Transport and Related Properties of Paint Films. I. Composition and Structure

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Synopsis

This is the first of a series of articles on ionic and molecular transport processes and related properties of paint films. The intention is to correlate adhesion and initiation of corrosion to these relevant physical and chemical properties. Chemical formulas and structure of three vinyl–three epoxy– and one polyurethane–paint system are given in this article. Each paint has been formulated to meet appropriate military specifications. Subsequent articles will deal with dynamic mechanical properties, small angle x-ray scattering measurements of porosity, and transport properties.

INTRODUCTION

The technology of painting for corrosion protection rests largely on an empirical basis, traceable to two major factors. First, corrosion protection by paints is a complex multivariable problem including polymer properties, surface properties, application conditions, and environment conditions. Second, the dispersion of manufacturers and users and the competitiveness of the business has not been conducive to a large-scale research and development effort to delineate and verify the relevant basic phenomena. The number of basic papers on transport properties of paints and the relation to corrosion protection is limited, and the papers are rather diverse in respect to paint systems, parameters measured, and theory.[1-24]

The present series of papers is based on research aimed at developing a coherent picture of ionic and molecular transport in paint films and the relation of these to loss of adhesion and the initiation of corrosion. The theoretical framework the transport studies[25] and results for a commercial airplane polyurethane[26] have been published. Through this work, a realization developed that transport properties should be related to composition, molecular weight, and structure of the paint systems as well as to performance. Required compositions and basic chemical properties of the commercial paints were unobtainable.

This first paper presents data on seven different paint systems formulated to meet military specifications of paint used by the Navy. These included seven resin systems: three vinyls, three epoxies, and one polyurethane. Unpigmented free films of all of these systems were prepared for various physical and chemical measurements. Chemical formulas, molecular weights, and structures of these resins are presented here. In addition, some data are presented for a commercial polyurethane and a commercial epoxy

used in the studies. Baseline infrared and ultraviolet spectra have been recorded for each system and will be used for comparison as required in later papers.

The accompanying paper[27] will deal with dynamic mechanical properties of the seven paints described here as well as an unpigmented commercial polyurethane. Planned subsequent papers will describe determination of pore size distribution based on small-angle X-ray scattering measurements and with transport properties. A primary objective is to correlate ionic and molecular transport behavior to the basic chemistry and structure of the films. Ionic and molecular transport in paint films play a dominant role in corrosion protection by paints.

PAINT FORMULATIONS

The paint systems were formulated to meet military specifications for Navy applications. Compositions and descriptions follow. The code names in parentheses will be used for designating the paints in future papers. All of the components for the seven paints were procured, and free films of all paints were made by spraying on decal paper and stripping in water. To date, only unpigmented films have been made.

Vinyl Resin Coating That Meets Mil-P-15328D (VR2) (Wash Primer Formula No. 117)

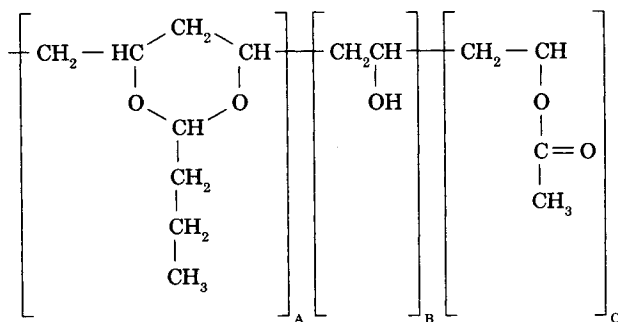The proportions by weight for an unpigmented coating are:

Base:

Bakelite vinyl butyral resin XYHL (Union Carbide Corp.)	8.0
n-Butyl alcohol	18.0
Isopropyl alcohol (99%)	50.3
Water	2.1

Diluent:

Phosphoric acid (85%)	4.0
Water	3.6
Isopropyl alcohol (99%)	14.0
	100.0

The base and diluent are stored separately and mixed just prior to use.

The structure of the Bakelite Vinly Butyral Resin XYHL can be best described by telling how it is made. Vinly acetate is polymerized to a linear polymer and then saponified to remove most of the acetate groups leaving hydroxyl groups. Part of these hydroxyl groups is reacted with butyralde-hyde, which forms an acetal with adjacent hydroxyl groups. The final product may be represented by the following structure:

$$\left[CH_2 - HC \underset{O}{\overset{CH_2}{\diagdown}} CH \atop \underset{CH_2}{\overset{CH}{\underset{CH_2}{\overset{|}{\underset{CH_3}{|}}}}} \right]_A \left[CH_2CH \atop OH \right]_B \left[CH_2 - CH \atop \underset{C=O}{\overset{O}{\underset{CH_3}{|}}} \right]_C$$
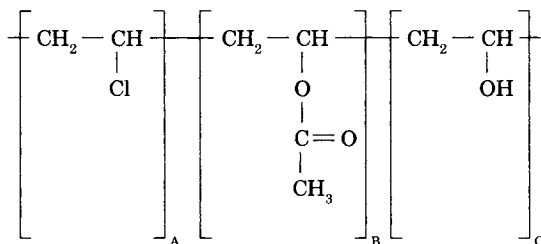
Units of A, B, and C are randomly distributed along the molecular chain. In Bakelite XYHL, there is approximately 80% by weight A, 19.5% by weight B, and 0.5% by weight C. The molecular weight is in the 38,000–45,000 range.

Vinyl Resin Coating That Meets MIL-P-15929C (VR3) (Formula 119)

The proportions by weight for an unpigmented system are:

Bakelite vinyl resin VAGH (Union Carbide Corp.)	22.2
Flexol plasticizer TCP (Union Carbide Corp.)	2.3
MIBK	39.1
Toluene	36.4
	100.0

Bakelite vinyl resin VAGH is a copolymer of vinyl chloride and vinyl acetate where a fraction of the acetate groups have been saponified to hydroxyl groups. It can thus be described as a copolymer of vinyl chloride, vinyl acetate, and vinyl alcohol, and can be represented by the formula

$$\left[CH_2 - CH \atop Cl \right]_A \left[CH_2 - CH \atop \underset{CH_3}{\overset{O}{\underset{C=O}{|}}} \right]_B \left[CH_2 - CH \atop OH \right]_C$$

These units are randomly distributed along the molecular chain. Bakelite VAGH is 91% by weight A, 3% by weight B, and 6% by weight C. The average molecular weight is 23,100 and it has a glass transition temperature of 79°C.

Tricresyl phosphate (TCP) is a plasticizer for the resin. It has the structure
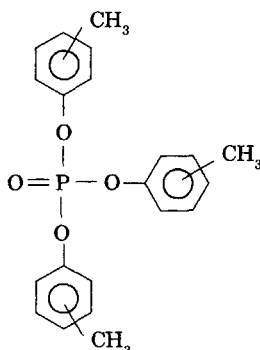
It does not react chemically but only dissolves in the vinyl resin.

Vinyl Resin Coating That Meets MIL-P-15931 (VR4) (Formula 121, Pigmented Formulation is Antifouling)

The proportions by weight for an unpigmented system are:

Rosin	12.3
Bakelite vinyl resin VYHH (Union Carbide Corp.)	12.3
Flexol TCP (Union Carbide Corp.)	4.7
MIBK	42.7
Xylene	28.0
	100.0

Bakelite Vinyl Resin VYHH is a random linear copolymer of vinyl chloride (86% by weight) and vinyl acetate (14% by weight). Again, tricresyl phosphate is the plasticizer. The rosin in the formula is largely abietic acid with other related compounds. Abietic acid has the following structure:
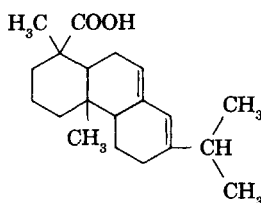
The rosin contributes to the hardness of the coating and helps adhesion. The coating dries by the evaporation of the solvent and no chemical reaction takes place between the components.

EPOXY RESIN COATINGS THAT MEET MIL-P-24441

#1 Epoxy-Polyamide (E Epoxy)
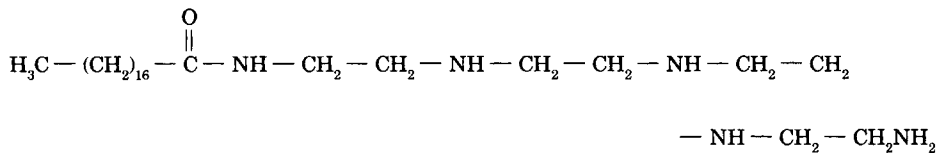
The proportions for an unpigmented coating are:
Component A:

GENAMIDE 2000 (General Mills Chemicals, Inc.)	3.3
VERSAMID 280B75 (General Mills Chemicals, Inc.)	54.0
Butyl alcohol	42.7
	100.0

Component B:
  EPON 815   73.2
  Super Hi-Flash Naptha   26.8
                                                            _____
                                                            100.0

The blend ratio for binder system is 74 parts component A to 100 parts component B, *by weight*. The recommended cure schedule for this coating is 16 h at 77°F plus 15 min at 125°F.

Excluding the pigment, this coating consists of an epoxy resin and a polyamide curing agent. First, the epoxy resin, Shell EPON 815 (in component B), is a mixture of the diglycidyl ether of bisphenol A (90% by weight), and butyl glycidyl ether (10% by weight). The structural formulas are

$$H_2C \overset{O}{\overbrace{}} CH - CH_2 - O - \langle\bigcirc\rangle - \underset{CH_3}{\overset{CH_3}{C}} - \langle\bigcirc\rangle - O - CH_2 - CH \overset{O}{\overbrace{}} CH_2$$

for diglycidyl ether of bisphenol A

$$H_3C - CH_2 - CH_2 - CH_2 - O - CH_2 - CH \overset{O}{\overbrace{}} CH_2$$

for butyl glycidyl ether

The curing agent is a more complex mixture. It is mainly Versamid 280B75. This is a 75% by weight solution of Versamid 280 in methyl ethyl ketone, which merely serves as a solvent. The other portion of the curing agent is Genamid 2000. The ratio of Versamid 280 to Genamid 2000, disregarding the MEK solvent, is 10.5 to 1.

Versamid 280 is a reaction product of dimer fatty acid, diethylene triamine, and the diglycidyl ether of bisphenol A. Dimer fatty acid is the reaction product of unsaturated fatty acids and has mainly the following structure:

$$
\begin{array}{c}
(CH_2)_7 - \overset{O}{\overset{\|}{C}} - OH \\
| \\
CH_3 - (CH_2)_7 - CH \overset{C}{\underset{H}{\diagdown}} \overset{O}{\underset{H}{\diagup}} C - (CH_2)_7 - \overset{\|}{C} - OH \\
CH_3 - (CH_2)_7 - CH \underset{\overset{|}{C}H}{\diagdown} CH \\
H
\end{array}
$$

To make the Versamid, this is first reacted with diethylene triamine. Representing the main body of the dimer acid by R, the reaction goes as follows:

$$HO - \overset{O}{\overset{\|}{C}} - R - \overset{O}{\overset{\|}{C}} - OH + H_2N - CH_2 - CH_2 - NH - CH_2 - CH_2 - NH_2 \rightarrow$$

$$H_2N - CH_2 - CH_2 - NH - CH_2 - CH_2 - \overset{H}{\overset{|}{N}} - \overset{O}{\overset{\|}{C}} - R - \overset{O}{\overset{\|}{C}} - \overset{H}{\overset{|}{N}} - CH_2 - CH_2$$
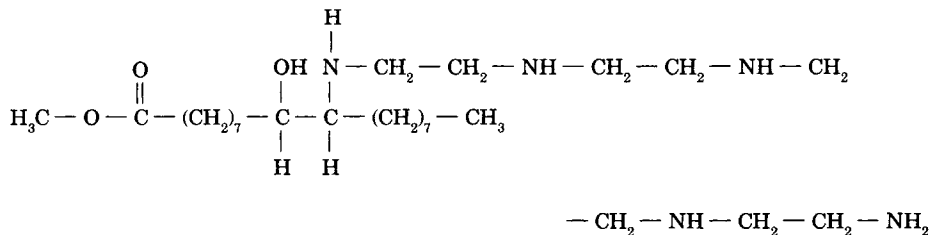
$$- NH - CH_2 - CH_2 - NH_2 + 2HOH$$

This serves as a curing agent because the amine hydrogens in this compound, of which there are six, will react adding to epoxy groups in an epoxy resin. The two amide hydrogen (marked with an asterisk) do not react. In the Versamid 280 the compound shown above is partially reacted with a small amount of the diglycidyl ether of bisphenol A. This increases the molecular weight but is not enough to crosslink the material.
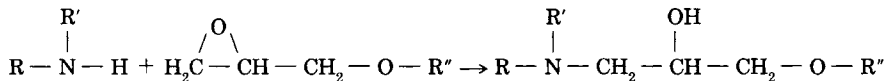
Genamid 2000, the other portion of the curing agent, is again a mixture. The two chemical structures present are:

$$H_3C-(CH_2)_{16}-\overset{\overset{\displaystyle O}{\|}}{C}-NH-CH_2-CH_2-NH-CH_2-CH_2-NH-CH_2-CH_2$$

$$-NH-CH_2-CH_2NH_2$$

and

$$H_3C-O-\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_7-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle \overset{\overset{\displaystyle H}{|}}{N}-CH_2-CH_2-NH-CH_2-CH_2-NH-CH_2}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-(CH_2)_7-CH_3$$

$$-CH_2-NH-CH_2-CH_2-NH_2$$

Again, in these two compounds, the amine hydrogens add to the epoxide groups in the epoxy resin by the following reaction:

$$R-\overset{\overset{\displaystyle R'}{|}}{N}-H+H_2C\overset{O}{\underset{}{\diagdown}}CH-CH_2-O-R''\rightarrow R-\overset{\overset{\displaystyle R'}{|}}{N}-CH_2-\overset{\overset{\displaystyle OH}{|}}{CH}-CH_2-O-R''$$

The epoxy group reacts with both amine hydrogens on the terminal primary amine groups.

These polyfunctional amines, the Versamid 280 and Genamid 2000, react by this simple addition reaction with the EPON 815 to give a crosslinked thermoset film.
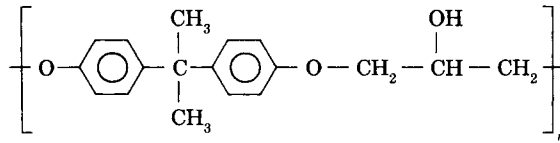
#2 EPONOL Resin Coating (A Epoxy)

The proportions by weight for an unpigmented system are:

Eponol 55-B-40 (Shell Chemical Co.)	22.2
Acetone	20.1
Toluene	33.3
Methyl ethyl ketone	6.6
Methyl isobutyl carbinol	8.9
Cellosolve acetate	8.9
	100.0

EPONOL 55 is a thermoplastic polyhydroxy ether resin related to epoxy

resin. The structure of the repeating unit is generally represented by the formula:

$$\left[O-\bigcirc-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\bigcirc-O-CH_2-\underset{\underset{}{\overset{\overset{OH}{|}}{CH}}}-CH_2 \right]_n$$

where n is about 25. There is some branching of the chain, and the end groups are probably phenol or alcohol groups. While the chemical structure is similar to the epoxy resins, the molecular weight is high enough that good films are formed merely by evaporation of the solvent without the need of a curing agent.

#3 Ketamine-Epoxy Coating (K Epoxy)

The proportions by weight for an unpigmented system are:

EPON 815 (Shell Chemical Co.)	73.5
50 wt % phenol in ethanol	4.4
EPON curing Agent H-2 (Shell Chemical Co.)	22.1
	100.0

The components are blended and mixed thoroughly and then held for one hour before laying down film. The cure is 24 hours at room temperature.

To explain the chemical composition of this coating, the ketimine curing agent (EPON Curing Agent H-2) and how it works is described. The ketimine is formed from ethylenediamine and methyl isobutyl ketone by the splitting out of water as follows:

$$H_2N-CH_2-CH_2-NH_2 + 2 \quad O{=}\underset{\underset{\underset{\underset{H}{|}}{\underset{H_3C\diagup|\diagdown CH_3}{C}}}{\underset{CH_2}{|}}}{\overset{\overset{CH_3}{|}}{C}} \longrightarrow$$

$$\underset{\underset{\underset{\underset{H}{|}}{H_3C\diagup|\diagdown CH_3}}{\underset{C}{|}}}{\underset{\underset{CH_2}{|}}{\overset{\overset{CH_3}{|}}{C}}}{=}N-CH_2-CH_2-N{=}\overset{\overset{CH_3}{|}}{C}\diagdown \quad +2HOH$$
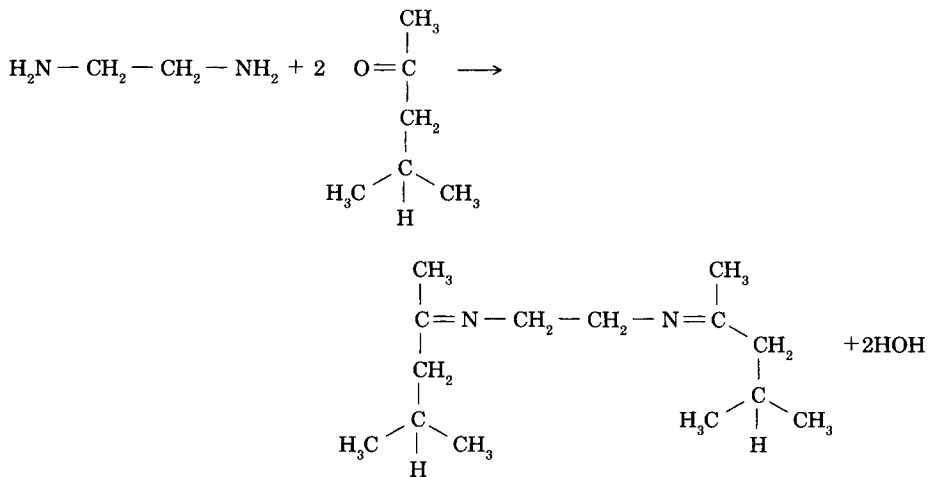
Ketimine H—2

When applied in a coating, this ketimine readily reacts with the moisture of the air and reverts to ethylenediamine and methyl isobutyl ketone. The methyl isobutyl ketone evaporates from the coating and the ethylenediamine is the curing agent. Ethylenediamine cures epoxy resins by a simple, cleancut addition of the amine hydrogen to the epoxide groups. This reaction

is shown in the following equation using a monoepoxide for illustrative purposes:

$$4R-O-CH_2-CH\overset{O}{\diagup\diagdown}CH_2 + H_2N-CH_2-CH_2-NH_2 \longrightarrow$$

$$
\begin{array}{cc}
\overset{\displaystyle OH}{\underset{}{\mid}} & \overset{\displaystyle OH}{\underset{}{\mid}}\\
R-O-CH_2-CH-CH_2 & CH_2-CH-CH_2-O-R\\
\diagdown & \diagup\\
N-CH_2-CH_2-N\\
\diagup & \diagdown\\
R-O-CH_2-CH-CH_2 & CH_2-CH-CH_2-O-R\\
\mid & \mid\\
OH & OH
\end{array}
$$

Since in the actual coating the epoxy resin is close to difunctional and the ethylenediamine tetrafunctional, the addition reaction gives a crosslinked system with well-defined structure.

The epoxy resin in this coating consists of two parts. It is mainly the diglycidyl ether of bisphenol A:

$$H_2C\overset{O}{\diagup\diagdown}CH-CH_2-O-\langle\bigcirc\rangle-\overset{CH_3}{\underset{CH_3}{C}}-\langle\bigcirc\rangle-O-CH_2-CH\overset{O}{\diagup\diagdown}CH_2$$

To lower the viscosity and cut down the crosslink density, this diglycidyl ether of bisphenol A is diluted with a minor amount (about 10%) of a monofunctional epoxy compound, butyl glycidyl ether.

$$H_3C-CH_2-CH_2-CH_2-O-CH_2-CH\overset{O}{\diagup\diagdown}CH_2$$

The phenol in the formula is merely present as a catalyst to speed up the reaction between amine hydrogens and epoxy groups.

Urethane Coating That Meets MIL-C-81773B A/S (N PUR)

This is a two-part coating. Part I is a solution of polyester resin having free hydroxyl groups. A typical product of this type would be prepared by reacting a glycol, phthalic anhydride, and a triol to yield the following resin structure:

$$H\left[O-R-O\right]_a\left[\overset{O\ \ O}{\underset{\langle\bigcirc\rangle}{\overset{\parallel\ \ \parallel}{C\ \ C}}-O}\right]_b\left[\overset{H\quad\ \ H}{\underset{H\ \ OH\ H}{\overset{\mid\quad\ \ \mid}{C-R-C}-O}}\right]_c H$$

Component II is a solution of Desomudur N. This is a biuret derived from hexamethylene diisocyanate:

$$3\ O = C = N - (CH_2)_6 - N = C = O + H_2O \xrightarrow{-CO_2}$$

$$O = C = N - (CH_2)_6 - N \begin{array}{c} \overset{O}{\underset{\|}{C}} - \overset{H}{\underset{\|}{N}} - (CH_2)_6 - N = C = O \\ \\ \underset{\underset{O}{\|}}{C} - \underset{\underset{H}{|}}{N} - (CH_2)_6 - N = C = O \end{array}$$

Desmodur N is sold by Mobay Chemical as a 75% solids solution in 1/1 by volume ethylglycol acetate/xylene solvent; designation of the solution is Desmodur N-75.

Crosslinking these systems results from the isocyanate-hydroxyl reaction to produce a urethane linkage:

$$R - N = C = O + R - OH \longrightarrow R - \underset{\underset{H}{|}}{N} - \underset{\underset{O}{\|}}{C} - O - R$$

Stoichiometry for this system is 1:1, Component I:Component II, *by volume.* Films of these coatings should be fully cured after eight hours at 77°F.

(O PUR) and (O Epoxy)

In addition to the specially formulated systems, two commercial airplane paints were studied. Both were in the unpigmented form. They were a polyurethane (Desoto, Inc., Chemical Coatings Div., Berkeley, Calif., meeting Boeing material specification, BMS-10-60D-TYII, and Mil C-83286) designated O PUR in this series of papers, and an epoxy (Koppers Co., Andrew Brown Div., Kent, Washington, BMS-10-11J-TYII) designated O Epoxy. Both were obtained from the Boeing Commercial Airplane Company, Seattle, Wash.

INFRARED SPECTROSCOPY

Infrared spectra were measured for the foregoing unpigmented paint systems to provide a basis for evaluating compositional and structural changes caused by exposure to various environments. Spectra were also determined for the various additives and curing agents used so that their contributions to the composite spectra could be identified. These spectra were measured using three different Perkin-Elmer spectrophotometers (Models 727-B, 283, and 257) for samples which were prepared as solvent-cast free films, by mixing with KBr and pressing into a disc,[28] and in liquid form. Infrared spectra obtained for the vinyl systems are presented and discussed to provide pertinent compositional and structural information for these systems. In addition, a brief discussion of the spectra obtained for the polyurethane and epoxy systems is provided.

Quantitative analysis of these infrared spectra involved the application of the Beer–Lambert law,[29] which relates the absorbance A to both the

samples thickness b (m) and the concentration of the absorbing species c (mol/m^3) by the molar absorptivity e (m^2/mol), viz.,

$$A = ebc \qquad (1)$$

The absorbance A, which was not directly provided by the instrument, was calculated from the incident intensity I_0 and the transmitted intensity I, using

$$-A = \log_{10} \frac{I}{I_0} \qquad (2)$$

The incident and transmitted intensities were determined applying the peak height from the baseline technique.[30] Representative baselines are shown in the spectra provided (see Figs. 1, 2, and 4). Since the molar extinction coefficient is greatly affected by environmental changes, the Beer–Lambert law is not always obeyed. Consequently, plots of band absorbance ratios were also used to correlate the infrared measurements to the composition and structure of these paints.

In addition to this quantitative treatment, frequency shifts were used to provide qualitative structural information on the extent and nature of the hydrogen bonding in these paints. Hydrogen bonding is known to alter the absorption frequencies of both the proton donor and acceptor in either a bending or stretching mode. In general, the stretching peak of a proton donor is moved to lower frequencies. The stretching frequency of the acceptor group is also shifted to lower frequencies, but to a lesser degree. In contrast, the bending vibration of the donor group is usually shifted to higher frequency, but to a lesser extent than that of the stretching mode. Specifically, hydrogen bonding shifts the OH stretching peak from the 3550–3650 cm^{-1} range to the 3350–3450 cm^{-1} range,[28,29] the NH stretching peak from approximately 3450 to 3300 cm^{-1},[28] and the C=O stretching mode from approximately 1742 to 1700 cm^{-1}.[28] The exact location of these bonded and unbonded peaks depends on the solvent, which in this case is the polymer, and the extent and nature of the hydrogen bonding. For example, West and Cooper[32] observed the hydrogen bonded and nonhydrogen bonded C=O stretching peaks at 1703 and 1733 cm^{-1}, respectively, for a polyurethane system.

Vinyl Systems

The infrared spectrum obtained for a solvent cast free film sample of VR2 is provided in Figure 1. A second spectrum obtained for a sample prepared by dispersing the polymer resin as supplied by Union Carbide Corp. in a KBr disc was found to be in excellent qualitative agreement with this solvent-cast free film spectrum. Furthermore, both of these spectra were in excellent agreement with the poly(vinyl butyral) spectra published by Haslam[33] and Hummel.[34] In all of these spectra, two strong and broad bands, which are characteristic of the ether structure (C—O—C) in this polymer, are observed at 1000 and 1140 cm^{-1}. Another characteristic of the poly(vinyl butyral) spectrum is the very broad and intense absorption band
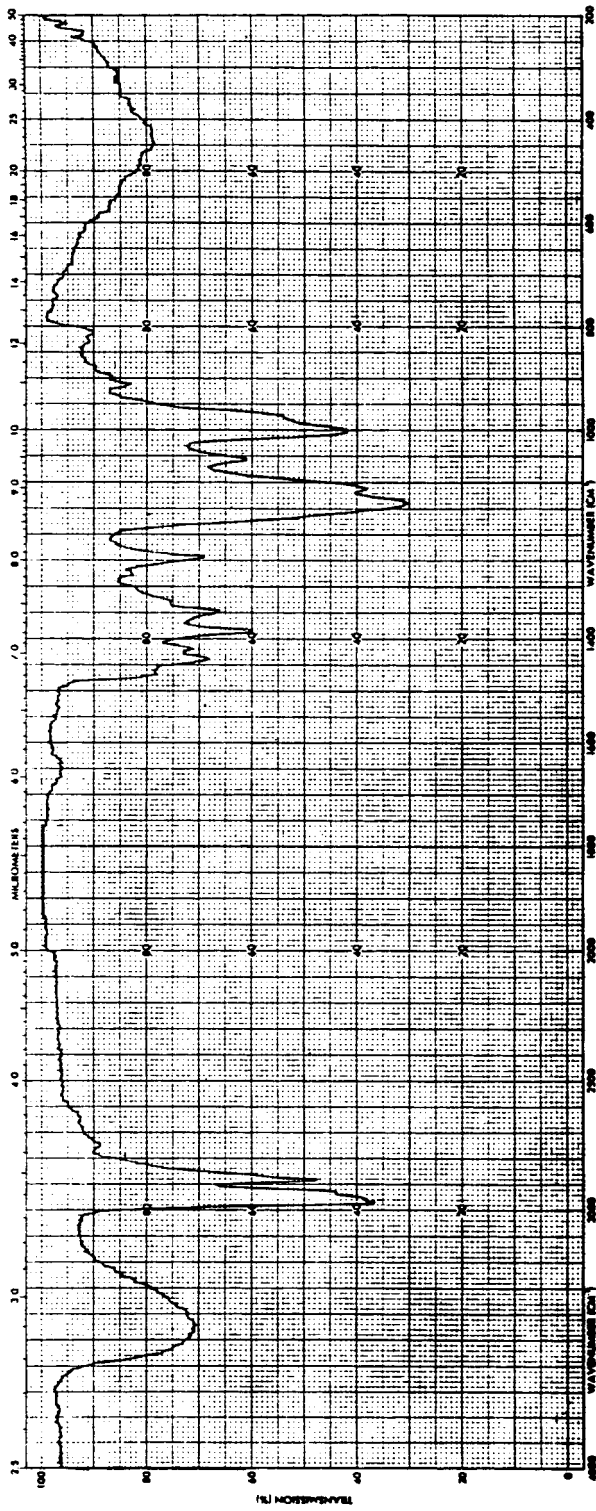
Fig. 1. Paint System VR2 obtained from a solvent-cast film.
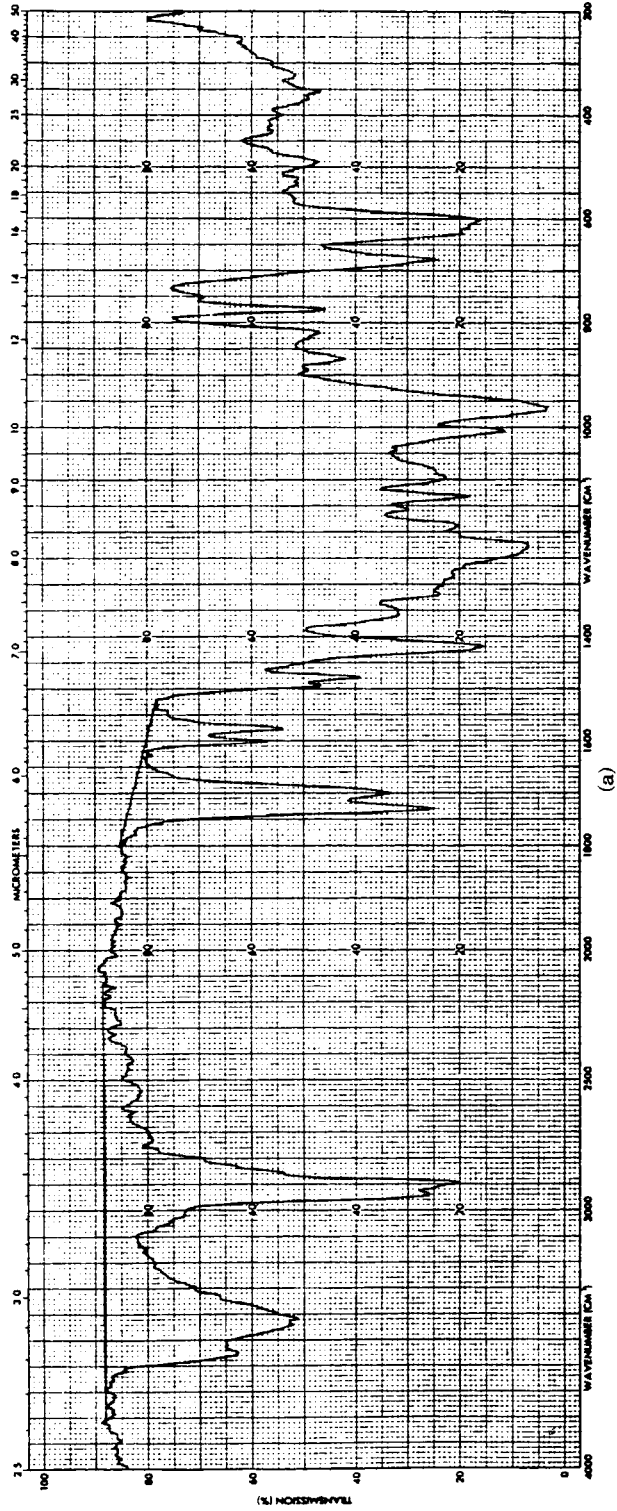
Fig. 2. (a) Paint System VR3 obtained from a solvent-cast film. (b) Copolymer of paint system obtained from a solvent-cast film. (c) Copolymer of paint system VR3 with 17.2% by weight TCP obtained from a solvent-cast film.
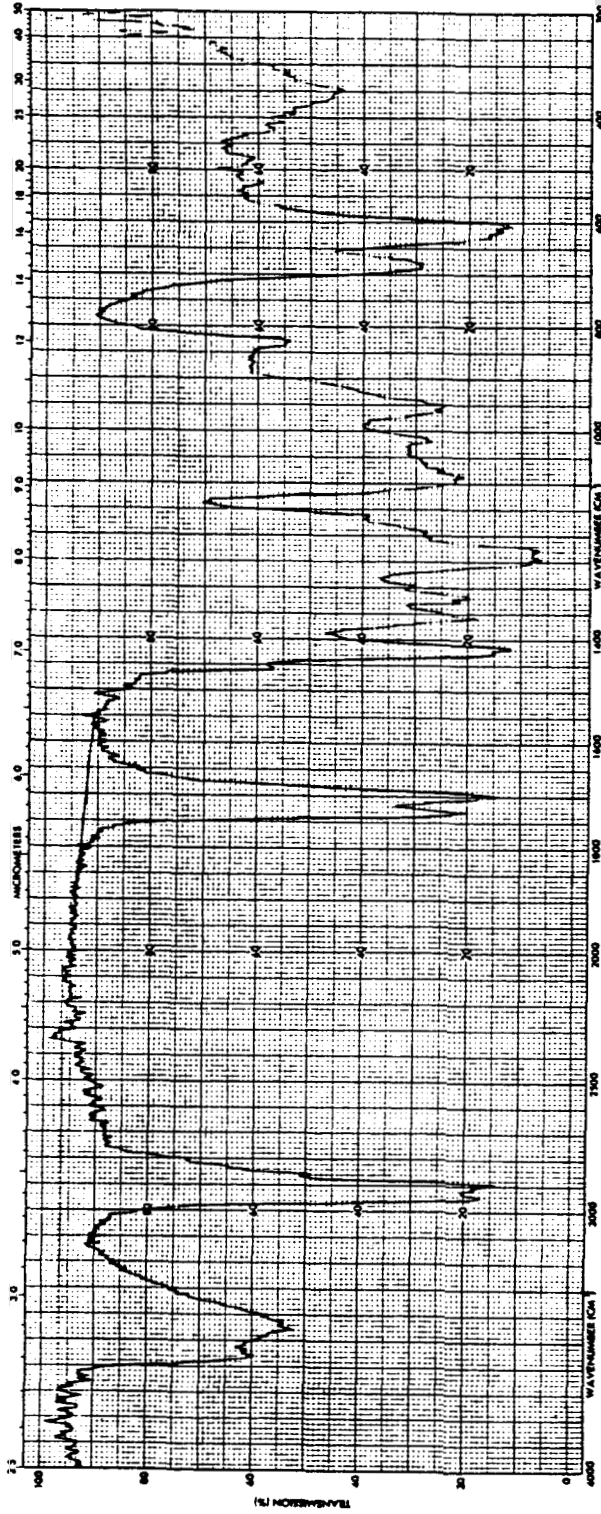
Fig. 2. (Continued from previous page.)
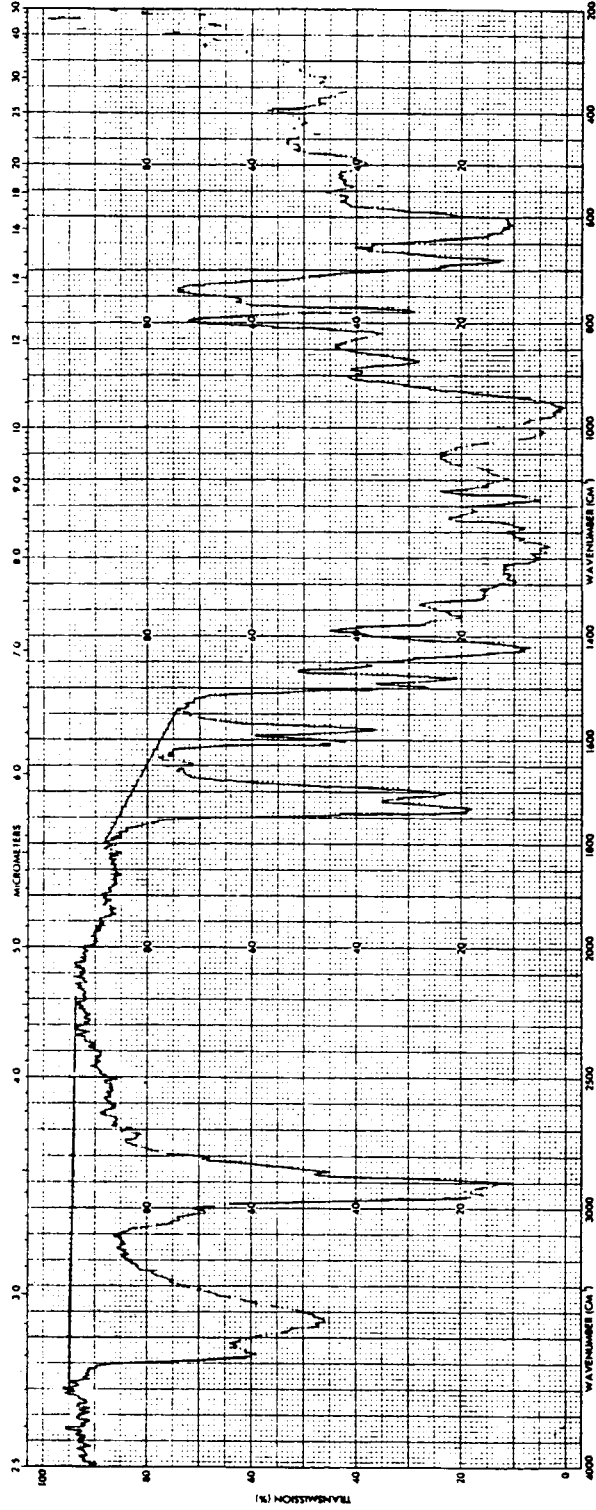
Fig. 2. (Continued from previous page.)

which covers the 350–700 cm^{-1} range. This band has been attributed to the overlap of a sequence of strong absorption bands due to the in-plane and out-of-plane C—O—C bending vibrations.[34]

The presence of residual poly(vinyl acetate) groups is usually indicated by a weak carbonyl absorption and a 1243 cm^{-1} absorption band.[33] The lack of the carbonyl absorption in the solvent-cast free film spectra is indicative of the low poly(vinyl acetate) content in this paint system. The approximately 20% vinyl alcohol content is characterized by the broad OH stretching peak observed at 3440 cm^{-1}. From the frequency location of this absorption it was concluded that the OH groups in this polymer are almost completely involved in hydrogen bonding.

Spectra for VR3, which contains 9.5% by weight TCP plasticizer, and two special formulations which contained 0 and 17.2% TCP by weight are provided in Figures 2. Direct comparison of these spectra allowed for the identification of six peaks (approximately 778, 1140, 1481, 1498, 1580, and 1603 cm^{-1}) associated with the TCP plasticizer. Examination and comparison with a spectrum measured for the TCP plasticizer only further confirmed the association of these peaks with the TCP plasticizer. Since the 1580 and 1603 cm^{-1} absorption peaks appear in a nonabsorbing region in the copolymer spectrum, they were chosen to monitor changes in the plasticizer composition due to exposure to different environments. Using a calculated weighted average density of 1.39 g/cm^3 for the copolymer and 1.17 g/cm^3 for the TCP plasticizer, and assuming that the volumes were additive, the molar absorptivity e was determined to be 10.2 $\pm$ 0.34 (m^2/mol) and 8.73 $\pm$ 0.79 m^2/mol for the 1580 and 1603 cm^{-1} bands, respectively.

The effect of the TCP plasticizer on the hydrogen bonding in these samples was examined using both the ratio of the 3440 and 3560 cm^{-1} absorbances (A_{3440}/A_{3560}) and the ratio of the 1703 and 1733 cm^{-1} absorbances (A_{1703}/A_{1733}). These ratios are plotted as a function of weight percent TCP plasticizer in Figure 3. Recalling the cause of each absorbance, it is readily seen that the increase in the A_{3440}/A_{3560} ratio indicates an increase in the extent of hydrogen bonding of the hydroxyl groups. In comparison, the decrease in the A_{1703}/A_{1733} ratio indicates a decrease in the hydrogen bonding of the carbonyl groups. From this result it was concluded that the TCP plasticizer hydrogen bonds only to the hydroxyl groups and as a result breaks bonds between the hydroxyl and carbonyl groups.

The spectrum obtained for the VR3 film which contained 0% TCP by weight was also compared with the results measured for a sample made by mixing the polymer powder as supplied by Aldrich Chemical Co., Inc. with KBr powder and pressing into a disc. The KBr and discs were carefully dried in an oven for that purpose. Close comparison of these two spectra showed two important differences. First, even though the hydroxyl group absorption was split into two peaks—one at 3560 cm^{-1} and the other at 3440 cm^{-1}—in both spectra their relative intensities were not the same. In the case of the KBr disc sample, the 3560 cm^{-1} absorption was greater than the 3440 cm^{-1} absorption, while for the solvent cast sample the opposite was observed. A second difference was that for the solvent cast film, the carbonyl absorption was split into two peaks—one at 1731 cm^{-1} and the
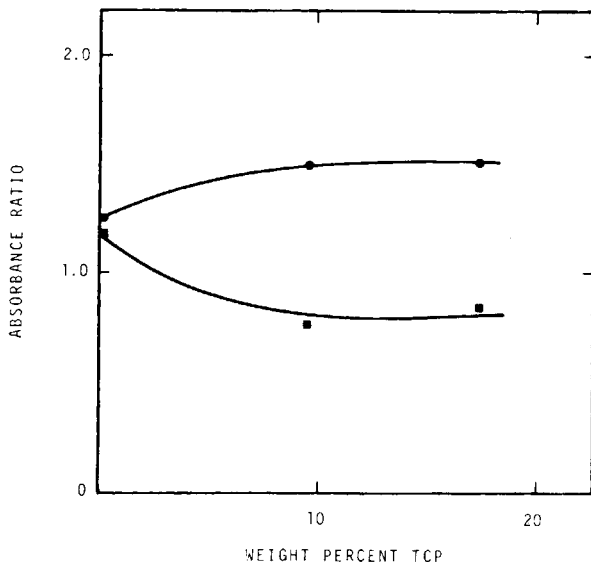
Fig. 3. The effect of TCP content on hydrogen bonding for Paint System VR3 monitored by plotting the following absorbance ratios: (●) A_{3440}/A_{3560}; (■) A_{1703}/A_{1733}.

other at 1701 cm^{-1}—while for the KBr disc sample only a single peak at 1735 cm^{-1} was observed. This single peak at 1735 cm^{-1} indicates that the disc was dry. These observations indicate an increased level of hydrogen bonding in the solvent-cast sample relative to the KBr sample. This difference was attributed to differences in the solvent interaction properties of these samples, since in the case of the KBr disc sample the solvent is the KBr, while in the solvent-cast film it is the polymer itself.

Spectra measured on solvent-cast film samples of the VR4 copolymer with 0 and 27.6% TCP plasticizer by weight are given in Figure 4. A second spectrum for the copolymer only, which was obtained from a KBr sample prepared with the resin powder as supplied by the Union Carbide Corp., was in excellent agreement with the corresponding spectrum in Figure 4.

The spectrum of the vinyl acetate–vinyl chloride copolymer is straightforward, because major bands for both the vinyl chloride and vinyl acetate components are evident. Strong vinyl acetate bands at approximately 1026, 1212, 1379, and 1739 cm^{-1}, and a strong vinyl chloride absorption at 615 cm^{-1} clearly identify the copolymer. The composition of a vinyl acetate–vinyl chloride copolymer can be accurately determined from the infrared spectrum using a number of quantitative methods involving measurement of the 1730–1740 cm^{-1} absorbance. Henniker[28] presented a calibration curve for the ratio of the 1730 and 1435 cm^{-1} absorbance bands as a function of percent vinyl acetate content. Using this calibration curve, along with the value of 2.60 calculated for this absorption ratio, the vinyl acetate content was calculated to be 14%. In addition, this spectrum compares well with a spectrum published by Haslam[33] for a sample with 16% vinyl acetate content. These observations are consistent with the 14% vinyl acetate content expected for this sample.
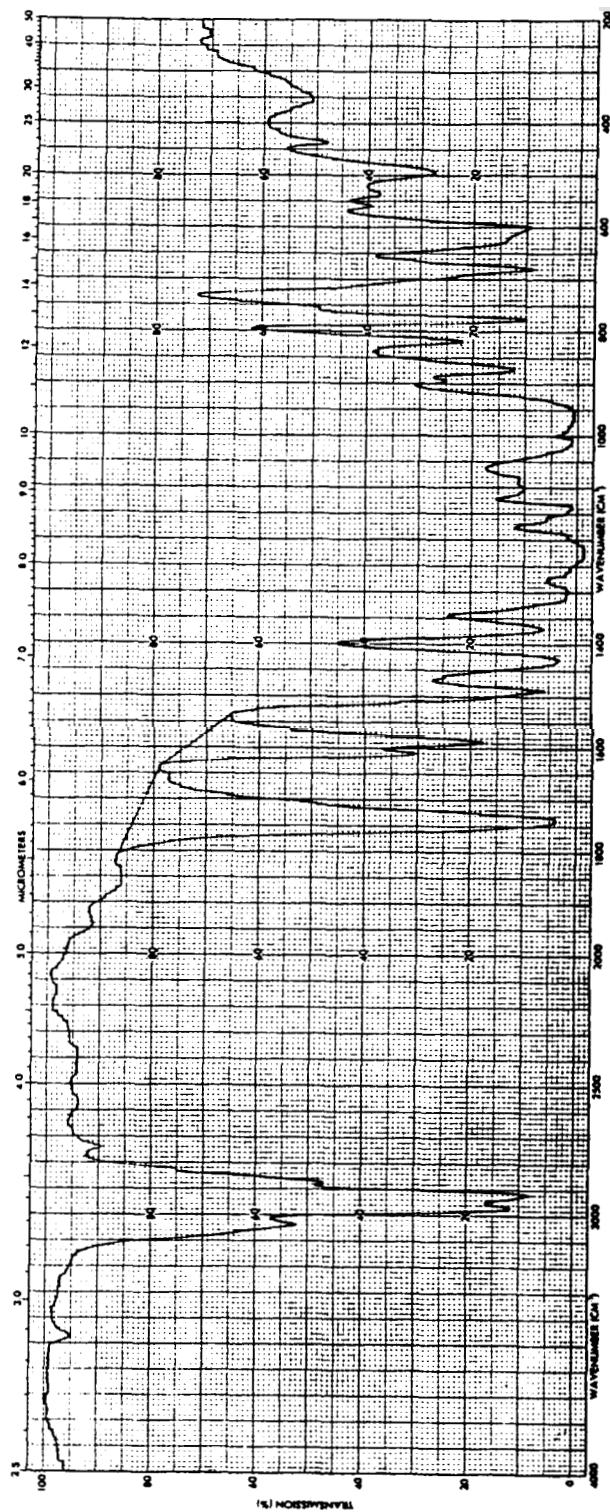
The location of the carbonyl peak at 1744 cm^{-1}, which has a slight shoulder in the 1700 cm^{-1} region, indicates a low degree of hydrogen bonding
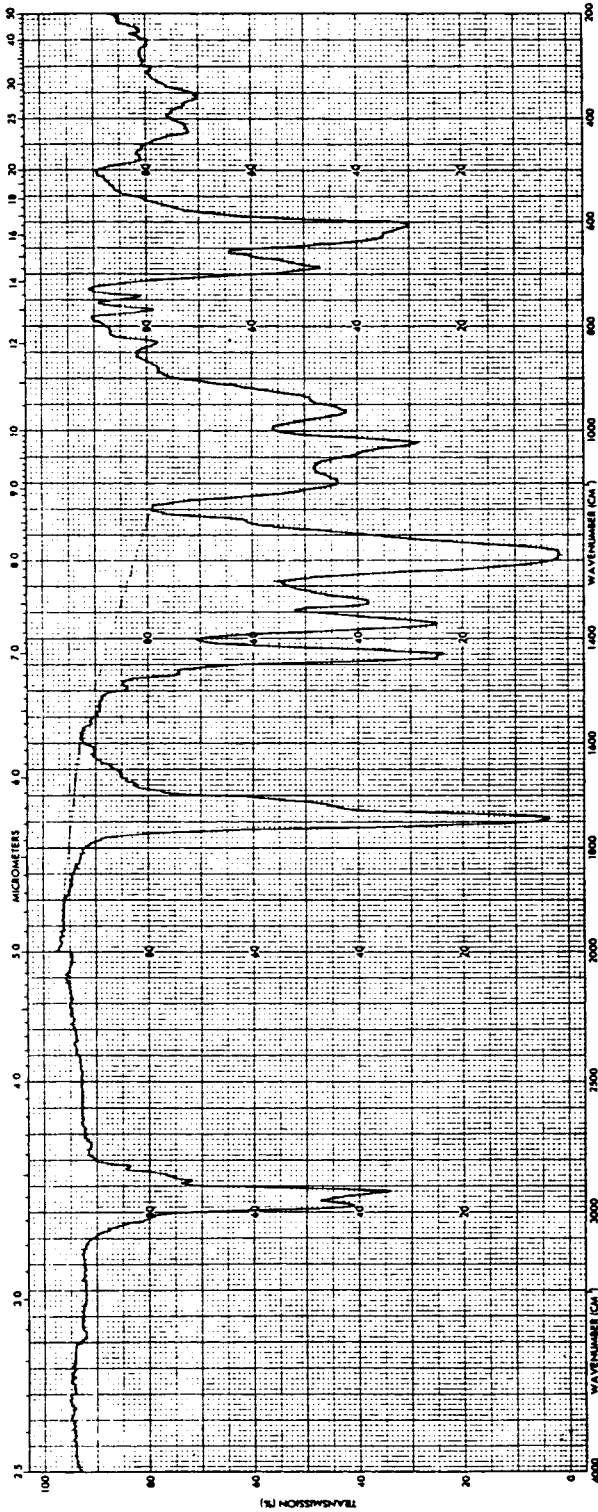
Fig. 4. (a) Copolymer of paint system VR4 obtained from a solvent-cast film. (b) Copolymer of paint system VR4 with 27.6% by weight TCP obtained from a solvent-cast film.

(b)

Fig. 4. (Continued from previous page.)

in this copolymer. Comparison of the two spectra provided in Figures 4 shows that the addition of TCP plasticizer has little if any effect on the location of the carbonyl absorption peak, indicating a low level of hydrogen bonding between the plasticizer and the copolymer. This observation is consistent with the preferential bonding of the TCP plasticizer to the hydroxyl groups observed in the VR3 paint system. Direct comparison of these spectra results in the identification of three peaks that are associated with the TCP plasticizer (778, 1588, 1610 cm⁻¹). Since both the 1588 and 1610 cm^{-1} absorbance peaks appear in a nonabsorbing region of the copolymer spectrum, they are especially suitable for monitoring the TCP plasticizer content in this paint system.

Spectra were also measured for various compositions of the copolymer, rosin hardener, and TCP plasticizer, but incomplete identification of the infrared spectrum for the rosin hardener[34] has hindered their interpretation.

Polyurethanes Systems

Infrared spectra were also obtained on the N Pur and O Pur paint systems. The preparations of thick samples, however, prevented complete resolution of these spectra. Nevertheless, information on the extent of hydrogen bonding was obtained from the location of the NH stretching absorption peak observed at approximately 3360 cm^{-1} for both polyurethane systems. From this observation and those of other investigators[35,36] it was concluded that there is extensive hydrogen bonding in both of these systems.

Epoxy Systems

Infrared spectra were also measured for the four epoxy paint systems and for each of the epoxide and amine curing components. A brief discussion of the results for the A, E, and K Epoxy paints is provided below.

The infrared spectrum for A epoxy was found to be very similar to the spectrum presented by Lee and Neville[37] for DGEBA, except for two important differences. First, the 910 cm^{-1} absorption due to the epoxide ring was not observed, and, second, the hydroxyl absorbance was observed to be slightly stronger. These observations are consistent with the fact that the epoxide end groups present in DGEBA effectively have been replaced by phenols and alcohols, while the main chain structure is essentially the same. The location of the OH stretch absorbance at 3440 cm^{-1} indicates a high degree of hydrogen bonding in this system.

Spectra measured for the E and K epoxy paints, which are both amine-cured systems, provided information of the extent of cure and level of hydrogen bonding in these paints. The absence of the 910 cm^{-1} epoxide ring absorbance in both of these systems indicates complete cure for both of the systems. Comparison to the work of Harrod,[38] who investigated hydrogen bonding in amine-cured epoxy systems, suggests that the broad absorbance at 3400 cm^{-1} indicates extensive hydrogen bonding in these systems.

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