentals should be investigated. However, at the minimum, a better understanding of the surface sensitivity and structure/orientation sensitivity is extremely useful in complementing ESCA for analysis of the topmost surface interface. It appears that these data will be extremely important in resolving the details of contact angle measurements with ESCA and ISS. Potentially, this information could be very useful in quality control and online analysis since contact angle measurements can be used more readily but backed up with detailed spectroscopic information to monitor surface processes like corona discharge treatments.

Finally, the potential of SIMS for polymers is quite exciting. Beyond the current low mass uses are unanswered and controversial questions about the limitation in ion formation at high mass. If overcome, the molecular weight distribution of the near surface region might be determined. When compared with the bulk molecular weight, segregation and processing effects could be known. Important surface properties related to segregation of low molecular weight species plague a variety of polymer interfacial adhesion and compatibility issues. In addition, the determination of chain orientation and intrachain bonding in the near surface region may be available from n-mer ion distributions. Hydrogen bonding in proteins in different conformations may be deduced from the probability of formation of specific ions. The average length in monomer units of the folds and loops in a polymer chain could be determined from the distribution of n-mer ions. All of these possibilities complement surface compositional information available from other methods and give hope that the future of applications of these methods will be bright for polymer analysis.

Acknowledgments

The author is appreciative of support for this research from the National Science Foundation Polymers Program of the Division of Materials Research (DMR 8720650); Mobil Films Division; Exxon Educational Foundation; and the Gelb Foundation. The contributions of J. H. Magill (University of Pittsburgh), R. L. Schmitt, J. H. Wandass, J. J. Schmidt, G. L. Grobe, III, P. A. Cornelio, K. J. Hook, T. J. Hook, L. Salvati (Perkin Elmer), R. L. Chin (Intel), T. G. Vargo, E. R. Mittlefehldt, M. B. Clark, Jr., H. Lee, C. A. Burkhardt, and P. L. Kumler (SUNY Fredonia) are gratefully acknowledged.

References

[1] (a) Burkstrand, J. M., *Journal of Applied Physics*, Vol. 52, 1981, p. 4795; (b) DiNardo, N. J., Demuth, J. E., and Clarke, T. C., *Chemical Physics Letters*, Vol. 121, 1985, p. 239; (c) Pireaux, J. J., Vermeersch, M., Grégoire, Ch., Thiry, P. A., Caudano, R., and Clarke, T. C., *Journal of Chemical Physics*, Vol. 88, 1988, p. 3353; (d) Grunze, M. and Lamb, R. N., *Surface Science*, Vol. 204, 1988, p. 183.

[2] Gardella, J. A., Jr., *Trends in Analytical Chemistry*, Vol. 3, 1984, No. 5, pp. 129–33.

[3] Gardella, J. A., Jr., *Applied Surface Science*, Vol. 31, pp. 72–102.

[4] Hercules, D. M., *Analytical Chemistry*, Vol. 58, 1986, p. 1177A.

[5] (a) Pireaux, J. J., *Journal of Electron Spectroscopy and Related Phenomena*, 1990, in press; (b) Dilks, A. *Analytical Chemistry*, Vol. 53, 1981, p. 802A.

[6] Nebesney, K. W., Masschoff, B. L., and Armstrong, N. R., *Analytical Chemistry*, Vol. 61, 1989, p. 469A.

[7] Gardella, J. A., Jr., *Analytical Chemistry*, Vol. 61, 1989, p. 589A.

[8] (a) Gardella, J. A., Jr. and Pireaux, J. J., *Analytical Chemistry*, Vol. 62, No. 11, 1990, p. 645A; (b) Schmitt, J. J., Gardella, J. A., Jr., and Salvati, L., Jr., *Macromolecules*, Vol. 22, 1989, p. 4489; (c) Vargo, T. G., Gardella, J. A., Jr., Meyer, A. E., and Baier, R. E., *Journal of Polymer Science*, Part A: Polymer Chemistry, 1991, Vol. 29, p. 555.

[9] (a) Benninghoven, A., *Journal of Vacuum Science Technology A*, 1985, A3(3), 451; (b) Benninghoven, A., Rudenauer, F. G., and Werner, H. W., *Secondary Ion Mass Spectrometry: Basic Concepts, Instrumental Aspects, Applications and Trends*, Wiley, New York, 1987, Chapter 5, pp. 672–753.

[10] Winograd, N., *Scanning Electron Microscopy*, Vol. III, 1985, pp. 919–26.

[11] Pachuta, S. J. and Cooks, R. G., *Chemical Reviews*, Vol. 87, 1987, p. 647.

[12] Colton, R. J., *Nuclear Instruments and Methods in Physical Research*, Vol. 281, 1983, pp. 276–86.

[13] (a) Gardella, J. A., Jr. and Hercules, D. M., *Analytical Chemistry*, Vol. 52, 1980, p. 226; (b) Gardella, J. A., Jr. and Hercules, D. M., *Analytical Chemistry*, Vol. 53, 1981, p. 1879.

[14] Briggs, D. and Hearn, M. J., *Vacuum*, Vol. 36, 1986, p. 1005.

[15] Brown, A., van den Berg, J. A., and Vickerman, J. C., *Spectrochimica Acta*, Vol. 40B, 1985, p. 871.

[16] (a) Bletsos, I. V., Hercules, D. M., Greifendorf, D., and Benninghoven, A., *Analytical Chemistry*, Vol. 57, 1985, p. 2384; (b) Bletsos, I. V., Hercules, D. M., vanLeyen, D., and Benninghoven, A., *Macromolecules* Vol. 20, 1987, p. 407.

[17] Horrell, B. A. and Cooke, D. L., *Catalysis Reviews—Science and Engineering*, Vol. 29, No. 4, 1987, pp. 447–491.

[18] Hook, T. J., Schmitt, R. L., Gardella, J. A., Jr., Salvati, L., Jr., and Chin, R. L., *Analytical Chemistry*, Vol. 58, 1986, p. 1285.

[19] Hook, K. J., Gardella, J. A., Jr., and Salvati, L., Jr., *Macromolecules*, Vol. 20, 1987, p. 2112.

[20] Vargo, T. G. and Gardella, J. A., Jr., *Journal of Vacuum Science and Technology*, Vol. A7, No. 3, 1989, p. 1733.

[21] Schmitt, R. L., Gardella, J. A., Jr., Magill, J. H., Salvati, L., Jr., and Chin, R. L., *Macromolecules*, Vol. 18, 1985, p. 2675.

[22] Schmitt, R. L., Gardella, J. A., Jr., and Salvati, L., Jr., *Macromolecules*, Vol. 19, 1986, p. 648.

[23] Hook, T. J., Gardella, J. A., Jr., and Salvati, L., Jr., *Journal of Materials Research,* 1987, Vol. 2, No. 1, p. 117.
[24] Hook, T. J., Gardella, J. A., Jr., Salvati, L., Jr., *Journal of Materials Research,* Vol. 2, No. 1, 1987, p. 132.
[25] Vargo, T. G., Gardella, J. A., Jr., and Salvati, L., Jr., *Journal of Polymer Science*: Part A: Polymer Chemistry, Vol. 27, 1989, p. 1267.
[26] Gardella, J. A., Jr., Novak, F. P., and Hercules, D. M., *Analytical Chemistry,* Vol. 56, 1984, p. 1371.
[27] Bletsos, I. V., Hercules, D. M., Magill, J. H., vanLeyen, D., Niehus, E., and Benninghoven, A., *Analytical Chemistry,* Vol. 60, 1988, p. 938.
[28] Bletsos, I. V., Hercules, D. M., vanLeyen, D., Benninghoven, A., Karakatsanis, C. G., and Rieck, J. N., *Analytical Chemistry,* Vol. 61, 1989, p. 2142.
[29] Hook, K. J., Hook, T. J., Wandass, J. H., III, and Gardella, J. A., Jr., *Applied Surface Science,* Vol. 44, 1990, pp. 29–41.
[30] (a) Briggs, D., *Organic Mass Spectrometry,* Vol. 22, 1987, p. 91; (b) Hearn, M. J., Ratner, B. D., Briggs, D., *Macromolecules,* Vol. 21. 1988, p. 2950.
[31] Clark, M. B., Jr., and Gardella, J. A., Jr., *Analytical Chemistry,* Vol. 62, No. 8, 1990, pp. 870–875.
[32] Hook, K. J. and Gardella, J. A., Jr., *Journal of Vacuum Science Technology,* Vol. A7, 1989, p. 1795.
[33] Cornelio, P. A. and Gardella, J. A., Jr., *Langmuir,* Vol. 7, 1991, p. 2454.
[34] Hearn, M. J., Briggs, D., Yoon, S. C., and Ratner, B. D., *Surface and Interface Analysis,* Vol. 10, 1987, p. 554.
[35] Briggs, D., Hearn, M. J., and Ratner, B. D., *Surface and Interface Analysis,* Vol. 6, 1984, p. 184.
[36] Valenty, S. J., Chera, J. J., Olson, D. R., Webb, K. K., Smith, G. A., and Katz, W. J., *Journal of the American Chemical Society,* Vol. 106, 1984, p. 6155.
[37] Russell, T. P., Deline, V. R., Wakharkar, V. S., and Coulon, G., *MRS Bulletin,* Vol. XIV, No. 10, 1989, p. 33.
[38] Aono, M. and Souda, R., *Japanese Journal of Applied Physics,* Vol. 24, No. 10, 1985, p. 1249.

Paint Failure and Defects

Anne M. Millon[1] *and James M. Julian*[2]

FTIR Techniques for the Analysis of Coating Problems: Solid Sampling Accessories

---

REFERENCE: Millon, A. M. and Julian, J. M., "**FTIR Techniques for the Analysis of Coating Problems: Solid Sampling Accessories,**" *Analysis of Paints and Related Materials: Current Techniques for Solving Coatings Problems, ASTM STP 1119*, American Society for Testing and Materials, Philadelphia, 1992, pp. 173–195.

ABSTRACT: The many advantages provided by Fourier transform infrared (FTIR) spectrophotometers over dispersive instrumentation have made infrared spectroscopy even more valuable for the analysis of difficult coating samples. Established surface analysis techniques, such as attenuated total reflectance (ATR) and specular reflectance, still find wide-spread use as problem-solving techniques for cured coating systems. However, the increased energy throughput of FTIR instrumentation has made possible the development of many additional sampling accessories that have greatly simplified the analysis of coating problems. Among these new accessories are the diffuse reflectance (DRIFTS) accessory, the infrared microscope, and the photoacoustic cell. A description of these accessories, associated sampling techniques, and the use of each for the analysis of coatings and surfaces will be discussed.

KEY WORDS: diffuse reflectance, infrared microspectroscopy, photoacoustic spectroscopy, coatings analysis, surface analysis, solids analysis, Fourier transform infrared (FTIR), infrared accessories

Infrared spectroscopy is an extremely informative and versatile tool for the analysis of coatings of all types and in all forms. Almost all organic compounds absorb infrared radiation whether they be in a solid, liquid, or gaseous form. The characteristic frequencies at which chemical functional groups absorb infrared radiation, as well as the factors which might cause these frequencies to be shifted, have been thoroughly studied and documented [*1*,*2*]. Extensive compilations of the infrared spectra of large numbers of chemical compounds [*3–6*] and polymeric materials [*6–9*] are available to the spectroscopist, making positive identifications of unknown materials possible. In addition, infrared spectroscopy provides a means of obtaining compositional information from small amounts of material in a very short period of time relative to other analytical techniques.

Because of its versatility, infrared (IR) spectroscopy becomes even more valuable for the analysis of materials in their irreversible solid forms, such as the cured films and substrate surfaces commonly encountered in the coatings industry. Not only is IR spectroscopy one of the few analytical tools capable of obtaining compositional information from both organic and inorganic solid materials, but most of the IR solid sampling techniques provide a nondestructive means of analysis such that additional testing may be performed on a single specimen.

The overall purpose of any coating is two-fold. One is to provide protection of the substrate to which it is applied. The other purpose is to provide decorative surface treatment. It is,

---

[1] Nalco Chemical Co., Naperville, IL 60566.
[2] DSM Desotech, Inc., Elgin, IL 60120.

therefore, the case that true coating failures are often observed only after a coating has been applied to a substrate and fully cured. A coating's inability to protect can take many forms, such as adhesion failure (peeling or flaking), susceptibility to weathering (erosion), or tacky or soft films due to insufficient cure. Examples of decorative failure include the presence of grit particles, craters, or a gradual fading or loss of gloss.

For many years the IR analysis of cured films was limited to predominantly attenuated total reflectance (ATR) or specular reflectance techniques. ATR has been used to study surface affects due to weathering. Specular reflectance, on the other hand, has found use for monitoring changes in the bulk characteristic of films coated on reflective substrates that have, for example, been subjected to various cure conditions (bake ladder studies). The usefulness of these techniques however, can be limited by factors such as pigment content or changes in surface morphology. The introduction of Fourier transform technology has permitted the development of many new sampling accessories, most of which find usefulness for the analysis of solid materials. The optical efficiency of these accessories tends to be very low (<20% relative energy throughput in many cases), which would have made them impractical or in some cases even impossible to use with dispersive instrumentation. Fourier transform infrared (FTIR) spectroscopy has so revolutionized the field of analytical chemistry that it is difficult to find an analytical laboratory in which this piece of instrumentation does not play an integral role. Simplified spectrophotometer design and manufacturing cost reductions have also made the FTIR a valuable tool for routine manufacturing in-process control applications.

The many inherent advantages of the interferometer method for IR spectral data collection and of FTIR spectrophotometer design over that of dispersive instrumentation have been extensively discussed in many excellent volumes [*10–13*]. For most accessories, the greatest of the FTIR advantages is the much larger quantity of IR energy made available to the sample (Jacquinot advantage). The optical efficiency of the Michelson interferometer and the absence of restrictive slits results in an FTIR beam area (at the interferometer) that is 75 to 100 times greater than the slit width of a dispersive system. In addition, the multiplex advantage, which is the simultaneous analysis of all IR frequencies, allows many scans to be rapidly co-added, resulting in spectra with considerably less noise. These spectra are routinely generated in a few seconds rather than the several minutes necessary to generate a single-scan spectrum using dispersive instrumentation. Thus, even accessories with low optical efficiencies can be used to acquire useful infrared data in a very short period of time.

The ability for rapid data acquisition and the superior data-handling capabilities of FTIR microprocessors has also resulted in the development of many combined analytical techniques. Examples include GC/FTIR, HPLC/FTIR, and SFC (supercritical fluid)/FTIR for the analysis of components separated from complex mixtures. Also available are TGA (differential thermogravimetric analysis)/FTIR and EGA (evolved gas analysis)/FTIR for decomposition studies on polymeric materials.

IR solid sampling techniques previously established on dispersive instrumentation, such as internal reflection (ATR) spectroscopy and reflection-absorption (specular reflectance) spectroscopy, are also finding increasingly wide-spread application as a result of FTIR technology. An additional reflection accessory, the CIRCLE® (cylindrical internal reflectance) cell, has also recently been developed and is finding applications predominantly for liquid sample analysis rather than solid sampling. This accessory makes use of a cylindrical zinc selenide internal reflection element affixed at the center of the cell to be filled with the analyte (flow-through, micro, and variable temperature cells are also available). This technique is ideal for the analysis of aqueous solutions since the strong absorptivity of the hydroxyl band in the shorter wavelength region is weakened relative to other organic group frequencies at longer wavelengths.

The sampling accessories that will be discussed here are limited to three of the more recently developed tools finding use for the examination of solid materials. These include the diffuse reflectance accessory, the infrared microscope, and the photoacoustic cell. These three were chosen due to the fact that they have been instrumental in simplifying the analysis of materials that were previously considered difficult or impossible to analyze. In fact, many of the techniques involved with each of these accessories require very minimal or no sample preparation.

Diffuse Reflectance Spectroscopy

When light impinges upon a material, two types of reflections occur. One type is specular reflection, which is the mirror-like reflection in which the angle of the reflected light from the surface is the same as the angle of the incident light. The other type of reflection is due to diffusely reflected light. This occurs when light is absorbed into the material and subsequently undergoes varying degrees of reflection, diffraction, and scattering before emerging from the sample in all directions. The degree to which a material scatters light is highly dependent on particle size. As the particle size of a material decreases, the amount of diffusely reflected light is increased.

Diffuse reflectance accessories developed for use with FTIR spectrophotometers make use of a large parabolic mirror to collect the diffusely reflected IR radiation over a wide solid area. A schematic diagram of Harrick Scientific's "praying mantis" model diffuse reflectance accessory is shown in Fig. 1 [*14*]. As illustrated in this design, a second parabolic mirror is used to condense and focus the source radiation to a small area of the sampling platform as a means of increasing the sensitivity of the method. The flat optical mirrors are used to direct the beam from the source and to the detector.

This design also illustrates an example of using an off-axis parabolic mirror to reduce specular reflection. The center of each of these mirrors is placed in a plane slightly behind

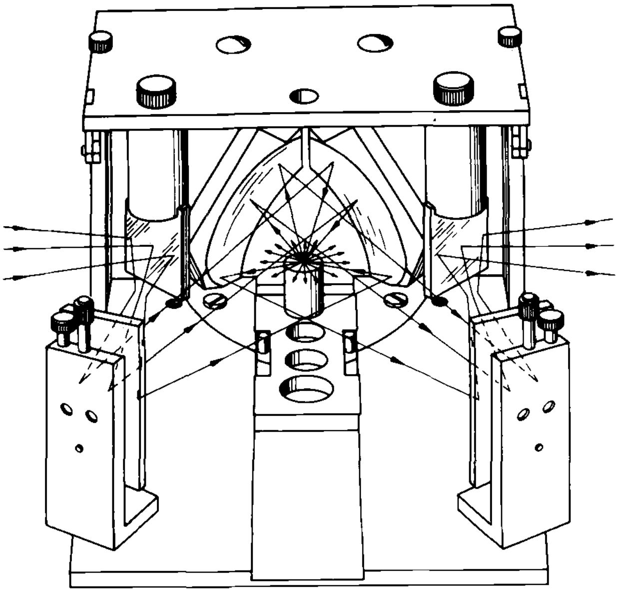


FIG. 1—*Harrick Scientific Corporation's "praying mantis" model diffuse reflectance accessory* [13].

that of the sample. By placing the mirrors adjacent to one another, rather than directly opposite from one another, much of the specularly reflected radiation is not collected. Specular reflectance causes an interference in the diffuse reflectance measurement, which results in derivative-shaped or inverted absorbance bands (referred to as reststrahlen bands). The specular component can also be reduced by using a number of other techniques. These include changing the sample orientation to the incident beam (tilting or turning the specimen), diluting or covering the analyte with a nonabsorbing powder, or using a physical barrier (such as the Spectra-Tech Blocker) perpendicular to the sample surface at the point of irradiation.

The diffuse reflectance accessory was originally developed as a means of collecting spectra of highly scattering materials, specifically powders [*15,16*]. When powders are analyzed by conventional reflectance techniques (ATR), it is only the specular surface component that is analyzed, not any bulk characteristics. Preparing powders for analysis by transmission techniques, either in the form of alkali halide pellets or mulls, can prove tedious and time-consuming, as well as holding the possibility for altering the composition through extensive grinding or use of high pressures. The diffuse reflectance accessory allows for powders to be analyzed either in neat form or, more often in the case of strongly absorbing materials, through dilution in an alkali halide matrix.

The use of diffuse reflectance is hardly restricted to the use of powders, however. The major requirements for collecting good quality diffuse reflectance spectra is that the material absorbs IR radiation and that it scatters light. A smooth and glossy coating film sampled directly will not produce good reflectance spectra due to the high level of the specular component reflected from the surface. On the other hand, a pitted film (weathered), coated embossed panels, or polymer foams will yield good spectra due to the higher degree of scattering. Furthermore, such irregularly shaped materials might prove difficult to analyze by ATR techniques due to the reduced area in intimate contact with the crystal.

In spite of the relatively low energy throughput of this accessory, diffuse reflectance provides extremely high sensitivity. The spectra in Fig. 2 represent approximately 1 and 10 μg of an acrylic resin absorbed onto the surface of cesium iodide powder. The spectra were

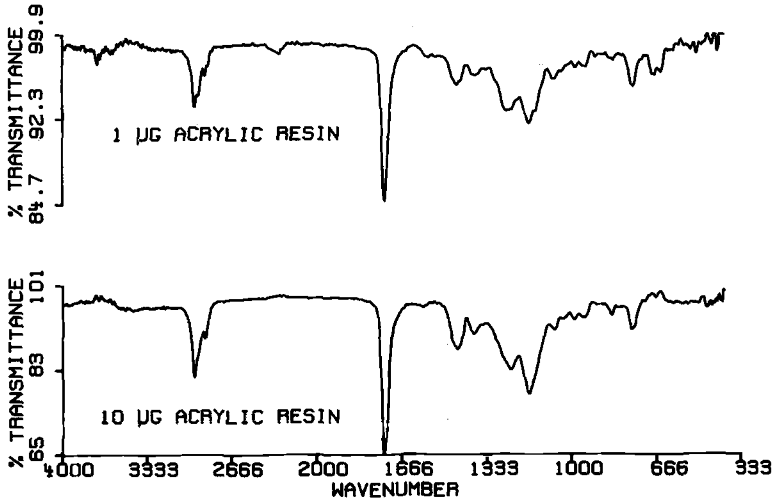


FIG. 2—*Low-level acrylic resin solutions absorbed on CsI powder [dueterated triglycine sulfate (DTGS) detector, 300 scans].*

obtained by first filling the microsampling cup with cesium iodide powder and smoothing the surface with a spatula. A spectrum of the powder was collected into the background file. An aliquot of chloroform solution containing approximately 10 μg of resin was placed on the powder surface. Solvent evaporation at room temperature required less than 1 min before the spectrum was obtained. The process was repeated for the 1-μg aliquot. These spectra suggest that spectra from nanogram levels of material could be routinely obtained.

A number of other diffuse reflectance sampling techniques may be used depending on the nature of the material being analyzed. For films and coated substrates, three techniques are predominantly used. These include direct sampling, alkali halide powder overlay, and silicon carbide sandpaper abrasion. Spectra illustrating the use of these three techniques are given in Fig. 3. The materials analyzed include a pigmented poly(vinylidene fluoride)-acrylic based low gloss coating on an aluminum substrate and coated optical fibers.

Direct Sampling

This technique involves simply placing the specimen directly on the sampling platform. The specimen can be raised or lowered to maximize signal and tilted or rotated to minimize specular reflection. Spectra are ratioed to a totally reflecting background, typically the optical alignment mirror. As the two spectra labeled (A) in Fig. 3 indicate, the high absorptivities of these organic materials result in intense, unresolved absorbance bands.

In instances where speed and nondestructive analysis are more essential than a high degree of spectral quality, diffuse reflectance direct sampling can prove useful. For example, Suzuki et al. [*17–19*] have described the use of the direct sampling diffuse reflectance technique as a screening tool for the identification of metallic automotive paints for forensic applications. In their studies, panels from the Reference Collection of Automotive Paints (Col-

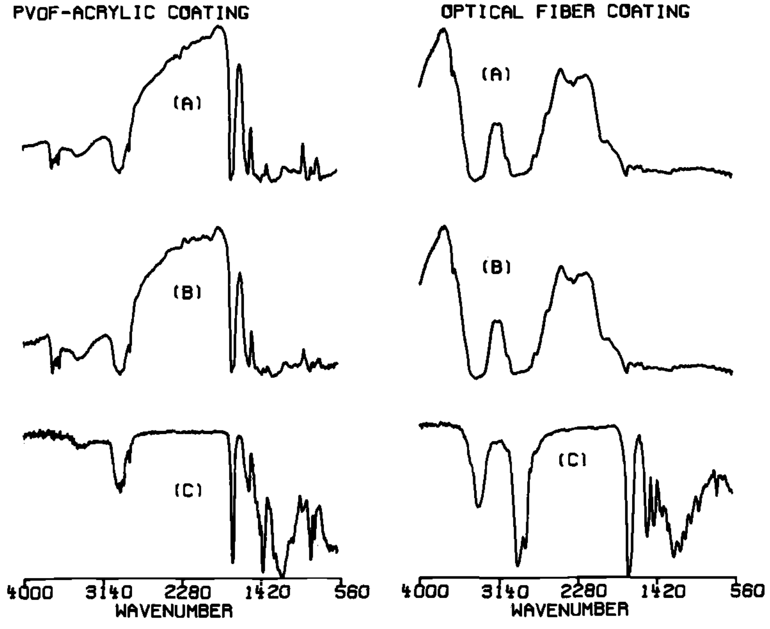


FIG. 3—*Comparison of sampling methods for obtaining diffuse reflectance spectra from coated surfaces: (A) direct sampling, (B) CsI powder overlay, (C) silicon carbide abrasion.*

laborative Testing Services, Inc.) containing metallic flake pigments were analyzed using direct sampling diffuse reflectance. Their studies indicated that coatings containing a high density of flake pigment yielded good-quality spectra similar to those obtained by transmission (Diamond Anvil Cell) techniques. The IR spectrum of panels containing medium- or low-density pigment were improved by tilting the parabolic collection mirror. Though spectral quality was poor, some generalities about the coating system could be obtained. Even though the DRIFTS technique was not intended as a means to definitively identify the make, model, and year of the vehicle from which an unknown specimen was obtained, a large number of possibilities can be quickly eliminated by this technique.

Alkali Halide Overlay

In theory, another method for reducing the effects of high absorptivities and specular reflection is to sprinkle a thin layer of a nonabsorbing powder (e.g., KBr or CsI) over the surface of the specimen. The high surface area of the overlay powder promotes scattering of both the incident and reflected radiation, considerably reducing the amount of specular reflection. In addition, the specimen remains intact for further testing, if necessary.

In practice, the use of the KBr overlay technique is highly dependent on the amount and particle size of the overlay powder, which can make this an extremely tedious technique to use. The spectra labeled (B) in Fig. 3 were obtained by sprinkling a thin layer of KBr over the sample surface. Commercially available KBr was first ground for 30 s using a Wig-L-Bug® grinder. As the spectra illustrate, the overall band intensities were not significantly affected; however, there is an increase in the amount of noise due to the decreased signal. As the amount of KBr overlay was further increased, a corresponding decrease in signal was observed, resulting in spectra that were unusable.

Some alkali halide powder overlay considerations and the application of this technique as a depth-profiling tool for a thin bilayered polymer film were studied by Culler et al. [*20*]. The film examined was a 1.5-μm layer of poly(vinylidene fluoride) over a 29-μm poly(ethylene terephthalate) film. In their study, the authors varied the amount of both a fine and coarse grade of KBr powder over the film and examined the spectral contribution of the two components in the 3200 to 2700 cm^{-1} region of the IR spectrum. As Fig. 4 illustrates, the contribution from the bottom (PET) layer decreases as the amount of KBr is increased. This is due to the increase in the amount of scattering before the light reaches the film surface, which reduces the overall depth to which the light is absorbed. Their study also determined that the use of finer KBr particles (<75 μm) resulted in the need for less of a KBr surface layer to eliminate the contribution of the bottom layer. This is due to greater scattering of the smaller particles.

Silicon Carbide Abrasion

Another sampling technique, which is almost as easy as direct sampling, is the use of silicon carbide sandpaper to gently abrade the surface of a material. This effectively converts the solid into a fine powder, resulting in the sufficient scattering necessary for obtaining good reflectance spectra. Spectra are recorded directly from the surface of the sandpaper with no need for further sample dilution. Spectra are ratioed to the spectrum of a fresh piece of sandpaper. Increased gain settings are typically necessary for this technique, due to the nonreflective nature of the silicon carbide substrate. However, as Fig. 3(C) indicates, the improvement in spectral quality more than makes up for the decreased sensitivity.

Use of the silicon carbide abrasion technique is ideal for the analysis of cured, hard, shiny, and irregularly shaped materials. Powdered samples may also be analyzed by this technique

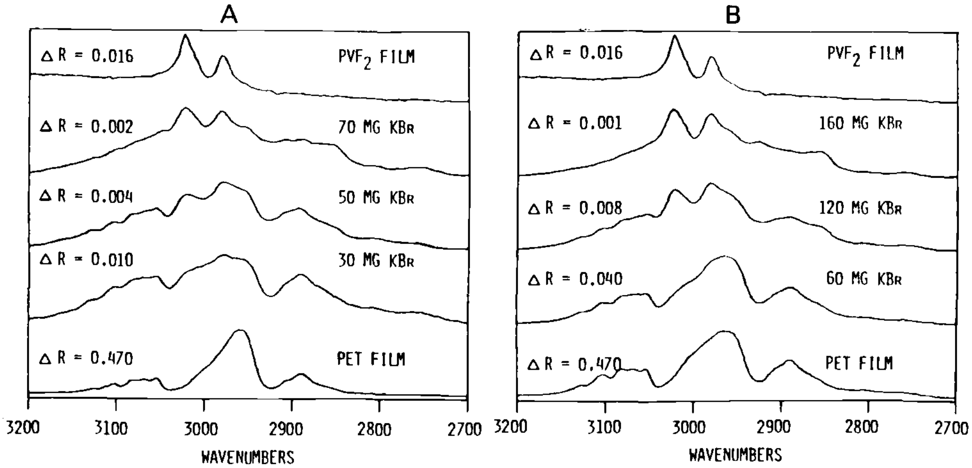


FIG. 4—*Use of KBr overlay technique for depth profiling study of 1.5 μm poly(vinylidene fluoride) on poly(ethylene terephthalate):* (a) *fine KBr powder (<75 microns),* (b) *coarse KBr powder (>75 μm).*

by simply sprinkling a small amount on the sandpaper surface. This technique provides the added advantage for remote sampling. For field failures, it is often necessary to obtain small pieces of a specimen either by cutting a small section of the coated substrate from the bulk or obtaining paint chips from the substrate. Both of these techniques leave obvious visual appearance defects. However, it would be an impossible task to determine the exact spot from which paint was abraded from the cinder block walls of our laboratory walls to obtain the spectrum shown in Fig. 5.

The silicon carbide sandpaper technique proved particularly useful for a problem in which it was necessary to analyze a primer on coated automotive panels that had failed gravel impact testing. A coarse grade of sandpaper was used to first abrade away the topcoat from a panel representative of coating that failed testing. After the primer had been exposed, a fresh piece of sandpaper was used to abrade a small amount of the black primer from the substrate. Comparison of the spectrum from the primer on the failed panel to control panels coated with primer formulations containing different levels of melamine (as represented by the absorbance band at 815 cm^{-1} in Fig. 6) indicated that the failed panel was coated with a primer containing an insufficient amount of melamine for this application.

Analysis of Low-Level Components by Diffuse Reflectance

As referred to earlier, solids in solution can be analyzed using diffuse reflectance techniques simply by evaporating a small amount of liquid onto an IR nonabsorbing powder such as potassium bromide or cesium iodide. This technique has been successfully used in our laboratory to identify substrate contaminants, coating additives, and coated surface "bloom" components.

In cases where severe adhesion failure occurs between coating and substrate, low-level processing materials (such as hydrocarbon or silicone oils) are often the cause. Examination of the substrate surface or the back of the failed paint chips by ATR can prove difficult for detecting small amounts of contaminants due to the strong spectral contribution from the bulk materials. By rinsing the coating or substrate surface with a nonpolar solvent such as heptane, small amounts of residue can be obtained for analysis. Figure 7 is the spectrum of

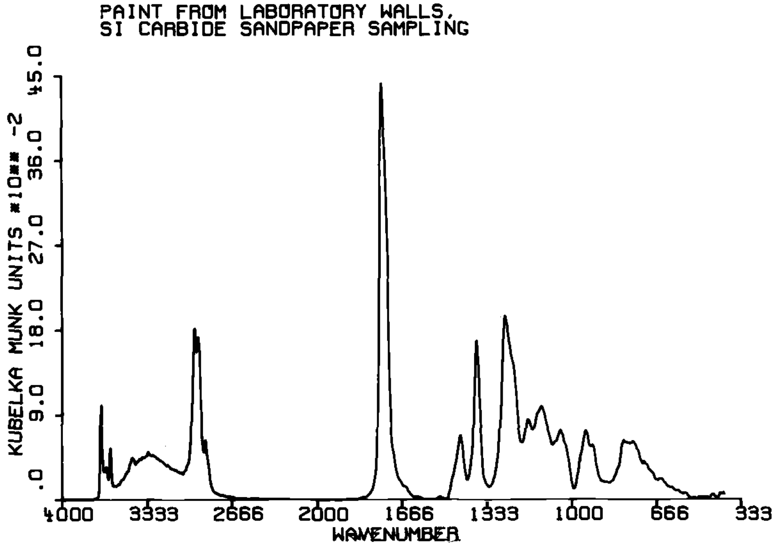


FIG. 5—*Diffuse reflectance spectrum obtained using silicon carbide abrasion technique (DTGS detector, 500 scans).*

the residue rinsed from an untreated piece of aluminum stock test panel used in our development laboratories.

Since many coating additives are not an integral part of the coating cure mechanism, they will remain soluble after the coating is cured. This provides a means for examining low-

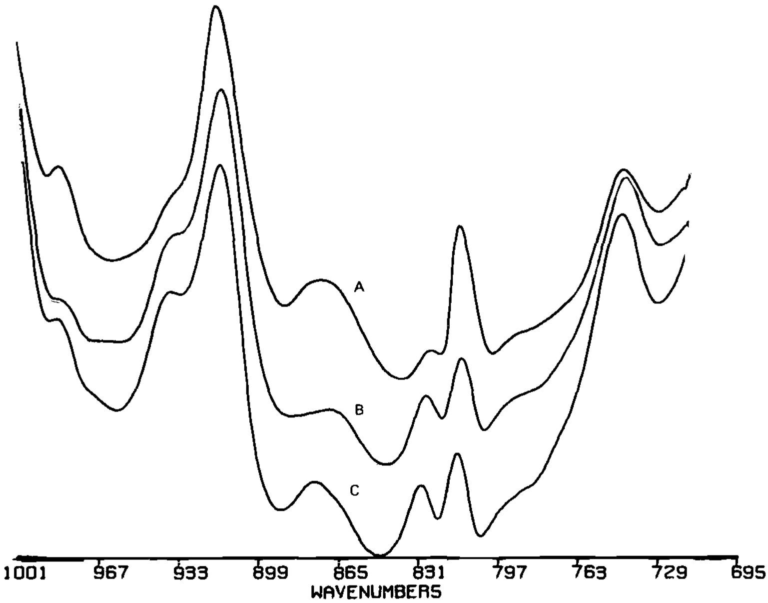


FIG. 6—*Diffuse reflectance spectra of primed automotive panels using silicon carbide abrasion technique: (A) control panel w/50% melamine; (B) control panel w/30% melamine; (C) failed production panel.*

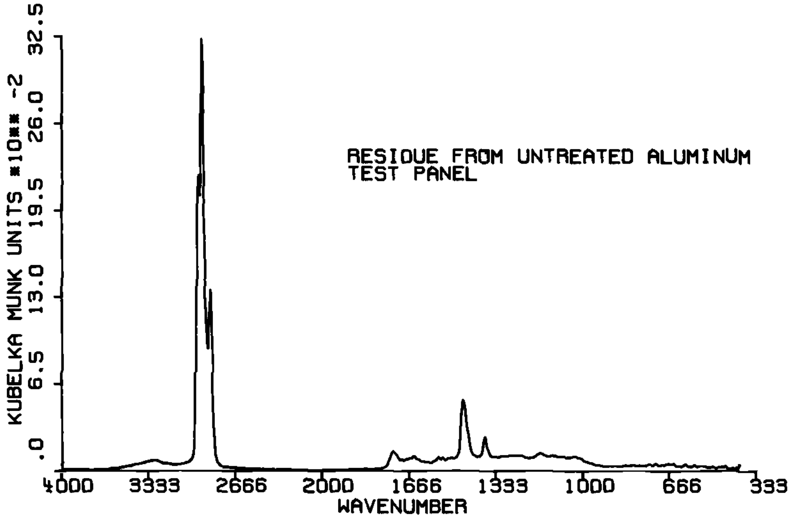


FIG. 7—*Hexane wash residue absorbed on CsI (DTGS detector, 300 scans).*

level additives that are not detected when examining total coating compositions. Figure 8 is a spectrum of the material extracted with heptane from a panel coated with an architectural coating. The hydrocarbon is the wax lubricant from the coating. The carbonyl ester is from a low molecular weight fraction of the acrylic resin portion of the coating.

In the course of testing a developmental aerospace high gloss topcoat, it was observed that a haze was developing over a period of time. This "bloom" component was isolated by gently rinsing the surface with heptane. The residue was then absorbed onto the surface of the CsI powder, filling the microsampling cup of the diffuse reflectance accessory. After the solvent had evaporated, the spectrum shown in Fig. 9 was obtained. This material was identified as the leveling agent used in this particular formulation. Alternately, a small

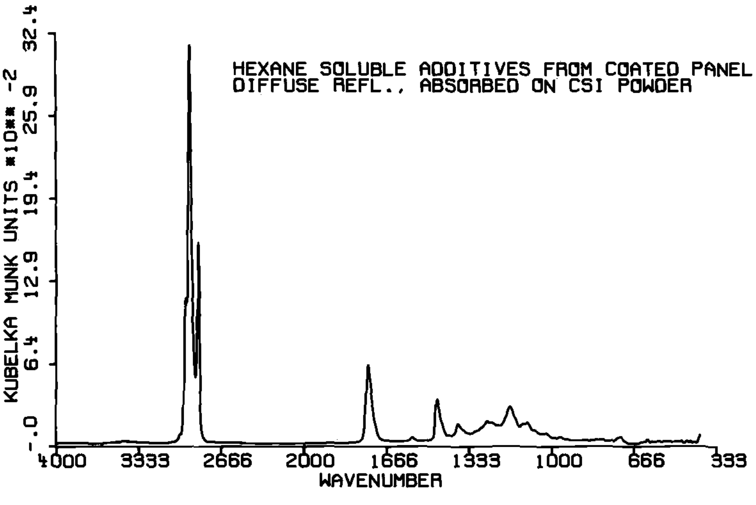


FIG. 8—*Use of absorption CsI technique for identification of low-level additives (DTGS detector, 300 scans).*

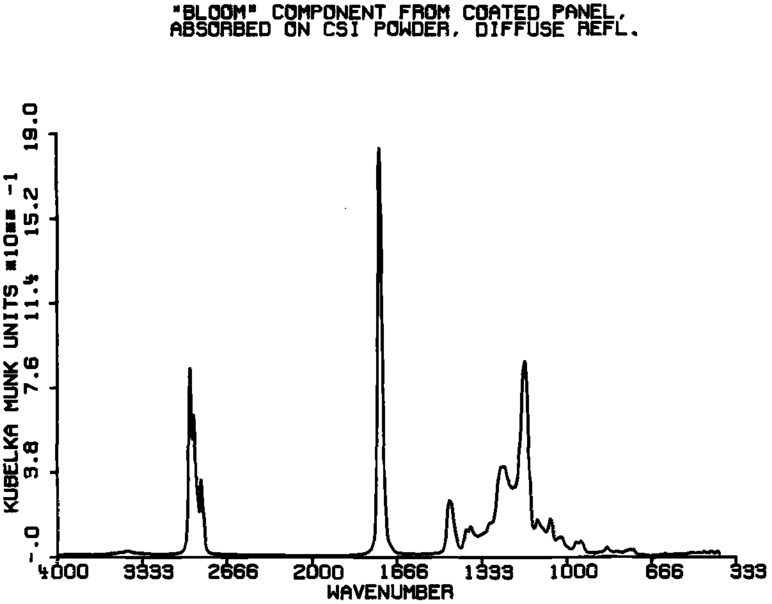


FIG. 9—*Identification of bloom on coated surface absorbed on CsI powder (DTGS detector, 300 scans).*

amount of KBr or CsI powder could have been used to remove the "bloom" by light surface abrasion and then transfer the powder to the sample cup.

Infrared Microspectroscopy

Undoubtedly, the accessory having the greatest impact on the analysis of minute coating defects has been the infrared microscope. Previously, microsampling was thought to be synonymous with the need for lengthy sample preparation. For example, the examination of seeds or particles on a coated film surface may have required several hours using a stereomicroscope, tediously removing dozens of particles from the film for use in a micro KBr pellet, whereas for microspectroscopic analysis only a single particle is required.

A schematic diagram of a typical infrared microscope is shown in Fig. 10. FTIR microscopes make use of transfer optics to direct the IR beam from the spectrophotometer source and when necessary back to the IR detector. Though not depicted in this diagram, many of the microscope accessories are equipped with their own high sensitivity mercury-cadmium-telluride (MCT) detector. Rather than using quartz objective lenses, which absorb infrared radiation, FTIR microscopes make use of the Schwarzchild-type Cassegrainian objective lens and condenser for IR data collection. These consist of large concave mirrors and a smaller convex mirror to collect and focus the IR beam. Normal glass refractive lenses are often included in order to provide sharper imaging for easier sample location and photomicrographic purposes.

FTIR microscopes are designed such that the optical light path and the IR beam path are the same, so that it truly is a case of "what you see (. . . through the optical eyepiece. . .) is what you get (. . . in the output from the spectrophotometer)." By making use of remote variable size apertures, which Fig. 10 shows placed in the imaging plane both above and below the sampling stage, very small areas of much larger samples can be quickly and easily

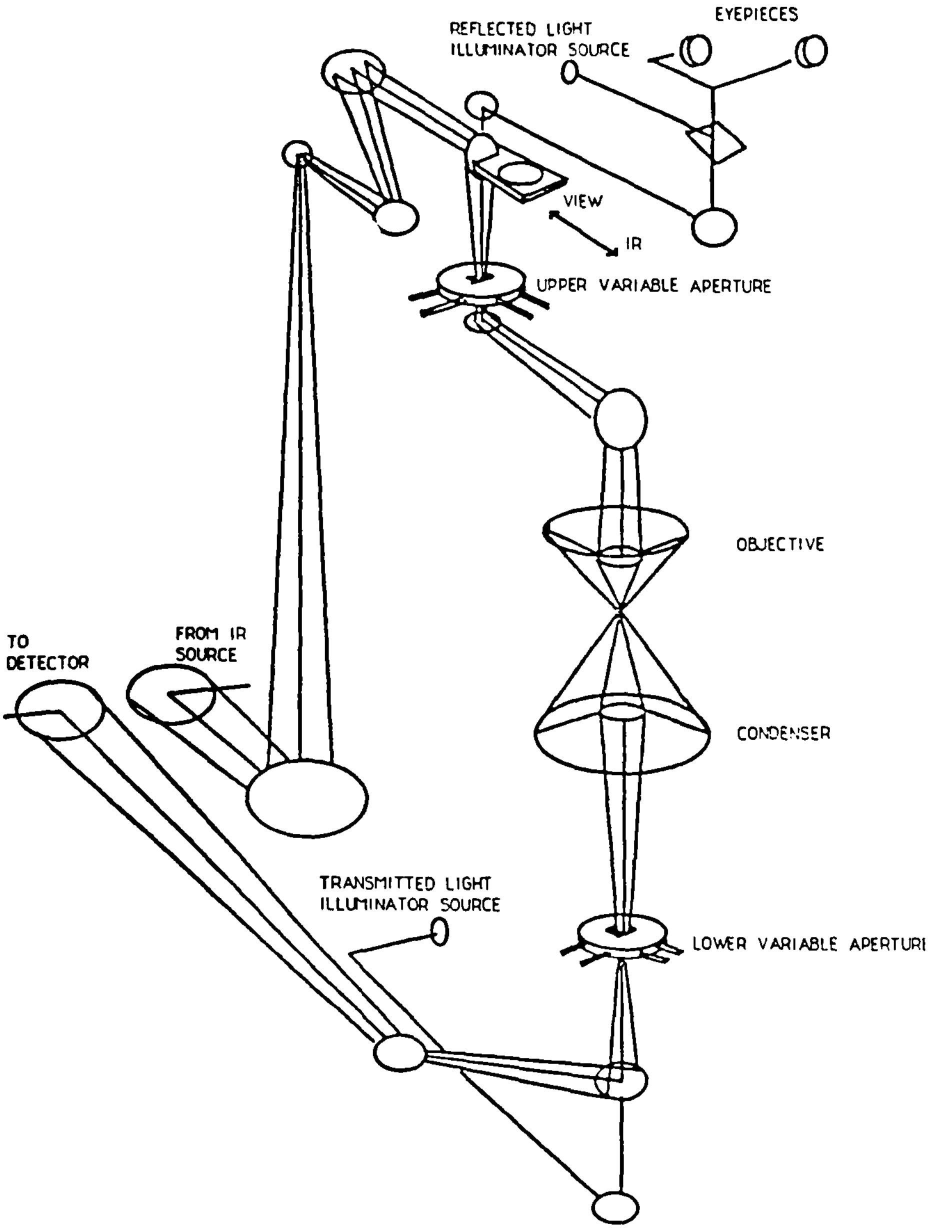


FIG. 10—*Schematic diagram of typical FTIR microscope (transmission mode). Sample located at focal point between objective and condenser lenses* [22].

isolated for analysis without the need for manual masking. The microscope mode is easily switched from optical viewing to the infrared beam by simply flipping a prealigned mirror into the path of the optical illuminator.

In addition, many FTIR-microscope accessories available today are capable of analyzing materials using either transmission or reflectance methods. This provides the spectroscopist with the capability of analyzing a wide variety of materials in their neat form. Two examples of materials ideally suited for examination in situ by reflectance techniques include can coatings and compact disk coatings (Fig. 11). In cases where the sample stage design permits, materials such as these need not even be cut in order to obtain an IR spectrum. For optimal spectral results, the materials analyzed using the microscope should be flat and thin. The specimen thickness required is dependent on the material, but may range from approximately 5 to 50 μm.

Sample Preparation Techniques

Unfortunately, not all coatings are applied at a thickness of 5 μm or less or applied to reflective substrates. More often than not, some type of sample preparation is required. A few basic microsampling tools can facilitate this process, however. These include a good stereomicroscope that will allow an ample work area for manipulating a specimen under some degree of magnification. Sharpened tungsten needles allow particles to be removed and transferred from films and surfaces. Scalpels or razor blades can be useful to slice thin shavings from thicker materials for analysis in the transmission mode.

For isolated particles and films that are still too thick for obtaining sufficient IR signal, slight pressure can be used to further flatten the material. Depending on the particle,

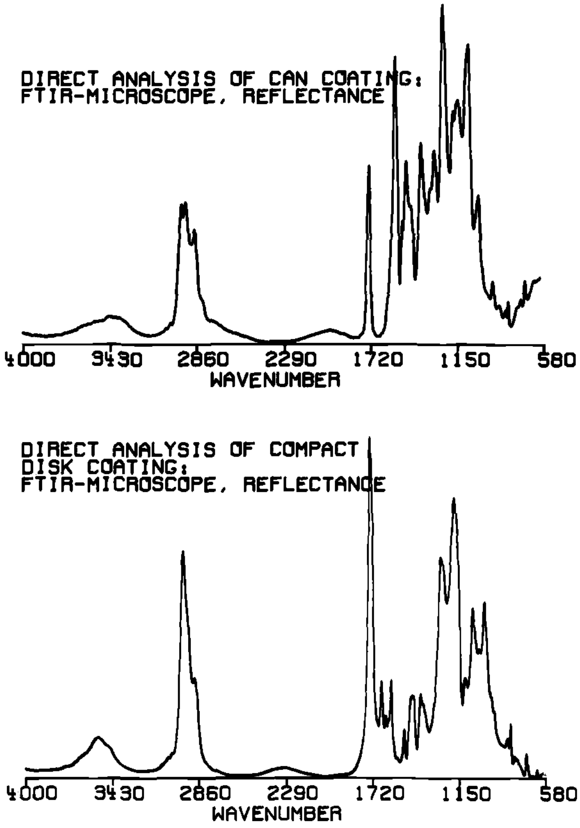


FIG. 11—*Sample spectra obtained using microscope accessory in reflectance mode (500 scans, 2 gain).*

squeezing between transmission windows may be sufficient. Harder particles may be placed on the flat die faces of a micropellet press such that higher pressures can be applied to the particle. The flattened particle is then removed from the die face and placed on the transmission window surface for analysis.

Diamond anvil cells have also been designed specifically for use with FTIR microscopes. Optically thick particles can be placed between the faces of the diamond anvils and a spectrum obtained while the particle is still under pressure. This is particularly convenient for resilient materials that return to their original thickness once pressure is removed.

Another method for preparing thin films of polymeric materials is the use of cryogenic microtome techniques. The most commonly documented application of this technique as a preparative tool is for the identification of the multiple layers in plastic laminates [*21*,*22*]. After a thin film has been prepared, the acquisition of an IR spectrum of each layer becomes a trivial matter. Each layer is simply isolated from the next layer by remote aperturing.

Selected Applications

As previously mentioned, the FTIR microscope is ideal for the analysis of defects on metallic substrates, including food and beverage cans. Corrosion of the interior walls of several juice cans prompted the examination of the interior coating in our laboratory. Though examination by other microscopic techniques indicated that the corrosion was attributed to mechanical abrasion of the protective epoxy coating, it was observed that the coating contained a large number of pinholes over its entire surface. These small craters measured 20 to 50 μm in diameter. Using circular remote aperturing accessories, the cratered areas were isolated for direct examination on the can surface. The spectra in Fig. 12 indicate that the craters are filled with a long chain aliphatic hydrocarbon component. Further investigation

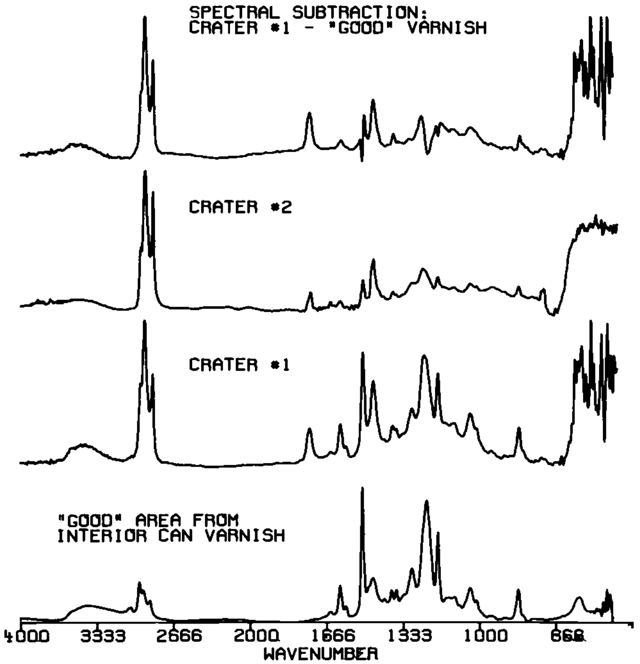


FIG. 12—*FTIR microscopic examination of can coating craters (300 scans, 16 gain).*

of the raw materials used during production traced the source for this material to a contaminant in the production lot of poly(propylene oxide)-based lubricant used in the coating.

Another problem presented itself as a result of soft drink beverage cans that became stuck in automatic dispensing machines. The customer had expressed concern that the cause may be due to insufficiently cured exterior overprint varnish. The sticky residue from the exterior of several of these cans was removed from the can surface and flattened onto a transmission window. Figure 13 indicates that the material is a carbohydrate that closely matches the nonvolatile material of the liquid beverage. The spectrum of the varnish, provided here for comparative purposes, was obtained directly from the can surface using the reflectance mode.

Another application for which microspectroscopic analysis becomes ideal is for grit particles or seeds in cured films. The white powdery "seeds" from a latex paint draw-down film were extracted using a needle probe and flattened onto the surface of a microscope transmission window. The infrared spectrum of each of the examined particles indicated an inorganic pyrophosphate (Fig. 14), suggesting a kickout of the dispersing agent, tetrapotassium pyrophosphate.

The "bubbles" from a piece of laminate used for food packaging were isolated by carefully cutting around the defective areas and peeling back the polyester and foil film layers. Using microspectroscopic reflectance techniques to directly analyze the foil surface indicates that the cause of the bubbles was the absence of adhesive in these areas (Fig. 15). In good areas of the laminate, adhesive is found to adhere to the foil film.

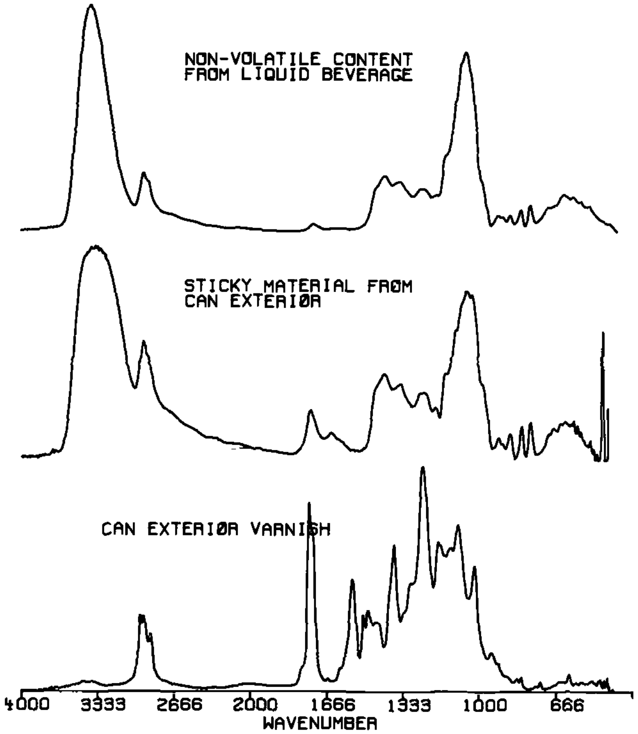


FIG. 13—*FTIR microscopic examination of beverage can materials (300 scans, 2 gain).*

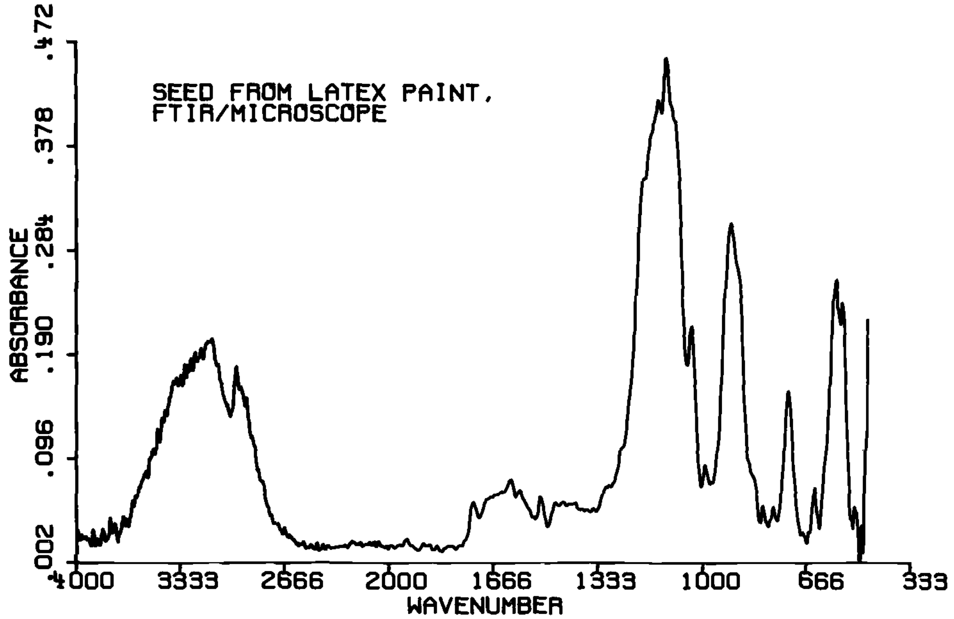


FIG. 14—*Obtained using transmission mode (MCT detector, 1000 scans, 16 gain).*

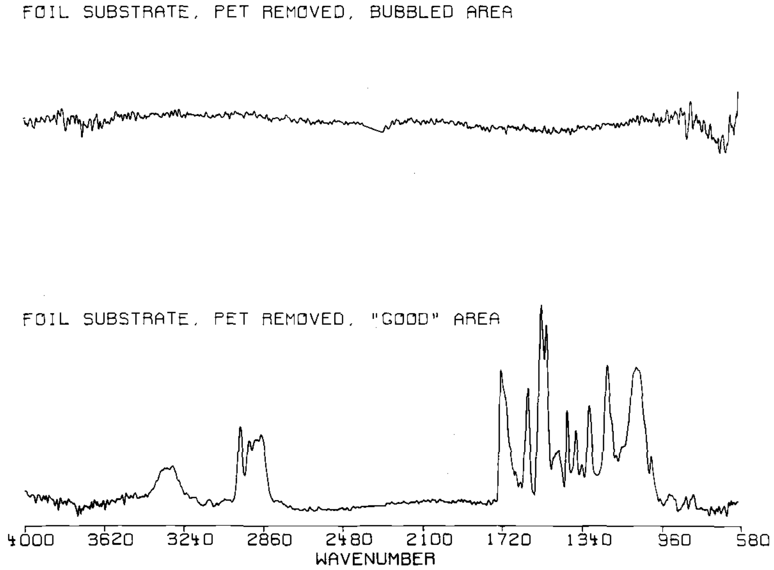


FIG. 15—*FTIR microscopic examination of bubbled laminate, reflectance mode (MCT detector, 500 scans).*

Further applications of the use of the FTIR microscope, as well as accessory design and sampling handling considerations, can be found in the literature [*23*,*24*].

Photoacoustic Spectroscopy

Another accessory recently finding a great deal of application in the analysis of coatings is the photoacoustic cell. Photoacoustic spectroscopy (PAS) is different from any other infrared technique in the respect that, rather than using an optical detector to measure the amount of light not absorbed by the analyte, this technique measures the sound generated by acoustic waves that are emitted from the material. When modulated infrared energy is absorbed by the specimen, the energy is converted into heat. As this thermal energy propagates to the surface of the analyte, pressure variations occur at the interface that generate periodic thermal waves into the surrounding atmosphere (Fig. 16). The resulting pressure variations are then detected by a sensitive microphone which converts the acoustic signal into an electrical signal. This brief description, needless to say, is PAS in its most rudimentary terms. For an in-depth explanation of the theory and sampling considerations of photoacoustic spectroscopy, one should consult Rosencwaig [*25*]. Excellent review articles are also available for a complete, yet succinct, treatment of the subject, as well as additional applications of this technique [*26*,*27*].

The photoacoustic effect was first observed in 1881 by Alexander Graham Bell [*28*]. Bell studied the effect of modulated sunlight impinging upon thin films isolated in a brass cell. The sealed cell was fitted at one end with a glass window to allow entry of the sunlight. Another side was fitted with a thin brass tube which served as a conductor for the sound to the detector, the human ear. The PAS cells of today, designed specifically for FTIR-PAS applications, are not dissimilar from Bell's original design. Many consist of two connected chambers made of a nonresonant material, such as brass. One of the chambers contains a sensitive microphone; the other small volume chamber functions as the sampling platform. The sampling chamber is fitted at one end with an IR transparent window that permits entry of the modulated IR beam into the air-tight cell. Although PAS spectra can be generated in ambient air, sensitivity can be greatly enhanced when the cell is purged with a coupling gas, such as helium, nitrogen, or argon. The criteria for a good coupling gas include infrared transparency and good thermal transfer properties.

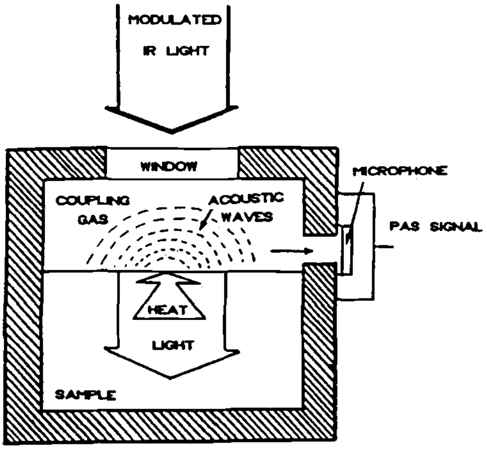


FIG. 16—*Schematic diagram of photoacoustic detection* [26].

The predominant advantage of PAS spectroscopy over other solid sampling techniques is that most materials can be analyzed in their neat form. The only sample preparation necessary is reducing the specimen to a size that can be accommodated by the sample chamber. Samples need not be diluted (e.g., with KBr for diffuse reflectance), nor is alteration necessary to make the sample optically thin (e.g., flattening samples for transmission microscopy).

Because the PAS signal is dependent on the thermal properties of the analyte rather than the optical properties, PAS becomes valuable for analyzing materials that are too optically opaque to be examined by other techniques. Examples of such materials include carbon-filled polymers and highly pigmented coatings. Spectra are generally ratioed to a spectrum of a totally IR absorbing material, such as carbon black.

Though PAS can be performed on a wide variety of materials, the quality of the spectrum is dependent on factors such as surface morphology and particle size of the analyte. Studies by Vidrine [*29*] and Yang and Fateley [*30*] have determined that the best PAS spectra are obtained from powdered materials. As the overall surface area of a material increases, so does the efficiency of the heat transfer between the solid and gas.

Further cell design improvements have been made that have greatly reduced the necessity for lengthy data collection times. Cells are so mounted and isolated that interference from environmental vibration has been minimized, significantly reducing the number of scans necessary to obtain PAS spectra containing little baseline noise. Such cell improvements have resulted in a resurgence of the applications of PAS toward the study of coating materials. The following are a few recent examples of the unique applications for which this technique has been used.

Depth Profiling

PAS allows another dimension in sampling not available from other surface techniques and that is the ability for controlled depth profiling studies. The depth to which the infrared radiation will be absorbed is directly related to the specimen's thermal diffusion length, that is, the depth within a sample from which heat will reach the outer surface. The thermal diffusion length is inversely proportional to the modulation frequency of the incident radiation. The modulation frequency of the midrange IR source is easily varied on modern FTIR spectrophotometers by simply changing the velocity of the moving mirror in the interferometer.

Earlier, in the section on diffuse reflectance, an example was provided which illustrated the ability to analyze a sublayer of poly(ethylene terephthalate) (PET) under a 1.5-μm surface layer of poly(vinylidene fluoride) (PVF_2) using the KBr overlay technique. These studies by diffuse reflectance techniques are limited to very thin surface layers, however. Urban and Koenig [*31*] have performed a similar experiment using 6 and 9-μm surface layers of PVF_2 over PET using photoacoustic spectroscopy. The spectra obtained at varying mirror velocities (Fig. 17) illustrate the increased contribution from the bottom layer (1730 cm^{-1} carbonyl band) as the mirror velocity is decreased. Note the quality of the absorbance bands below 1500 cm^{-1}. In the diffuse reflectance study, only the less intense absorbance bands in the 3000 cm^{-1} region were presented, likely because all other bands were unresolved due to intense absorption.

Drying and Curing

Salazar-Rojas and Urban [*32*] have used the PAS/FTIR technique to study the solvent evaporation and long-term curing process of a nonpigmented alkyd resin system. In their experiment, the spectral changes of a freshly coated steel substrate were monitored as a

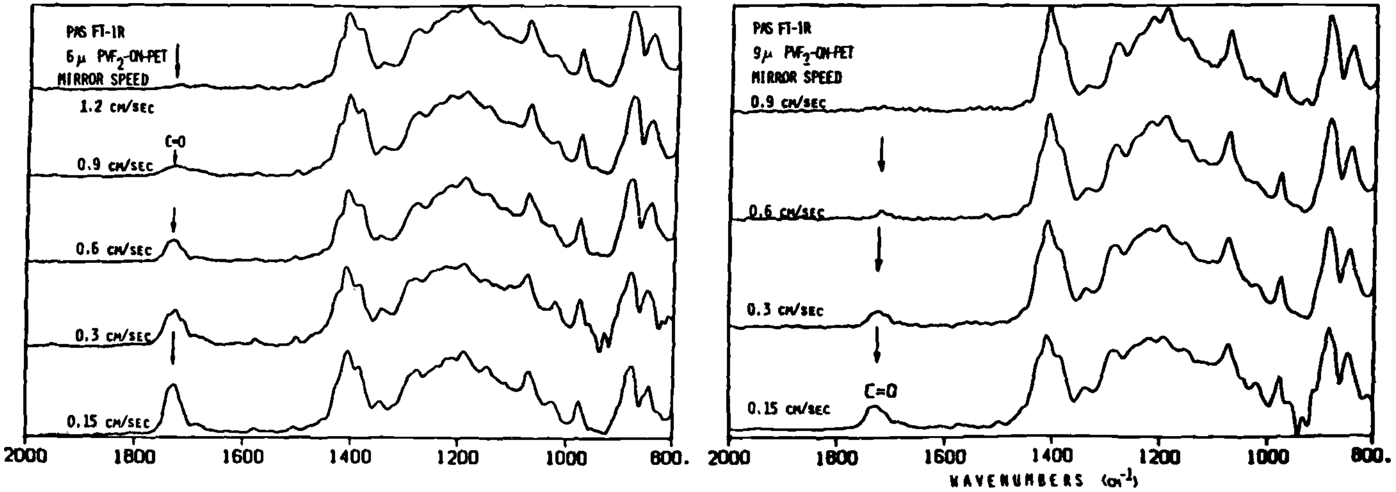


FIG. 17—*PAS depth profiling study of poly(vinylidene fluoride) on poly(ethylene terephthalate) by altering mirror velocity* [30].

function of time. The changes due to solvent loss (methyl isobutyl ketone, *n*-butyl acetate and methyl propyl ketone), as measured by the decrease in the 1380, 1252, and 1737 cm^{-1} bands, were found to cease after 20 min (Fig. 18). This data correlated with independent weight loss measurements on the same system. In addition, both gravimetric and PAS methods indicate that a significant level of solvent (approximately 33%) remains trapped in the film and possibly contributes to the further cross-link processes.

Using spectral subtraction techniques, the authors used PAS to further monitor the spectral changes that occur in the same film at various points over a period of one month. The authors were successful in identifying many stepwise functionality changes in the coating over that period of time, allowing them to propose a mechanism for the curing process and the role that the retained solvents play in the curing of the alkyd.

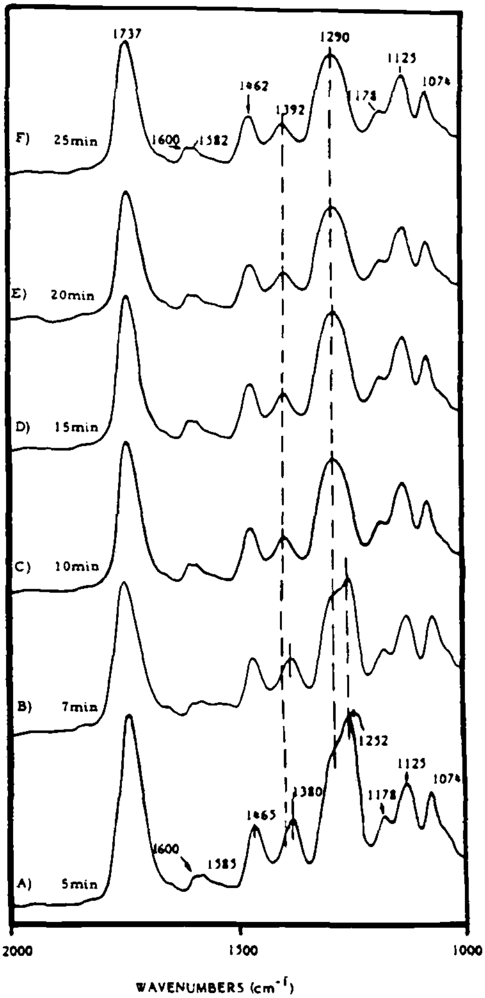


FIG. 18—*PAS spectra of alkyd coating recorded at varying air dry exposure times* [31].

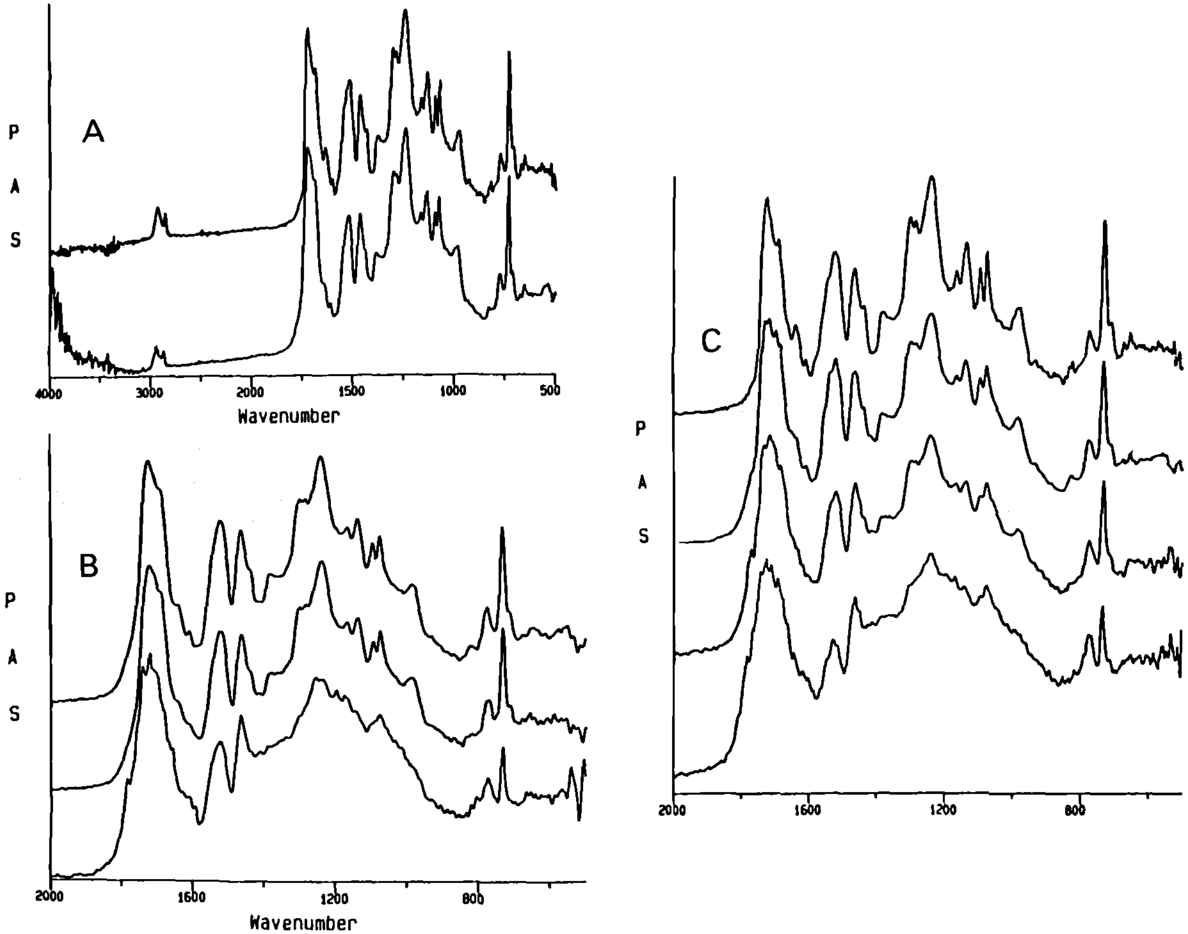


FIG. 19—*PAS spectra of polyester-urethane coatings weathered by* (a) *Florida exposure,* (b) *carbon arc, and* (c) *xenon arc* [33].

Weathering and Film Degradation

PAS is finding extensive use for weathering and degradation studies of pigmented paint films. Hodson and Lander [*33*] used this technique to determine the effects of several different white pigments on the weathering of an alkyd formulation in accelerated weathering testing. The authors chose this method over diffuse reflectance and ATR because of the decrease in spectral quality and intensity in the latter methods due to change in the surface morphology of the film upon weathering.

Studies were performed on formulations containing: anatase titanium dioxide, rutile titanium dioxide coated with alumina and silica, zinc oxide, and zirconium dioxide. PAS spectra were obtained after 3, 10, 17, and 24 days of accelerated weathering in a QUV Weatherometer®. For comparison, spectra were obtained at the same intervals from portions of the same films that had not been exposed to any weathering conditions. Spectral subtraction techniques were used in order to ascertain the spectral changes in weathered versus unweathered films.

The most significant spectral change noted in each of the weathered films was the loss of aliphatic hydrocarbon, believed to be due to chain scission of the alkyd as a result of free-radical attack. Using the relative loss of hydrocarbon as a measure of degradation, it was determined that the coatings exhibiting the least amount of binder degradation were those containing the pigments (zinc oxide and coated rutile titanium dioxide) that absorb greater amounts of UV radiation, thus serving to reduce the amount of UV energy absorbed by the binder.

Bauer, Peck, and Carter [*34*] have used PAS/FTIR to compare coating degradation in films exposed to artificial light sources to those subjected to Florida natural sunshine exposure testing. Figure 19 shows the spectra of pigmented polyester-urethane films that had been weathered in Florida by carbon arc exposure and by xenon arc accelerated weathering, respectively. The most notable difference in each film is the marked decrease of the 1560 cm^{-1} amide II band, which is believed to be due to scission of the urethane linkage. This degradation occurs to a much greater degree in the films exposed to artificial light sources. The spectra of accelerated weathered films show that, in addition to a decrease in the urethane linkage, a severe attack on the polyester portion of the resin occurs as well, as evidenced by the decrease in aromatic functionality (731 cm^{-1}) and the broadening of the carbonyl ester band (1730 cm^{-1}) due to photooxidation.

Conclusions

The added sensitivity provided by Fourier transform infrared spectroscopy has made possible the development of a number of accessories to assist the spectroscopist in the difficult problem-solving tasks encountered in the coatings industry. The addition of diffuse reflectance, infrared microscopy, and photoacoustic spectroscopy to our "arsenal" has allowed studies to be performed that previously would have either been a major undertaking or perhaps even impossible. Not only have these techniques provided the means for analyzing cured materials, optically opaque materials, and microscopic defects, they have made these tasks rather straightforward and routine in nature. The literature should be consulted for further applications of these techniques.

References

[*1*] Bellamy, L. J., *The Infrared Spectra of Complex Molecules,* Vol. 1, 3rd ed., Chapman and Hall, London, 1975.

[2] Bellamy, L. J., *Advances in Infrared Group Frequencies,* Methuen and Co. Ltd., Sussex, England, 1968.

[3] "Sadtler Standard Spectra," Vols. 1–51 cont., Sadtler Research Laboratories, Inc., Cambridge, MA.

[4] Pouchert, C. J., *The Aldrich Library of Infrared Spectra,* Aldrich Chemical Co., Milwaukee, WI, 1970.

[5] *Alphabetical List of Compound Names, Formulae and References to Published Infrared Spectra,* Vol. 3, American Society for Testing and Materials, Philadelphia, 1969.

[6] *An Infrared Spectroscopy Atlas for the Coatings Industry,* Federation of Societies for Coatings Technology, Philadelphia, 1980.

[7] Hummel, D. O., *Infrared Spectra of Polymers,* Wiley-Interscience, New York, NY, 1966.

[8] Hummel, D. O., *Infrared Spectra of Polymers, Resins and Additives: an Atlas, Vol. 1: Plastics, Elastomers, Fibers and Resins, Part 1,* Wiley-Interscience, New York, NY, 1971.

[9] Hummel, D. O. and Scholl, F., *Infrared Spectra of Polymers, Resins and Additives: an Atlas, Vol. 2: Additives and Processing Aids,* Verlag Chemie, Weinheim, Germany, 1973.

[10] Bell, R. L., *Introductory Fourier Transform Spectroscopy,* Academic Press, New York, 1972.

[11] Griffiths, P. R., *Chemical Infrared Fourier Transform Spectroscopy,* Wiley-Interscience, New York, 1975.

[12] Ferraro, J. R. and Basile, L. J., Eds., *Fourier Transform Infrared Spectroscopy,* Vol. 1, 1978, Vol. 2, Academic Press, New York, 1979.

[13] Griffiths, P. R. and deHaseth, J. A., *Fourier Transform Infrared Spectrometry,* Wiley-Interscience, New York, 1986.

[14] *Optical Spectroscopy: Sampling Techniques,* Harrick Scientific Corp., Ossining, NY, 1987.

[15] Fuller, M. P. and Griffiths, P. R., "Diffuse Reflectance Measurements by Infrared Fourier Transform Spectroscopy," *Analytical Chemistry,* Vol. 50, No. 13, 1978, p. 1906.

[16] Fuller, M. P. and Griffiths, P. R., "Infrared Microsampling by Diffuse Reflectance Fourier Transform Spectrometry," *Applied Spectroscopy,* Vol. 34, No. 5, 1980, p. 533.

[17] Suzuki, E. M. and Gresham, W. R.,"Forensic Science Applications of Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS). I. Principles, Sampling Methods, and Advantages," *Journal of Forensic Science,* Vol. 31, No. 3, 1986, p. 931.

[18] Suzuki, E. M., "Forensic Science Applications of Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS). IV. Direct Analysis of Metallic Paints—Sampling Considerations," *Journal of Forensic Science,* Vol. 34, No. 1, 1989, p. 164.

[19] Suzuki, E. M. and Brown, J. A., "Forensic Science Applications of Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS). V. Direct Analysis of Metallic Paints—Screening of Panels," *Journal of Forensic Science,* Vol. 34, No. 1, 1989, p. 180.

[20] Culler, S. R., McKenzie, M. T., Fina, L. J., Ishida, H., and Koenig, J. L., "Fourier Transform Diffuse Reflectance Infrared Study of Polymer Films and Coatings: A Method for Studying Polymer Surfaces," *Applied Spectroscopy,* Vol. 38, No. 6, 1984, p. 791.

[21] Reffner, J. A., Coates, J. P., and Messerschmidt, R. G., "Chemical Microscopy with FTIR Microspectrometry," *American Laboratory,* April 1987.

[22] Harthcock, M. A., Lentz, L. A., Davis, B. L., and Krishnan, K., "Applications of Transmittance and Reflectance Micro/FTIR to Polymeric Materials," *Applied Spectroscopy,* Vol. 40, No. 2, 1986, p. 210.

[23] Messerschmidt, R. G. and Harthcock, M. A., Eds., *Infrared Microspectroscopy: Theory and Applications,* Marcel Dekker, Inc., New York, NY, 1988.

[24] Roush, P. B., Ed., *The Design, Sampling Handling and Applications of Infrared Microscopes, ASTM STP 949,* American Society for Testing and Materials, Philadelphia, 1987.

[25] Rosencwaig, A., *Photoacoustics and Photoacoustic Spectroscopy,* Wiley-Interscience, New York, 1980.

[26] Jasse, B., "Fourier-Transform Infrared Photoacoustic Spectroscopy of Synthetic Polymers," *Journal of Macromolecular Science, Chemistry,* Vol. A26, No. 1, 1989, p. 43.

[27] Urban, M. W., "Recent Advances in Coatings Characterization by Photoacoustic FTIR Spectroscopy," *Progress in Organic Coatings,* Vol. 16, 1989, p. 321.

[28] Bell, A. G., *Philosophical Magazine,* Vol. II, 1881, p. 510.

[29] Vidrine, D. W., "Photoacoustic Fourier Transform Infrared Spectroscopy of Solid Samples," *Applied Spectroscopy,* Vol. 34, 1980, p. 314.

[30] Yang, C. Q. and Fateley, W. G., *Journal of Molecular Structure,* Vol. 146, No. 25, 1986.

[31] Urban, M. W. and Koenig, J. L., "Depth-Profiling Studies of Double-Layer PVF$_2$-on-PET Films by Fourier Transform Infrared Photoacoustic Spectroscopy," *Applied Spectroscopy,* Vol. 40, 1986, p. 994.

[32] Salazar-Rojas, E. M. and Urban, M. W., "Curing of Non-Pigmented Alkyd Coatings Detected by In-Situ Photoacoustic Fourier Transform Infrared Spectroscopy (PA FT-IR)," *Progress in Organic Coatings*, Vol. 16, 1989, p. 371.
[33] Hodson, J. and Lander, J. A., "The Analysis of Cured Paint Media and a Study of the Weathering of Alkyd Paints by FTIR/PAS," *Polymer*, Vol. 28, No. 2, 1987, p. 251.
[34] Bauer, D. R., Peck, M. C., Paputa, and Carter, R. O., "Evaluation of Accelerated Weathering Tests for a Polyester-Urethane Coating Using Photoacoustic Infrared Spectroscopy," *Journal of Coating Technology*, Vol. 59, No. 755, 1987, p. 103.

Kenneth B. Tator[1] *and Dwight G. Weldon*[1]

Failure Analysis of Applied Coatings

REFERENCE: Tator, K. B. and Weldon, D. G., "**Failure Analysis of Applied Coatings,**" *Analysis of Paints and Related Materials: Current Techniques for Solving Coatings Problems, ASTM STP 1119,* American Society for Testing and Materials, Philadelphia, 1992, pp. 196–203.

ABSTRACT: When protective coatings are properly formulated and applied, they are usually expected to last ten years or more with periodic maintenance. However, occasionally, premature failure occurs, with expensive cost ramifications. The investigation of a field coating failure is considerably different than routine paint analysis, even though the same laboratory equipment is used. Instead, a forensic analysis technique is required, which relies heavily on background information, field sampling and observations, and laboratory testing and analysis.

This paper will describe how one coating consulting company conducts the field and laboratory investigation of coating failures. The structure of failure analysis will be illustrated by three different failures. The first failure involves an alkyd applied over concrete; the second failure involves the delamination of a urethane topcoat from an epoxy primer; and the third failure involves the cohesive failure of an inorganic zinc-rich primer topcoated with a vinyl system.

KEY WORDS: coatings, microscope, FTIR, saponification, ultraviolet light, inorganic zinc-rich primer, cure

Despite the improvements in coatings technology over the past ten or twenty years, paint failures still occur. Such failures include blistering, poor adhesion, cracking, fading, and premature corrosion. Ironically, in some cases, the problems are related to the sophistication of the coatings themselves, which require an equal sophistication on the part of the applicator that, in some cases, is not achieved. In other instances, the coating itself may be at fault. Since coatings play an important role in our industrialized society and since coating failures can prove costly, a need exists to be able to determine the cause of such failures and, hopefully, to resolve them.

If anything, the field of analytical chemistry has grown at a much faster pace than that of coating technology. With the sophistication of modern analytical instrumentation, it would seem an easy task to resolve the problem of coating failures. However, the accuracy of analytical results still depends to a large extent on the nature of the sample and the amount of information known about its composition and history. Take, for example, the problem of a coal tar epoxy delaminating from primed structural steel in a wastewater treatment plant. Not only are the exposure conditions of the samples unknown and almost impossible to reconstruct, but the composition of the coal tar epoxy topcoat and the primer is also unavailable except for the meager information printed on the company's product data sheets or material safety data sheets. Even in those rare instances where the coating manufacturer agrees to supply the analyst with a formula, samples of the raw material involved are usually impossible to acquire.

Despite the above difficulties, it is often possible to determine the cause of a paint failure. While a "cookbook" approach to failure analysis is probably not possible, our company has

---

[1] KTA-TATOR, Inc., 115 Technology Drive, Pittsburgh, PA 15275.

developed a loosely structured framework in which to approach such problems. Generally speaking, this approach involves acquiring both field and laboratory data. The laboratory data will almost always start with a careful visual and microscopic examination of samples. Depending on what is seen and the complexity of the problem, any number of analytical techniques can also be utilized. The preparation and testing of panels, often as a function of application parameters (thickness, cure time, etc.), may also be done.

The importance of field data cannot be overemphasized. The individual who conducts the field investigation, takes samples, documents the extent and nature of the failure, and obtains background information is critical to the success of the laboratory investigation.

The individual conducting the field investigation should be well versed in coatings and coating characteristics and be familiar with the laboratory techniques commonly brought to bear on coating failures. This includes requirements regarding sampling size and type. Providing appropriate photographic documentation and obtaining suitable background information regarding the events up to the time of the failure are also important. Quite often, prior to going out to investigate a coating failure or problem, the consultant confers with the laboratory staff in order to anticipate the samples that may be obtained and seek laboratory direction regarding the amount of sample required and sampling techniques that may be employed. As might be expected, when investigating a blistering failure (either gaseous or liquid-containing blisters), the field investigator may utilize sampling equipment that would be different than if the failure were one of peeling or delamination.

After the field investigation, it is incumbent upon the field investigator to brief the laboratory investigator such that the laboratory has a good understanding regarding the nature of the problem and suspected causes. As a general rule, the field investigator, upon his return from investigating the failure, has made a determination as to whether or not deficient surface preparation and/or excessive or deficient coating thickness and other application irregularities are principal to the cause of the problem. Application-related factors are the cause of many problems and are the easiest to investigate and to prove or disprove. Often there are application-related irregularities that occur on the jobsite but are not felt to be principally responsible for the problem, although they may be aggravating factors. On other occasions, the application appears to be adequate or even good, although a massive coating problem has occurred. In these cases, the laboratory investigation is usually more involved and difficult, and the reliance on properly obtained, suitably sized samples becomes more critical.

Equipment

The major pieces of equipment used in investigating the failures presented here included the following:

1. *Microscope*—Stereo zoom microscope with magnification to ×40.
2. *Infrared Spectrometer*—A Fourier transform infrared spectrometer. Spectra were generally obtained from either potassium bromide pellets or cast films on potassium bromide plates. In some cases, spectra were obtained by purging the sample compartment with dry CO_2-free air using a Balston air purifier.

Failure No. 1

The first failure involved the softening and dirt retention of an alkyd enamel coating applied to a concrete floor. The floor was poured in late April and early May and was cured with the assistance of an alkaline curing additive which was added directly to the concrete mix. The concrete floor also had a postcuring compound applied to the surface to protect against moisture loss during cure. No compositional information was available on this product.

The paint system specified for the floor consisted of a two-coat alkyd enamel. The system had been previously applied to an old concrete floor in a similar facility with good results. Prior to the paint application in early June, the concrete floor was etched with a 1:1 mixture of muriatic acid and water, followed by a water rinse. The floor was allowed to dry for one or two days prior to the application of the alkyd enamel. Within a few weeks, it was noticed that the alkyd was softening and that dirt was sticking to the floor and could not be easily removed by normal cleaning procedures.

A number of observations were made during the site visit. These included the following:

1. On approximately one half of the floor, only one coat of alkyd paint was present. The paint was soft and was highly contaminated with dirt and construction residue. The dirt and residue was embedded in the soft paint and was difficult to remove with a wet cloth.
2. The paint had poor abrasion resistance and was worn off in several high traffic locations.
3. In the other half of the building, two coats of alkyd had been applied to the floor. The paint in these areas showed similar dirt and debris contamination. Additionally, in some locations, the topcoat had lifted, revealing a semiliquid, deteriorated primer coat underneath. In other locations, the paint was extremely soft and pliable and appeared to be almost completely uncured.
4. In several locations, when a small amount of deionized water was applied to the paint, the water rapidly dissolved some of the paint and turned cloudy.
5. pH measurements were conducted in several locations by applying a small amount of deionized water to the floor, lightly scraping with a paint scraper, and pressing a piece of pH paper into the moist surface. Readings of 8 to 12 were common.

During the course of the field observations, a number of samples were taken. These included both falling and nonfalling paint chips and scrapings and concrete cores with the coating attached. These samples were then submitted to the laboratory for analysis.

The first step in the laboratory investigation consisted of visual and microscopic observations. Generally, these observations supported those which were conducted in the field. In particular, when a few drops of water were applied to the back side of paint chips, the paint quickly began to soften, and when examined microscopically, a steady stream of whitish material could be seen flowing from the paint into the water. Generally, the softer and tackier the paint chips, the more readily this happened.

A concrete core sample was evaluated for pH by using a hammer and chisel to remove small chips of concrete within the upper 1/4 in. (0.635 cm) of the sample, pulverizing them, and extracting for 5 min in a small amount of deionized water. The pH was determined using a Beckman-Altex Model PHI-71 pH Meter and was found to be 12.1.

Infrared spectra were subsequentiy obtained on both nonfailing, hard, glossy coating, and on soft, failing, water-sensitive coating. Characteristic vibrations near 1730, 1275, 1130, and 1080 cm^{-1} identified the materials as being alkyds. However, the failing sample had an additional vibration near 1580 cm^{-1}, characteristic of carboxylic acid salts.

Based on both the field and laboratory results, the cause of the coating failure was identified as saponification of the alkyd coating due to the alkaline nature of the concrete floor. Alkyds are essentially oil-modified polyesters and as such are sensitive to moisture and alkalinity. This environment can degrade the resin due to saponification or alkaline hydrolysis. The process involves the breakdown of the ester linkages to produce alcohols and carboxylic acid salts. It was felt that the problem was aggravated by the fact that fresh concrete is somewhat more alkaline than aged concrete and also by the use of the alkaline-based curing compound added to the concrete mixture. Although the concrete was acid etched, this only neutralizes the surface, and alkalinity can still be brought to the surface by moisture, either as retained water from the concrete or water that may enter the concrete from exterior sources.

Failure No. 2

The second failure involved the delamination of a two-component urethane topcoat from a polyamide epoxy primer which was applied to the exterior aluminum sheeting, trim, and mullions on a high-rise building. The specification for the job required that the exterior aluminum surfaces be lightly blast cleaned and then primed with a brush application of the polyamide epoxy primer. The specification also required that the cured primer be sanded prior to the application of topcoat to remove any incidental depositions of sand, dirt, etc. Various inspection reports filled out at the time of coating application indicated that partial kits of paint were being used without the use of measuring devices and also that sanding between the epoxy primer and the urethane topcoat was not being performed. Several days to a few weeks elapsed between the primer application and the topcoat application.

Shortly after the job was finished, sporadic delamination began occurring between the urethane topcoat and the epoxy primer. The delamination progressively worsened over a period of months.

A site visit confirmed the fact that the topcoat had extremely poor adhesion to the epoxy primer. Indeed, in the worse locations, chips of topcoat several square inches in size could be easily peeled from the primer. In most cases, little or no dirt appeared to be present between coats when examined with a pocket magnifier, and the surface of the primer appeared to be smooth, indicating that it had not been sanded. A rough idea of the cure of the primer was assessed by rubbing with cotton swabs saturated with methyl ethyl ketone. A lack of color transfer after prolonged rubbing indicated that the primer had cured sufficiently.

Although there appeared to be little pattern to the failure, the adhesion was better in some areas that were sheltered from the environment. Several pieces of delaminated topcoat were removed, along with scrapings of the underlying epoxy primer, which in every case was well adherent to the aluminum substrate.

The field investigator also verified that application parameters (surface preparation, coating thickness, etc.) were normal and within the range of what could be expected to be a "good" job. Thus, during the course of the field visit, the field investigator did not have any idea as to the cause of the problem, although he considered many possibilities and rejected virtually all of them at the time of the visit. Accordingly, it was essential to obtain many good samples, to take several photographs, and to ask numerous questions in the hope that a possible failure mechanism might emerge. Ultimately, the field investigator returned to the laboratory with his samples and information and the opinion that application-related factors were not responsible for the problem. However, he had no preliminary opinion as to what an appropriate failure mechanism might be. Thus, if this problem were to be successfully resolved, it would be very dependent upon the results of the laboratory investigation.

Once again, the first step in the laboratory investigation consisted of a careful visual and microscopic examination of the samples. In most cases, the back side of the delaminated topcoat appeared clean and smooth. When dirt was present, it appeared to have been blown in after the coating had already been loosened. Coating thicknesses were also determined and ranged from approximately 37 to 62 μm, in accordance with the specification. No voids or porosity were noted in the urethane topcoat, which might otherwise have been an indication of a moisture problem.

Since it was reported that partial kits of paint were used without the benefit of measuring devices, one possible explanation for the poor adhesion appeared to be the mismixing of the epoxy primer, possibly producing a harder film to which the urethane would not adhere. This possibility was investigated by the preparation of test panels in the laboratory, varying the mix ratio of the epoxy primer. Since the adhesion failure was between coats, the nature of the substrate was felt to be unimportant, and blast-cleaned 4 by 6 in. (10.16 to 15.24 cm) hot-rolled carbon steel test panels were used.

In addition to varying the primer mix ratio, primed panels were cured under different conditions prior to topcoating with the urethane. The following cure conditions were observed:

1. Two days at laboratory ambient conditions of approximately 72°F (22.2°C) and 50% relative humidity.
2. Two weeks at laboratory ambient conditions with exposure to ultraviolet light and moisture.
3. Two weeks in a laboratory oven at 110°F (43.33°C).

The ultraviolet light was supplied by a QFS40 ultraviolet light tube (the type used in ASTM Recommended Practice for Operating Light- and Water-Exposure Apparatus (Fluorescent UV-Condensation Type) for Exposure of Nonmetallic Materials (G 53) accelerated weathering devices). Moisture was applied by misting the panels once a day with tap water. During the course of the experiment, it was noted that the epoxy primer exposed to ultraviolet (UV)/moisture developed an off-white or yellowish appearance which did not occur with any of the other test panels.

After the panels were cured as described above, the bottom 1 in. (2.54 cm) of each panel was lightly sanded and then the entire panel topcoated with the specified urethane topcoat. After a one-week cure time, the adhesion of the paint system was evaluated in accordance with ASTM Test Methods for Measuring Adhesion by Tape Test (D 3359), Method B. Briefly, the adhesion testing revealed very good adhesion regardless of the primer mix ratio. However, all panels exposed to UV/moisture displayed very poor adhesion, also regardless of primer mix ratio. In every case, the failure occurred as a clean delamination of the urethane topcoat from the epoxy primer, identical to the failure observed in the field. Furthermore, where the panels had been sanded, the adhesion of the topcoat was very good.

In addition to physical testing, both field and laboratory samples were evaluated by infrared spectroscopy. The purpose of the investigation was to determine if any interfering material was present on the back side of delaminated samples, including the test panels. The technique generally involved applying a small amount of chloroform to the back side of paint chips in such a way that the chloroform would run over the back face of the chip and collect in a small beaker. This process was repeated several times using the same volume of chloroform, which was then carefully evaporated onto potassium bromide plates.

Spectra were obtained from both the back side of a disbonded piece of field topcoat and from the back side of the laboratory-applied topcoat, which had been delaminated from primer which had been exposed to UV/moisture. Both spectra revealed bands characteristic of epoxy material, such as the aromatic vibration near 1510 cm^{-4}. This indicated that a small amount of degraded epoxy material from the primer was on the back side of the failing urethane topcoat, despite the fact that visual and microscopic observations indicated a clean adhesive break.

The cause of the failure, then, appeared to be related to the exposure of the epoxy primer to ultraviolet light and moisture prior to topcoating. This produces a thin, weak layer of degraded epoxy which compromises the adhesion of the subsequently applied urethane topcoat. Furthermore, the laboratory physical testing also tended to rule out mismixing of the epoxy primer as the cause of the problem. Since the duration of the laboratory ultraviolet exposure was only two weeks, this indicates that the paint system is very susceptible to normal environmental factors and at the very least suggests that suitable warnings should be issued for its use.

Failure No. 3

The third failure involved the application of a two-coat vinyl system to an inorganic ethyl silicate-based, zinc-rich primer. The project was the structural steel and steel piping for a coal-handling conveyor system. The specification required that the steel surface be cleaned in accordance with SSPC-SP6: Commercial Blast Cleaning, and that the zinc/vinyl/vinyl system be totally shop applied. The inorganic zinc was to be applied at 50 to 100 μm, with the two coats of vinyl each applied at a minimum thickness of 75 μm. The specification further required that the inorganic zinc primer be applied to dry overnight prior to application of the finish coats in accordance with the recommendation of the coating manufacturer.

The entire job was performed in a fabricating shop in a midwestern state in the fall, winter, and spring. The steel was then shipped to the jobsite, and erection was completed in the early spring. Considerable delamination of the paint system was noted during shipping, handling, and erection.

Several observations were made during the site investigation, including the following:

1. Several areas were noted where the steel had been impacted, perhaps during handling or erection. The coating adjacent to many of these areas had lifted. In the worst area examined, the lifted coating covered approximately 1 ft^2 (0.09 m^2). When this piece of coating was removed, zinc-rich primer was present on both the back side of the coating and also on the underlying steel substrate.
2. In addition to mechanically damaged areas, occasional blisters were noted in the paint. The blisters were hollow, generally less than 1/4 in. (0.63 cm) in diameter, and widely scattered. When the blisters were broken open, a moderate-to-strong odor of solvent was noted. Once again, zinc-rich primer was present both on the back side of the blistered coating and on the underlying steel surface.
3. The adhesion in areas which appeared to be visually intact was evaluated in accordance with ASTM D 3359 and was found to be extremely poor in eight of eleven locations. Once again, the failure occurred as a cohesive break within the zinc-rich primer.
4. The sensitivity of the inorganic zinc-rich primer to softening by solvent (a measure of cure) was evaluated by rubbing a cloth saturated with methyl ethyl ketone (MEK) on the surface of the zinc. Only a few rubs were required to soften the coating and transfer it to the cloth, indicating poor cure.
5. The appearance of the coating was generally smooth and free of noticeable application defects, although some pinholes were noted in the topcoat. Thickness measurements indicated an average of 65 μm for the primer and 100 to 125 μm for each of the two vinyl coats, generally in accordance with the specification.

In addition to several paint chips and scrapings, fresh 5-gal samples of the various coatings were obtained for laboratory analysis along with a section of coated steel plate removed from one of the conveyor tubes.

Previous work conducted in this laboratory has shown that topcoated inorganic zinc-rich primers can fail in a cohesive fashion similar to that observed here if they have not cured sufficiently prior to topcoating. This is thought to be the result of softening of the primer by solvents in the topcoat, followed by the introduction of a weakened plane within the primer as the topcoat cures and imparts shrinkage stress.

Certainly, the poor solvent resistance of the primer applied to the structural steel is indicative of inadequate curing. However, rather than relying solely on this simple test, the cure of the primer was also evaluated by infrared spectroscopy, as described in the literature [*1*].

It has been shown that the cure of an inorganic zinc-rich primer can be followed by monitoring the absorbance ratios of the silicate vibrations near 1100 cm^{-1} to that of the carbon-hydrogen stretching vibrations near 2900 cm^{-1}. As the ethyl silicate vehicle cures, the intensity of the carbon-hydrogen stretching vibrations decrease relative to the silicate vibration. Therefore, a term called "cure ratio" can be obtained by dividing the silicate absorbance by the carbon-hydrogen absorbance with larger numbers corresponding to a greater degree of cure.

Test panels were prepared with the control samples of zinc-rich primer and cured under both laboratory ambient conditions (approximately 70°F (21.1°C), 50 to 60% relative humidity), and at approximately 70°F (21.1°C) and 100% relative humidity. Spectra were then obtained of these samples at various times during cure and compared with the results obtained from field samples.

The results are shown in Table 1 and clearly show that the primer cures sluggishly unless exposed to high humidities. Indeed, when cured per the manufacturer's recommended time of 24 h at 70°F (21.1°C) and 50% relative humidity, the cure ratio of 17.8 was only 10% of the "full cure" achieved in 96 h at 100% relative humidity. The data also clearly show the relationship between infrared cure ratio and solvent resistance.

The data also show cure ratios of approximately 25 to 30 for the field samples, suggesting that the shop-applied, zinc-rich primer did receive at least the minimum cure time recommended by the manufacturer prior to topcoating.

Based on the field observations of poor cohesive strength of the zinc-rich primer, solvent odor and solvent sensitivity, and laboratory infrared and solvent resistance testing, the cause of the poor adhesion was felt to be the topcoating of inadequately cured zinc-rich primer. Furthermore, the fault in this case does not appear to be due to poor application, but rather to a coating which simply does not have the proper cure characteristics for shop application. Indeed, the laboratory results clearly showed that even when the primer was cured as

TABLE 1—*Infrared cure ratios and solvent resistance of field and laboratory samples.*

Sample	Cure Ratio	MEK Double Rubs
Lab, 4 h ambient	18.4	1–2
Lab, 24 h ambient	17.8	1–2
Lab, 48 h ambient	29.2	2–3
Lab, 96 h ambient	31.7	2–3
Lab, 4 h 100% RH	21.1	1–2
Lab, 24 h 100% RH	47.4	40–50
Lab, 96 h 100% RH	177.0	>100
Field 1	31.9	
Field 2	43.6	
Field 3	30.0	
Field 4	24.2	
Field 5	26.5	

required by the manufacturer, it had very incomplete cure and poor solvent resistance, factors which had a direct bearing on the failure. It is quite likely that had the specification called for shop priming only, with topcoating to be done at the jobsite, the failure would not have happened. The delay between shop application and field topcoating likely would have given the primer enough time, and possibly exposure to humidity, to have effected adequate cure.

Summary

The above examples illustrate the integrated approach to failure analysis incorporated by our laboratory. This approach depends heavily on observations, background information, effective sampling, and finally, analysis and testing. Hopefully, the examples illustrate the need for a basic understanding of both application and coatings technology. Without such an understanding, the laboratory approach can tend to be haphazard and extremely time consuming. With such guidance, the laboratory approach tends to be more focused and hopefully more efficient.

Reference

[*1*] Weldon, D. G., et al., "The Cure and Topcoating of Inorganic Zinc-Rich Primers," *Journal of Protective Coatings and Linings*, Vol. 6, No. 4, 1989, p. 21.

ISBN 0-8031-1465-6