

Analysis of

Paints and Related Materials:

Current Techniques for Solving
Coatings Problems

William C. Golton, editor



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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.

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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.

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.

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Analysis and Characterization of Whole Paint

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.

¹BASF 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 cor-

rection, 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.

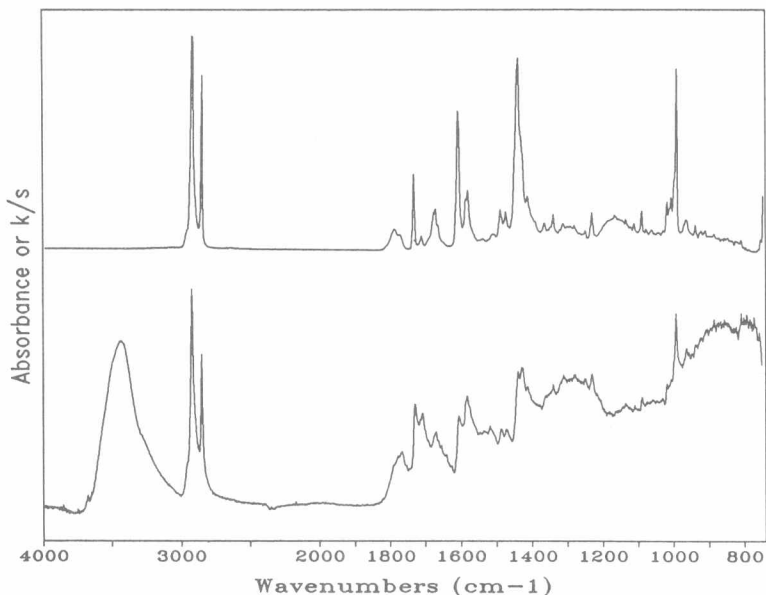


FIG. 1—Infrared spectra of a mixture of an Indanthron pigment and aluminum flakes. Top: diffuse reflectance spectrum; bottom: KBr pellet.

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

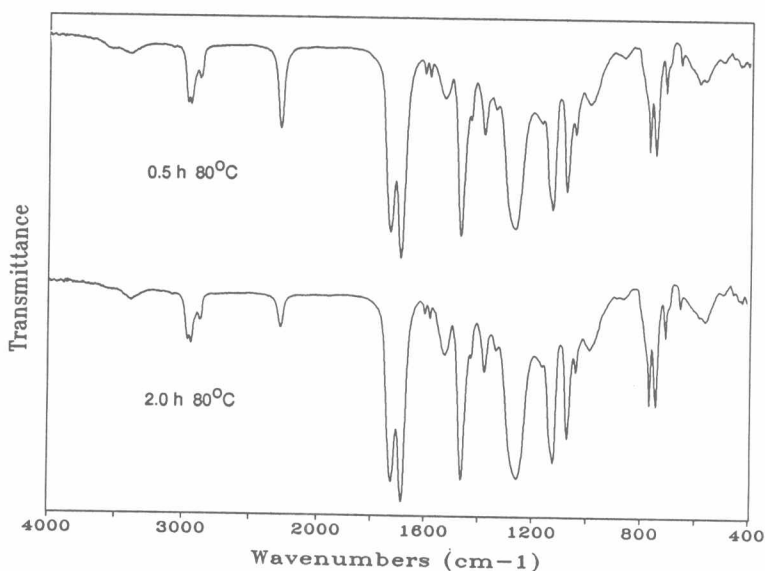


FIG. 2—ATR spectra of a two-component polyurethane coat cured under different conditions: KRS-5 crystal, 45°.

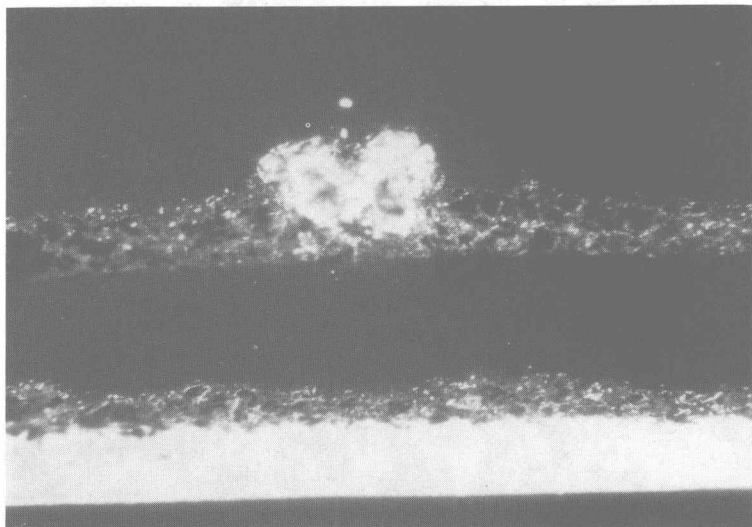


FIG. 3—Photomicrograph of an inclusion in a repair base coat.

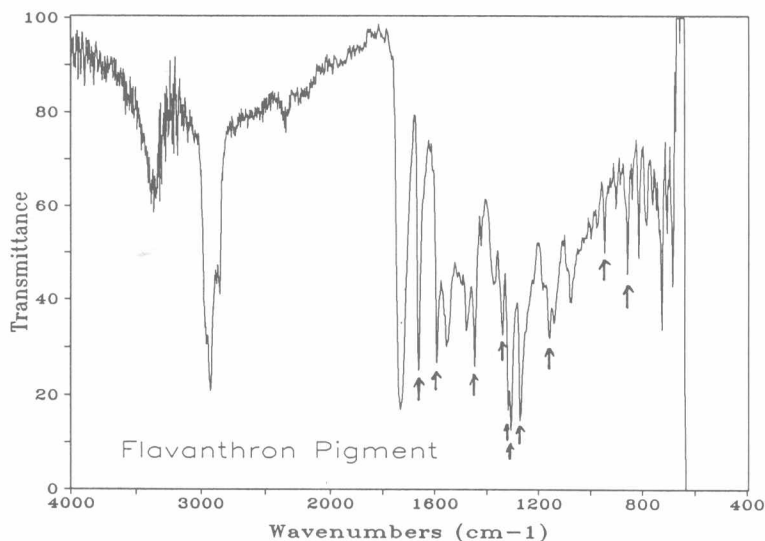


FIG. 4—Spectrum of the inclusion in a base coat recorded with the help of the infrared microscope; sampling area is about 30 by 30 μm .

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-

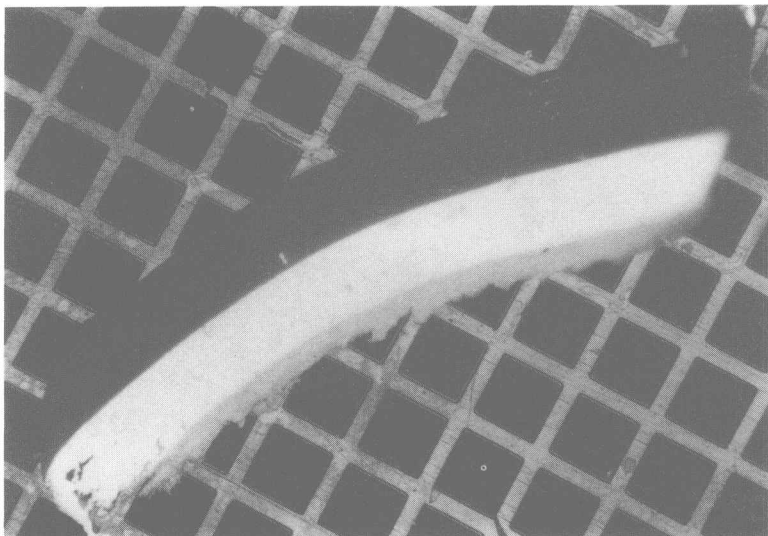


FIG. 5—Photomicrograph of a cross section of a three-layered coating. Bottom: E-coat; medium: primer surfacer; top: top coat.

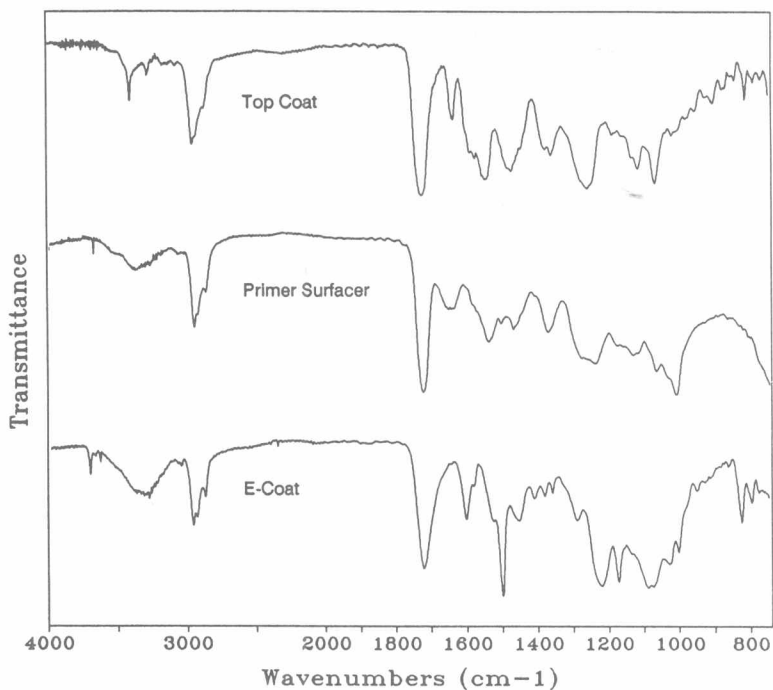


FIG. 6—Microscope infrared spectra of the individual layers of a three-layered coating.

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 ^{13}C -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 ($> 4.7\text{ T}$) 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 ^{13}C -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

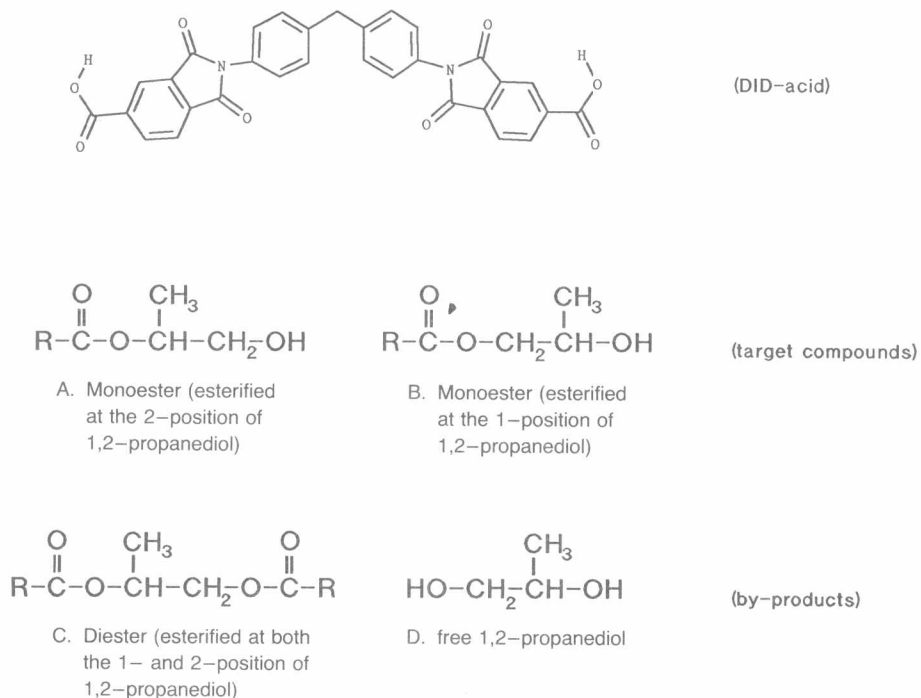


FIG. 7—Reaction products of DID acid and 1,2 propanediol.

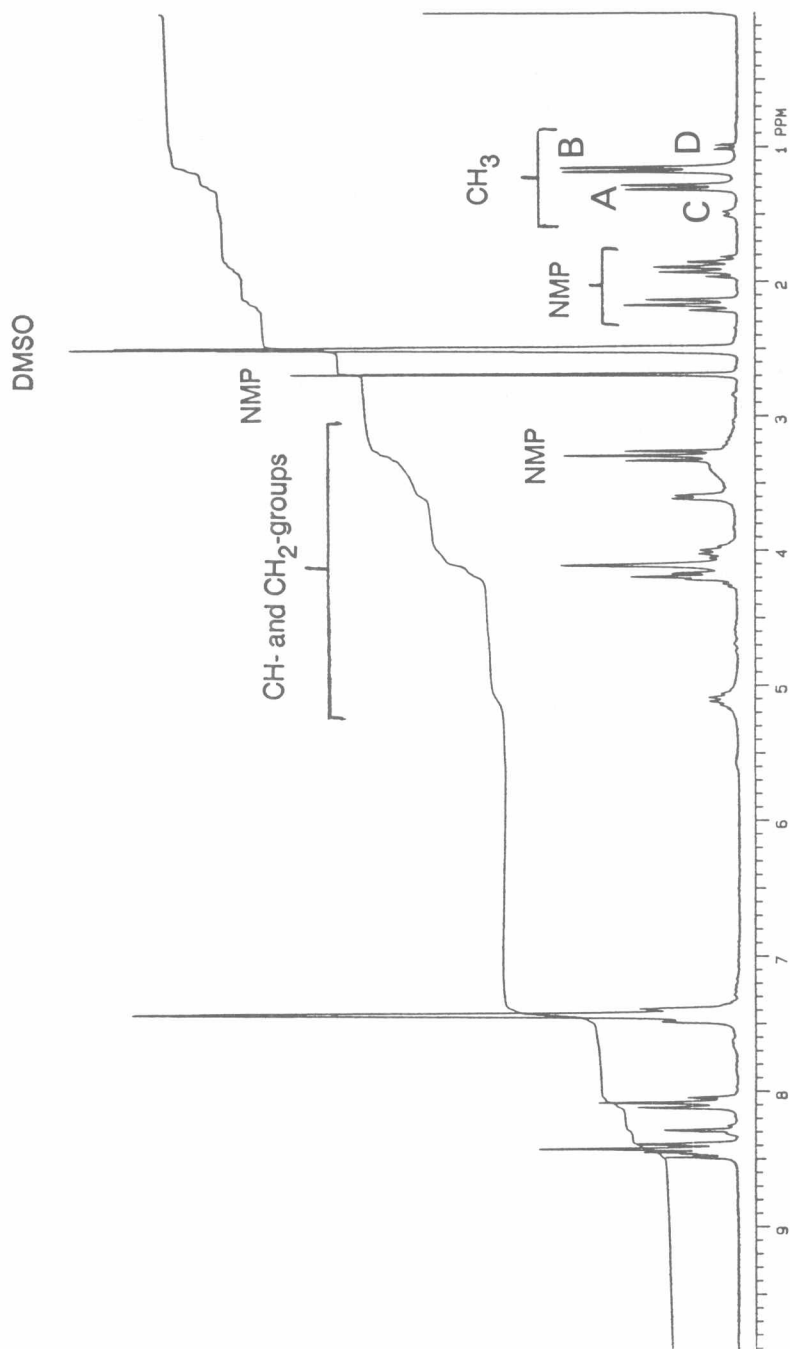


FIG. 8— ^{13}C -NMR and ^1H -NMR spectrum of the reaction products of DID acid and 1.2 propanediol. NMP = *N*-methyl pyrrolidone; DMSO = dimethyl sulfoxide.

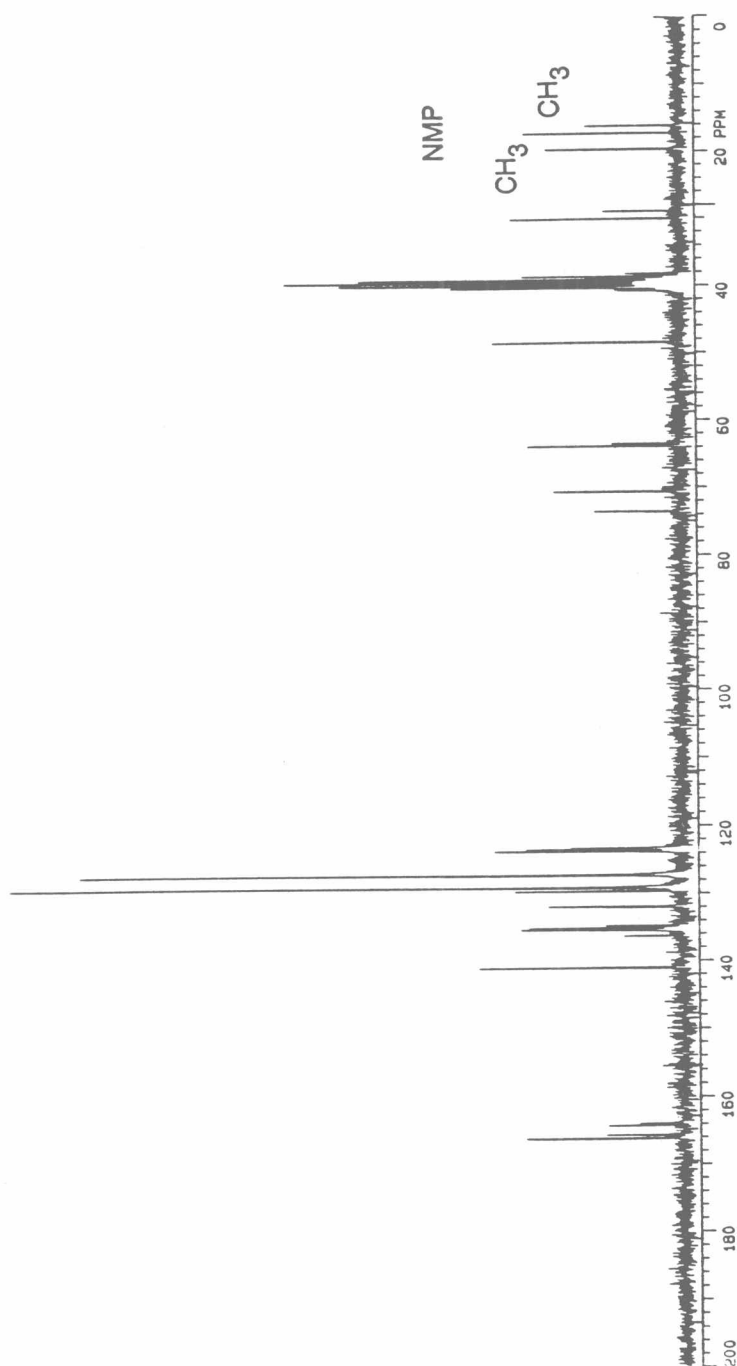


FIG. 8—(Continued).