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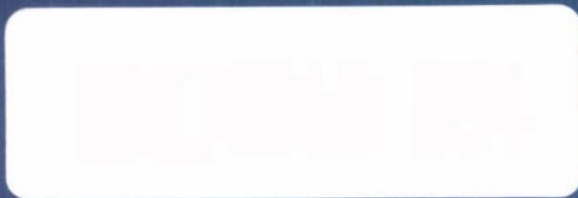


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Alcohol-Sensitive Epoxy Formulations for Temporary or Repairable Embedment

June 1976



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U.S. Army Materiel Development
and Readiness Command

HARRY DIAMOND LABORATORIES

Adelphi, Maryland 20783

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Repairable embedding epoxy formulations have been developed that are alcohol sensitive and hence can be readily removed with an alcohol without damage to the embedded components. The alcohol sensitivity is greatly enhanced with poly(N-vinyl-2-pyrrolidone) as filler. Some basic thermal, electrical, and mechanical properties of the cured epoxies were found to be satisfactory. Being inherently more hydrophilic than the regular epoxy, the materials are not intended for the continuous use in an environment of high		

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humidity. For occasional exposures, a low filler level or an application of a protective thin coating of a regular epoxy is advisable.

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1. INTRODUCTION

Epoxy resin is widely used for embedding or potting electronics. The purpose of potting is to provide protection from environmental effects and handling abuse and to give mechanical support and additional electrical insulation. Usually one expects the potting to be solid and permanent. However, situations may arise later where it is necessary to remove the potting material or to depot in order to reach the components inside for reasons such as repair or failure analysis. This need is particularly true when the work is in the development stage or when the potted assembly or components are expensive. Unfortunately, there is no magic key to depotting. It is a process that is expensive and time consuming, yet often ends up with damage to the components. This is a dilemma and a problem that has existed in industry and in our laboratories.

Many solvents and reagents have been used for depotting. There are proprietary reagents called "strippers" commercially available for this purpose. The reality is that when the solvents or reagents are active enough to swell or attack the potting epoxy, they are usually active enough to attack the insulation plastics and the metals of the components.¹⁻³ Therefore, when preservation of the components is desired, commercial strippers have to be used with caution, and quite often the use of some known solvent is preferred. Depotting usually involves soaking, swelling, picking, and machining, and the steps are repeated with patience. A commercial depotting-process vendor claims in his brochure that "potting can be removed without damage to components or insulation in most cases." At the same time, he strongly suggests the use of repairable potting compounds in the first place whenever practicable, in order to avoid trouble later in depotting. Indeed, repairable potting compounds are available in the market. These materials are usually soft and hence repairable. In fact, some of them are gels and cannot stand even a light finger pressure. Generally, it is not practicable to expect much thermal stability or mechanical protection from such potting materials. Obviously, a demand exists for the development of some better repairable potting compounds.

Although a perfect solution might be difficult to reach, we believed that it was possible to formulate repairable potting compounds that possess better properties, yet that can be removed with some specific

¹S. Ringel, *SPE Journal*, 25 (1969), 44-47.

²Comparative Test of Seven Epoxy Stripping Solutions, Motorola Government Electronics Division, Test Memorandum No. 1121 (10 August 1966).

³P. W. Erickson and J. M. Augl, Solvent Removal of EC-2273 Potting Compound from F-4 Aircraft Electrical Components, Naval Ordnance Laboratory NOLTR 71-35 (14 May 1971).

solvents causing the least damage. Reasoning along this line, we proposed to formulate an epoxy compound that is sensitive to alcohols or removable with an alcohol. Alcohols are particularly desirable because they are nonsolvents for essentially all the insulation materials commonly used. Consequently, an alcohol causes little or no damage when used for depotting.

To make a repairable epoxy that is alcohol sensitive (hereafter referred to as an "RA" material), our approach is to incorporate an alcohol-soluble organic polymer as filler to an epoxy system that is more hydrophilic than the standard bisphenol-A type. Under these conditions, we have chosen a low viscosity epoxy with a flexible polyoxyalkylene chain such as DER 736 of Dow Chemical Co. to modify the conventional epoxy Epon 815 of Shell Chemical Co. The resin system is to be cured with a flexible polyoxypropyleneamine such as Jeffamine D230 of Jefferson Chemical. Among a number of polymeric materials considered and tried as the desired filler, poly(N-vinyl-2-pyrrolidone) (abbreviated as PVP) has been found to be compatible with the resin system and effective in promoting the alcohol sensitivity. This report is to introduce the development of the RA epoxy formulations with these materials.

2. EXPERIMENTAL

2.1 Materials

Materials used in this work are listed in table I. Their infrared spectra are enclosed in appendix A.

TABLE I. MATERIALS USED

Name	Supplier	Description
Epoxy resin Epon 815	Shell Chemical Co.	A conventional bisphenol-A type epoxy; epoxy equivalent weight (EEW), 175 to 195
Epoxy resin DER 736	Dow Chemical Co.	A low-viscosity epoxy with a flexible polyoxyalkylene chain; EEW, 175 to 205
Jeffamine D230	Jefferson Chemical	A flexible low-viscosity epoxy hardener, a polyoxypropyleneamine; primary amine content, 8.30 meq/g
Accelerator 298	Jefferson Chemical	Amines used with D230 as accelerator
PVP	GAF Corp.	Poly(N-vinyl-2-pyrrolidone), a water-soluble polymer, off-white powder; grades K15 and K30 average 10,000 and 40,000 mol wt, respectively
Hysol PC-17-M	Hysol Corp.	A conformal coating epoxy, bisphenol-A type epoxy cured with polyamide and others; toluene as solvent; conforming to MIL-I-46058C
Epoxy 70/30-DETA	HDL formulation	Formulated with Epon 815, polysulfide LP-3, and DETA in a weight ratio of 70/30/7, cured at 70°C for 2 to 3 hr after gelation; for potting and general use

2.2 Instruments

A Perkin-Elmer model 337 grating infrared spectrophotometer was used for identification and cure study. A DuPont thermal analyzer 990 was employed to investigate thermal properties. The analyzer provides three kinds of analysis: differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and thermomechanical analysis (TMA).

2.3 Procedure for the Pretreatment of PVP

The PVP samples of about 90 g each were weighed from a 25-lb drum, which had been kept sealed from unnecessary moisture exposure. Each sample was evenly spread in a Petri dish of 5.75 in. i.d. to form a powder layer about 0.5 in. deep and was dried for 3 hr at 70°C under vacuum (ca 3 Torr). The dried PVP was kept in a sealable container and used for all the experiments described in this report.

2.4 Testing of the Cured RA Materials

2.4.1 Gel Time and Peak Exotherm

The gel time and peak exotherm of the formulations were measured according to American Society for Testing and Materials (ASTM) D2471-71. A 50-ml beaker of 5.5-cm height and 4-cm diam was used to hold a 30-ml sample. Gel time was recorded with a Mol-Rez gel timer, while the exotherm was followed with a Honeywell 19 recorder. The thermocouple wires were inserted into a thin glass well, whose bottom end was positioned at the center of the epoxy mass in the beaker.

2.4.2 Tensile and Adhesion

The tensile test was run according to ASTM D638-71a using specimen type IV. Specimens were cast and machined to specifications. Adhesive tensile was determined per ASTM D2094-69 and D2095-69. Aluminum rods were used as the adherends for the test.

2.4.3 Volume Resistivity

For determining volume resistivity, ASTM D257-66 was followed. The cast disc specimens were brush painted on both sides with DuPont conductive silver paint No. 4817 to achieve satisfactory contact with electrodes. The specimens were conditioned at 50-percent relative humidity (RH) before resistance measurements, which were made with a model 260-A Q-meter of the Doonton Co. A dc potential of 500 V was applied for 1 min, during which time six readings were taken and afterwards averaged.

2.4.4 Water and Moisture Absorption

Water absorption was determined by the long-term immersion method according to ASTM D570-63. Moisture absorption was measured at room temperature and at both 52- and 93-percent RH. Cast specimens of 2-in. diam $\times$ 1/4-in. thickness were kept in desiccators, in which atmospheres of the chosen relative humidity were maintained with the saturated salt solutions recommended by ASTM E104-51.

3. RESULTS AND DISCUSSION

3.1 Pretreatment and Properties of PVP

3.1.1 Pretreatment

Several grades of PVP are available with average molecular weights varied from 360,000 to 10,000. For better compatibility with the basic resins, two grades of the lowest molecular weight, K30 and

K15, were chosen for the formulations. Efforts were made to determine the degree of sensitivity to moisture of the PVP, which is known to be hygroscopic, and its content of low molecular weight volatiles, because both would have pronounced effects on the mechanical and electrical properties of the proposed formulations.

Preliminary sublimation experiments under vacuum at 220°C showed that both K15 and K30 gave off water vapor, and that K15 also released some low molecular weight volatiles. In practice, a much lower temperature should be used for moisture removal. Therefore, a 70°C vacuum-drying process was evaluated. In a vacuum oven, batches of the PVP samples of about 90 g each were spread in Petri dishes of 5.75-in. i.d. to form PVP powder layers about 0.5 in. deep. Figure 1 shows the weight loss during the drying processes of both the samples taken from the drum containers as received and the samples that had been conditioned in an atmosphere of 52-percent RH for 72 hr. Evidently, K30 contained more moisture at the beginning and hence should be considered to be more hygroscopic than K15.

Since it is known that PVP retains moisture like hydrated water reported for various proteins,⁴ no exhaustive attempt was made to dry it. To obtain consistent results, all PVP used for the formulation development was dried for 3 hr at 70°C under vacuum, as described in the pretreatment procedure in section 2.3.

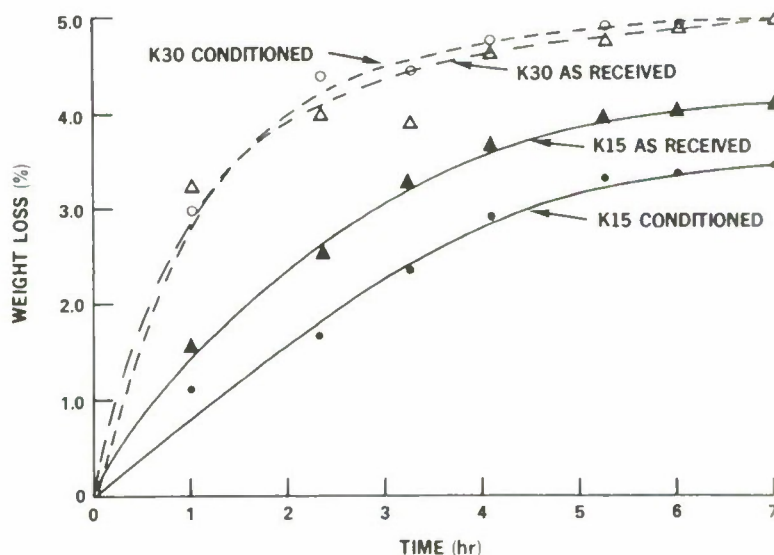


Figure 1. Weight loss of poly(N-vinyl-2-pyrrolidone) K15 and K30 at 70°C under vacuum.

⁴D. H. Lorenz, *N-Vinyl Amide Polymer*, *Encyclopedia of Polymer Science and Technology*, Vol. 14, Interscience Publishers, New York (1971), 239-251.

3.1.2 Moisture Absorption

To learn how fast PVP can pick up moisture from air, the pretreated samples in Petri dishes were exposed to the laboratory atmosphere whose relative humidity varied from 52 to 57 percent. Figure 2 shows that both K15 and K30 picked up moisture rapidly and that their moisture content reached 10 to 15 percent in 1 day. Relatively, K15 showed lower moisture affinity and picked up less than 1 percent of moisture in the first hour. Therefore, it is not difficult to handle K15 in air, if precautions are taken to ensure minimum air exposure.

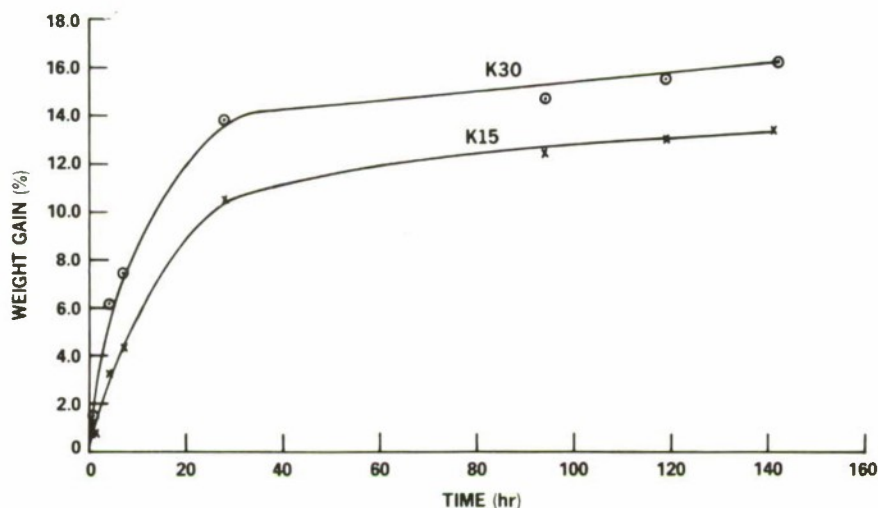


Figure 2. Moisture absorption from air by poly(N-vinyl-2-pyrrolidone) K15 and K30 at room temperature and 52 to 57 percent relative humidity.

3.1.3 Thermal Stability

The pretreated PVP was subjected to thermal analysis with a DuPont thermal analyzer. The changes of physical appearance were visually examined during heating with a Fisher-John melting-point apparatus. The data obtained are summarized in table II. Apparently, K30 is a little more stable than K15, which has lower molecular weight. The 2- to 3-percent weight loss before 70°C is probably due to moisture either residual or picked up during the preparation of the experiments (the sample size was about 10 mg). Some low molecular weight volatiles also could be lost in the course of heating. The data suggest that it is not advisable to expose the two materials above 100°C for any long duration, even though neither showed melting visually observable before 170°C.

TABLE II. THERMAL DATA OF PRETREATED POLY(N-VINYL-2-PYRROLIDONE)

Method ¹	K15	K30
TGA	Weight loss onset at 50°C, 2% total loss at 70°C, 5% total loss at 100°C and loss rate slowed down, 8% total loss at 190°C	Weight loss onset at 50°C, 3% total loss at 70°C, 8% total loss at 115°C and loss rate leveled off, 9% total loss at 190°C
DSC	Gradual endotherm onset at 38°C and peaked at 100°C, major endotherm onset at about 120°C, no exotherm before 200°C	Major endotherm onset at 40°C and peaked at 115°C, no exotherm before 200°C
Appearance	Shrinking after 120°C, melting slowly after 170°C	Shrinking after 170°C, softening after 200°C, turning brown at 210°C

¹The samples were heated from room temperature at a rate of 10°C/min for thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) and of about 4°C/min for the appearance observation.

3.2 Formulations

A blend of Epon 815 and DER 736 in a ratio of 70/30 by weight was chosen to make the epoxy resin system with balanced properties. The hardener Jeffamine D230 and accelerator 298 were used in stoichiometric amounts as suggested by the manufacturer. Filler PVP is not very soluble in DER 736 alone and tends to settle, but the resin blend can be filled with PVP up to 80 parts per 100 of resin (80 phr) without settling. Due to the low viscosity of both the resin blend and the hardener, it is possible to use these high levels of PVP filler and have compounds fluid enough for casting. Between the two grades of PVP, K15 is miscible readily with the resin blend at all levels, whereas K30 tends to float up gradually unless it is present in the higher concentrations. The final formulations⁵ developed in this work are shown below:

RA Formulations

<u>Ingredient</u>	<u>Part by wt</u>
Epoxy Epon 815	70.0
Epoxy DER 736	30.0
Jeffamine D230	26.5
Accelerator 298	5.3
Pretreated PVP, K15 or K30	0 to 80

Cure cycle: Gelling at room temperature plus 70°C for 3 hr.

⁵S. Yen Lee, U.S. Patent 3,929,717 (30 December 1975).

The designations of the RA formulations are illustrated by the following examples:

RA15-20	filled with K15, 20 phr
RA15-80	filled with K15, 80 phr
RA30-20	filled with K30, 20 phr

Grade K30 was initially used for all formulations, but was replaced with K15 when the advantages of K15 were well established. In the evaluation of the RA formulations, epoxy 70/30-DETA was used as the control. It is a flexible formulation developed earlier at the Harry Diamond Laboratories for potting and general use.

3.3 Curing Conditions

The gel time and peak exotherms at room temperature of the RA formulations were determined according to the ASTM method, using a sample volume of 30 ml (ca 21 g). The data in table III show that their gel times vary from 3 to 17 hr, depending on the level of PVP, whereas their peak exotherms are negligibly small.

TABLE III. GEL TIME AND PEAK EXOTHERM

Formulation ¹	Gel time (hr)	Peak exotherm	
		Temperature (°C)	Time (min)
RA30-0	17.1	28.0	10.5
RA30-20	14.5	28.5	16.0
RA30-80	2.9	26.0	7.0
Control	4.5	32.5	12.5

¹Sample size: 30 ml.

The curing rate was studied at 70°C. This temperature was chosen because it is the usual temperature limit that many electronic components can tolerate. The infrared spectroscopic data summarized in table IV indicate that PVP tends to slow down curing. The DSC data in table V reveal that curing can be essentially completed in 3 hr at 70°C. Standing at room temperature for 3 days or heating at 120°C for 1 hr also can effect a similar degree of cure according to some other DSC runs. For consistent practice, the standard cure cycle adopted in this work is a 3-hr cure at 70°C after gellation at room temperature.

TABLE IV. INFRARED SPECTRAL STUDY OF CURING AT 70°C

Formulation	Epoxied absorption at 910 cm^{-1}	Hydroxyl absorption
RA15-0	Essentially disappeared by 2 hr	Intensity increased accordingly
RA15-20	Intensity decreased sharply in first 2 hr, then stabilized	Intensity increased accordingly
RA15-40	Intensity decreased grad- ually in first 4 hr, then stabilized	Intensity increased accordingly

TABLE V. DIFFERENTIAL SCANNING CALORIMETRY STUDY OF CURING AT 70°C (HEATING RATE: 5°C/min)

Formulation	Cure time (hr)	Exotherm peak near 100°C (area units/mg)	Apparent cure (%)
RA15-20	0	12.6	0
	1	3.2	71
	2	1.1	83
	3	0.8	94
RA15-40	0	12.6	0
	0.5	8.9	29
	1	4.3	66
	2	2.2	83
	3	0.6	95
	4	0.6	95

3.4 Alcohol Sensitivity

Alcohol sensitivity was evaluated by immersing the RA-formulation specimens at room temperature in the alcohol selected. The weights of the specimens were periodically checked, and the physical changes were noted. The specimens were cast discs of 2-in. diam $\times$ 1/4-in. thickness. Before each weighing, the surface solvent was absorbed and wiped off with dry paper tissues. Table VI records the sensitivity to methyl alcohol, and figure 3 shows the pictures of specimens both before and after immersion. The effect of PVP is distinctly demonstrated. Disintegration took place in 2 hr for RA15-20, which has the lowest level of PVP (20 phr). Formulation RA15-0, which has no PVP, gave no sign of disintegration after 48 hr of soaking. However, its alcohol sensitivity was shown by its rapid alcohol absorption and by its being readily crushable by finger pressure after immersion. In contrast, the control sample was not affected at all.

TABLE VI. SENSITIVITY TO METHYL ALCOHOL

Immersion time (hr)	Formulation									
	Control		RA15-0		RA15-20		RA15-40		RA15-80	
	W ¹ (%)	P ²	W (%)	P	W (%)	P	W (%)	P	W (%)	P
2	1.1	0	16.4	I	13.5	III	15.1	III	33.8	IV
4	1.8	0	25.2	II		IV		IV		
6	2.3	0		II						
24	4.8	0		II						
48	-			II						
96	13.6	0								

¹W = net weight gain in percentage (solvent absorption minus poly(N-vinyl-2-pyrrolidone) dissolution, which increased with time).

²P = physical changes, as coded:

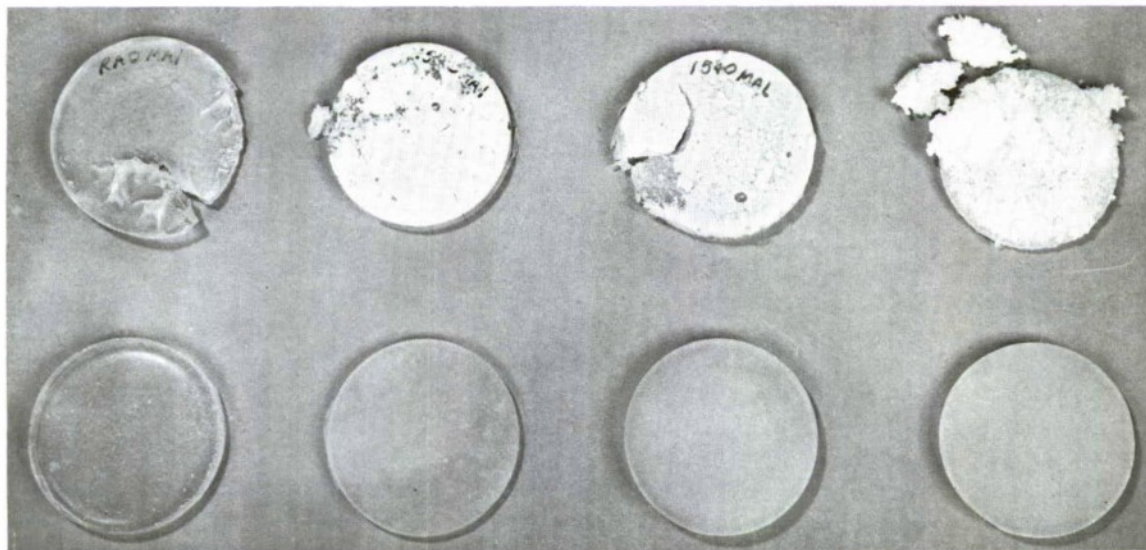
0 = no apparent change

I = warped, chippable with fingernails

II = chippable readily, crushable to powder by finger pressure

III = disintegration started

IV = disintegration



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Figure 3. Immersion in methanol of alcohol-sensitive repairable epoxies: (top) immersed; compounds and immersion time (hr) from left to right: RA15-0, 5; RA15-20, 4; RA15-40, 3; RA15-80, 2; (bottom) corresponding compounds not immersed.

A similar sensitivity trend was observed with isopropyl alcohol, but the degree of sensitivity is much lower, as described in table VII. Propyl alcohol and ethylene glycol were found to be similar to isopropyl alcohol. Obviously, methyl alcohol is the choice for depotting the RA materials.

TABLE VII. SENSITIVITY TO ISOPROPYL ALCOHOL

Soaking time (hr)	Formulation							
	Control		RA15-0		RA15-20		RA15-40	
	W ¹ (%)	P ²	W (%)	P	W (%)	P	W (%)	P
2	0		2.4	I		I	2.5	II
4	0		4.2	I	1.5	I	3.7	II
6	0.5	0	5.2	I	1.5	I	4.7	III
24	0		10.1	I	2.9	I		IV
48	0.8	0		I	4.8	II		

¹W = net weight gain in percentage (solvent absorption minus poly(N-vinyl-2-pyrrolidone) dissolution).

²P = physical changes as coded:

0 = no apparent change

I = some softening, chippable with finger, but hard

II = chippable with fingers

III = disintegration started

IV = disintegration

3.5 Thermal, Electrical, and Mechanical Properties

The results of thermal analysis of the cured RA materials are summarized in table VIII. The materials all showed earlier exotherms and a little higher weight loss than the control. The higher weight loss is apparently due to the high moisture affinity of the formulations. The isothermal TGA of RA15-20 at 70°C showed no change in 7 hr after the initial 1.7 percent of weight loss, which was probably moisture. The PVP filler appears to slightly improve the thermal stability of the cured materials. The fact that none of the DSC thermograms showed thermal changes below 100°C certainly indicates that they are stable at least up to 100°C. For long-term thermal aging effects, a comprehensive study should be conducted.

The basic electrical and mechanical properties of the cured materials at room temperature are illustrated by the volume resistivity, tensile and elongation, and adhesion tensile data as recorded in tables IX and X. The RA materials appear to have equal or slightly higher volume resistivity than the control. Their tensile strengths and adhesion tensile are distinctly superior. The PVP filler tends to

decrease elongation or to increase rigidity. However, the 5- to 12-percent range of elongation is a positive indication of their flexibility at room temperature. Their low-temperature properties and the environmental effects on electrical properties, of course, remain to be investigated.

TABLE VIII. THERMAL ANALYSIS OF CURED ALCOHOL-SENSITIVE REPAIRABLE EPOXY FORMULATIONS

Formulation ¹	Differential scanning calorimetry (DSC)	Thermogravimetric analysis (TGA)
RA15-0	Gradual exo ² from 140°C, no endo ² peak before 196°C	Wt loss onset at 65°C, 0.5% total loss at 70°C, 2.8% total loss at 190°C
RA15-20	Gradual exo from 100°C, no endo peak before 196°C	Wt loss onset at 50°C, 0.5% total loss at 70°C, 4% total loss at 190°C
RA15-40	Gradual exo from 170°C, no endo peak before 196°C	Wt loss onset at 66°C, 0.3% total loss at 70°C, 6.8% total loss at 190°C
RA15-80	Gradual exo from 150°C, no endo peak before 196°C	Wt loss onset at 40°C, 1.2% total loss at 70°C, 5.1% total loss at 190°C
RA15-20		Isothermal at 70°C: 1.7% wt loss in first 37 min, no more loss in next 7 hr
Control	Exo onset at 200°C, small and gradual endo onset at 90°C	Wt loss onset at 50°C, 0.3% total loss at 70°C, 1.2% total loss at 190°C

¹The samples in the analyses were all heated at a rate of 10°C/min, except RA15-0 for DSC and RA15-20 for TGA, which were run at a rate of 5°C/min.

²Exo: exotherm; endo: endotherm.

TABLE IX. VOLUME RESISTIVITY OF CURED FORMULATIONS (PER ASTM D257-66, 50-PERCENT RELATIVE HUMIDITY)

Formulation	Volume resistivity (ohm-cm)
RA15-0	2.6×10^{13}
RA15-20	5.3×10^{12}
RA15-80	3.0×10^{13}
RA30-20	8.2×10^{12}
Control	8.7×10^{12}

TABLE X. TENSILE AND ADHESION OF CURED FORMULATIONS

Formulation	Tensile ¹		Elongation at break (%)	Adhesion tensile ¹ (psi)	Adhesion failure	
	At yield (psi)	At break (psi)			Cohesive (%)	Adhesive (%)
RA15-0	4,900	4,000	12	7,100	35	63
RA15-20	6,600	4,000	8	6,200	27	73
RA15-40	3,430	3,370	5	-	-	-
RA15-80	-	-	-	3,200	24	76
Control	2,380	2,480	44	3,700	-	-

¹Crosshead speed for tensile, 2 in./min; for adhesion tensile, 0.05 in./min.

3.6 Water and Moisture Absorption and Its Reduction with a Coating

The expected hydrophilic property of the RA formulations was shown by the standard water-immersion test. The weight gains due to water absorption described in table XI were directly proportional to the level of PVP, and PVP exudation took place in 2 to 6 days when its level was 40 phr or more. Without the PVP filler, RA15-0 appears to be only slightly more hydrophilic than the control.

To overcome the hydrophilic propensity of the RA formulations, the specimens were spray coated with a standard bisphenol A-type regular epoxy coating. The thin coating would protect the RA materials from excessive water absorption, yet could be readily removed by some simple mechanical means before depotting with an alcohol. In effect, the water absorption of all the specimens with a coating, except RA15-80, was cut down to the level of the control, as shown in table XI. No attempt was made to determine the water absorption over extended periods, since the more relevant test should be the moisture absorption from air.

TABLE XI. WATER ABSORPTION (ASTM D570-63, BY PERCENTAGE WEIGHT GAIN)

Immersion time (day)	Absorption								
	Formulation RA15-				Formulation coated ^a RA15-				Control
	0	20	40	80	0	20	40	80	
1	1.0	2.6	3.9	21.3 _b	0.2	0.4	0.6	0.7	0.4
2	-	3.8	5.6	32.4 _b	0.4	0.6	0.7	1.0	0.7
3	1.7	-	-	-	0.6	0.7	0.6	1.9	0.5
4	2.1	4.7	-	-	0.7	0.7	1.0	2.6	-
5	2.4	5.3	-	-	0.9	-	-	-	-
6	2.5	-	20.5 _b	-	-	-	-	-	1.1
7	2.8	-	-	-	-	-	-	-	1.1

^aThe specimens were spray coated with Hysol PC-17M and cured at 70°C for 1.5 hr. The coating thickness was 0.002 to 0.006 in.

^bExudation of poly(N-vinyl-2-pyrrolidone) was observed.

The moisture absorption at ambient temperature and 93 percent RH is recorded in table XII. A similar trend of the PVP effect is apparent. Formulation RA15-20 lasted only a little over 1 month before serious degradation was noted. Without PVP, RA15-0 again showed higher moisture absorption than the control, but retained its rigidity as the control did after 4 months. The high tensile of RA15-0 should be a factor that contributes to the maintenance of its rigidity.

TABLE XII. MOISTURE ABSORPTION AND HARDNESS CHANGES AT ROOM TEMPERATURE AND 93 PERCENT RELATIVE HUMIDITY

Time (day)	Formulation									
	RA15-0		RA15-20		RA15-40		RA15-80		Control	
	Wt ^a (%)	HD ^b	Wt (%)	HD	Wt (%)	HD	Wt (%)	HD	Wt (%)	HD
0	-	77	-	81	-	79	-	70	-	68
16	1.5	63	4.1	51	14.7	-- ^c	14.4	-- ^c	-	-
28	2.0	54	4.9	45	19.9 ^c		16.7 ^c		-	-
42	2.5	54	5.7	45					0.7	-
56	2.6	50	7.6 ^d	38 ^d					1.0	67
70	3.4	50							1.2	68
84	4.1	46							1.4	67
98	4.5	41							1.5	69
120	4.8	40							1.6	69

^aWeight gain.

^bHardness, Shore D.

^cBendable and sticky after 16 days, much worse after 28 days.

^dVery sticky, not bendable.

With a regular epoxy coating, the moisture absorption of the PVP filled specimens was tremendously slowed down (table XIII). Formulation RA15-40 remained good in appearance for 3 months, and RA15-20 would have lasted longer if the coating had not been defective. Nevertheless, the coating under such high humidity only slowed down, but did not prevent, the moisture penetration. The moisture absorbed tended to cause swelling beneath the coating, crack the coating at the weak or defective spots, and cause peeling of the coating. Even when the coating was perfect, RA15-40 became cheesy eventually. Therefore, the life of the coated RA15-20, the one with the lowest level of PVP in the experiment, would not be expected to be much over 2 months in terms of tolerable moisture absorption if it were exposed continuously to a high humidity.

It is noteworthy that the moisture absorption is reversible. In other words, the moisture absorbed is not all permanently retained. The uncoated RA15-40 and RA15-80 specimens, after the moisture absorption experiment at 93-percent RH, were left exposed to the laboratory atmosphere (about 50-percent RH). Their physical appearance recovered gradually, and they became as hard as they originally had been. The retained moisture decreased to about 5 percent after

TABLE XIII. MOISTURE ABSORPTION (WEIGHT GAIN) AT ROOM TEMPERATURE AND 93-PERCENT RELATIVE HUMIDITY OF SPECIMENS COATED WITH REGULAR EPOXY^a

Time (day)	Formulation			
	RA15-0 (%)	RA15-20 (%)	RA15-40 (%)	RA15-80 (%)
16	1.1	2.2	1.8	4.6
28	1.7	3.6	3.0	6.1
42	1.9	4.3	4.2	6.5
56	2.5	5.0	5.0	9.1
70	2.7	6.0	6.0	8.7
84	2.9	-	6.9	12.3
98	2.9	6.2 ^b	7.9	14.3
120	3.4	-	4.2 ^c	17.0 ^c
134	3.4	-	~11.2	-

^aSpray coated with epoxy Hysol PC-17M, 0.002 to 0.005 in. thick.

^bCoating wrinkled on one side after 42 days and blistered with some soft and sticky spots after 108 days.

^cSome tiny cracks of the coating on the edge found after 98 days; some peeling after 120 days, except one RA15-40 specimen, which had intact coating but became cheesy after 134 days.

3 months, from over 20 percent right after the 93-percent RH experiment. Further drying at 70°C under vacuum lowered the retained moisture to about 3 percent.

Being inherently hygroscopic, the RA materials are not designed to be used under conditions where a continuous exposure to high humidity is expected. It is, therefore, more practical to examine the moisture absorption in a somewhat normal atmosphere. Also, it is unnecessary to have a PVP level higher than 40 phr, which makes it too hygroscopic for the slight gain in alcohol sensitivity. Table XIV records the moisture absorption and hardness data collected at room temperature and 52-percent RH. All the materials, including the control, showed some moisture absorption, but the absorption appeared to level off after 5 months, as illustrated in figure 4, and the level off persisted after 10 months. Formulations RA15-20 and RA15-40 behaved practically the same and equilibrated with the atmosphere at about 2.5-percent moisture absorption. The moisture decreased their hardness slightly. Formulation RA15-0 had slightly higher absorption than the control and kept about 1-percent moisture gain after 5 months. The leveling off of moisture absorption by RA15-40 at 2.5 percent appears to fall in line with Miller and Hamm's report⁶ that every mole of PVP monomer unit tends to keep 1/2 mole of hydrated water. According to calculation, RA15-40 and RA15-20 could retain respectively 1.9- and 1.1-percent moisture due to PVP. Since RA15-0 absorbed 1-percent moisture and there should be

⁶L. E. Miller and F. A. Hamm, *J. Phys. Chem.*, 57 (1953) 110.

some moisture retained in the material at start, the 2.5 percent total seems to be reasonable. For reliable results, the experiment is being continued to observe their long-term behavior.

In summary, the results of the water and moisture absorption experiments clearly indicate that it is impractical to use the RA materials continuously in an atmosphere of high humidity. In consideration of its positive effect on hygroscopicity, the PVP level

TABLE XIV. MOISTURE ABSORPTION AND HARDNESS CHANGES AT ROOM TEMPERATURE AND 52-PERCENT RELATIVE HUMIDITY

Time (day)	Formulation							
	RA15-0		RA15-20		RA15-40		Control	
	Wt ¹ (%)	HD ²	Wt (%)	HD	Wt (%)	HD	Wt (%)	HD
0	-	70	-	82	-	80	-	67
14	0.2	71	1.1	67	1.1	66	0.1	68
28	0.2	68	1.2	64	1.2	64	0.6	69
42	0.5	69	1.5	64	1.6	65	0.4	66
56	0.2	68	1.5	63	1.5	63	0.5	68
70	0.5	70	1.8	65	1.7	65	0.4	67
84	0.8	66	2.2	62	2.0	62	0.4	68
98	0.7	67	2.0	63	1.9	64	0.6	67
120	1.0	67	2.4	65	2.3	65	0.6	69
134	0.9	70	2.3	65	2.2	66	0.8	69
148	1.0	67	2.3	63	2.4	63	-	-
198	1.1	-	2.6	-	2.4	-	0.8	71
220	1.1	72	2.6	66	2.5	67	0.8	68

¹Weight gain.

²Hardness, Shore D.

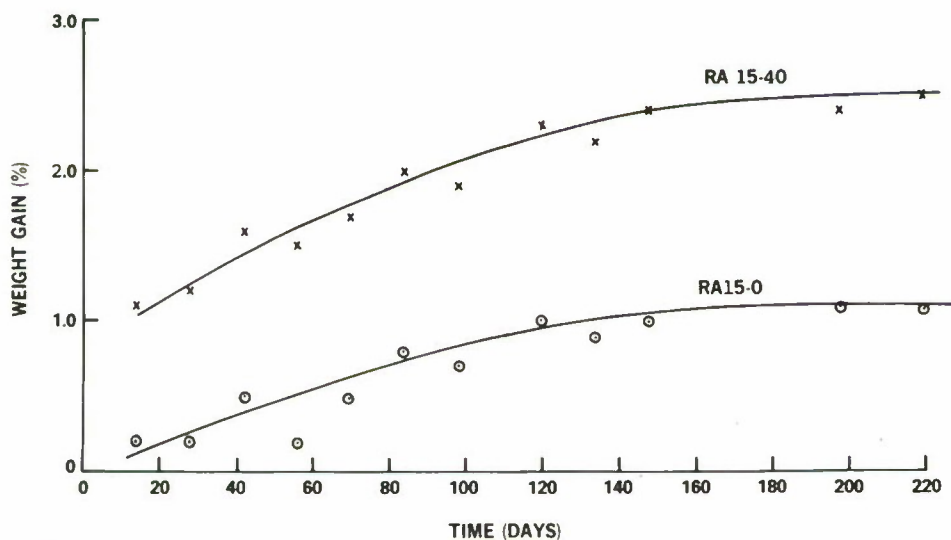


Figure 4. Moisture absorption at room temperature and 52-percent relative humidity.

should not be more than 40 phr. A level of 20 phr would be more desirable if occasional brief exposures (not over 1 month at one time) to high humidity are anticipated. The moisture absorption is reversible. To slow down the moisture absorption, a thin coating of regular epoxy can be applied, which can be removed readily by some simple mechanical method before depotting with methanol. At 52-percent RH, some moisture absorption was observed. The weight gain leveled at about 2.5 percent after 5 months for both RA15-20 and RA15-40.

3.7 Future Actions

This preliminary work is to introduce the development of the RA formulations and demonstrate their applicability in terms of some of their basic properties. Further actions will be necessary to evaluate the following properties before they can be used with confidence for permanent potting:

- a. Mechanical and other properties at both military storage temperature limits
- b. Thermal shock resistance
- c. Environmental effects on electrical properties
- d. Thermal and oxidative aging.

4. CONCLUSIONS

Seven conclusions can be drawn from the work:

- a. The RA formulations have been demonstrated to be sufficiently alcohol sensitive to meet the requirement for a repairable potting material. Methanol is the choice for depotting.
- b. Adding PVP, preferably K15, can tremendously enhance the alcohol sensitivity. Without PVP as filler, RA15-0 can be softened by methanol, but does not disintegrate.
- c. The RA materials are thermally stable at least up to 100°C. They showed stronger mechanical and adhesion strength than the control and gave comparable electrical resistivity when measured under standard laboratory conditions.
- d. Hygroscopicity is the shortcoming of the RA formulations. Therefore, it is impractical to use them continuously in high humidity.
- e. The PVP level should not be more than 40 phr. A level of 20 phr or less would be more advisable if occasional brief exposures (not over 1 month at one time) to high humidity were expected. Without

PVP as filler, RA15-0 showed only slightly higher moisture absorption than the control under all conditions. A high level of PVP up to 80 phr should be used only for temporary potting and for quick depotting later.

f. The moisture absorption is reversible. To slow down the moisture absorption, a regular epoxy thin coating can be applied, which can be readily removed by some simple mechanical means before depotting with methanol.

g. At room temperature and 52-percent RH, the moisture absorption of both RA15-20 and RA15-40 leveled off after 5 months at about 2.5-percent weight gain.

ACKNOWLEDGEMENT

We wish to thank S. Clark, Jr., and J. Warwick for the measurements of electrical resistivity and mechanical strength.

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APPENDIX A.--INFRARED SPECTRA OF MATERIALS USED

Figures A-1 to A-6 show the infrared spectra of the materials used to formulate the alcohol-sensitive epoxies.

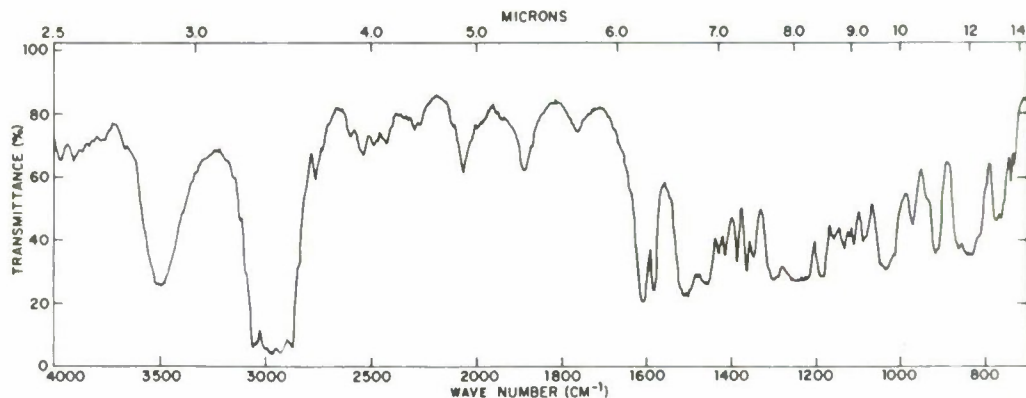


Figure A-1. Epoxy Epon 815.

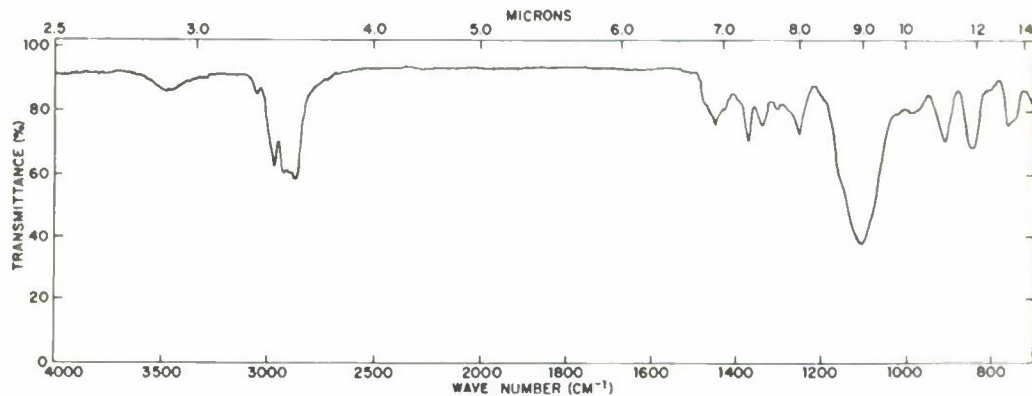


Figure A-2. Epoxy DER 736.

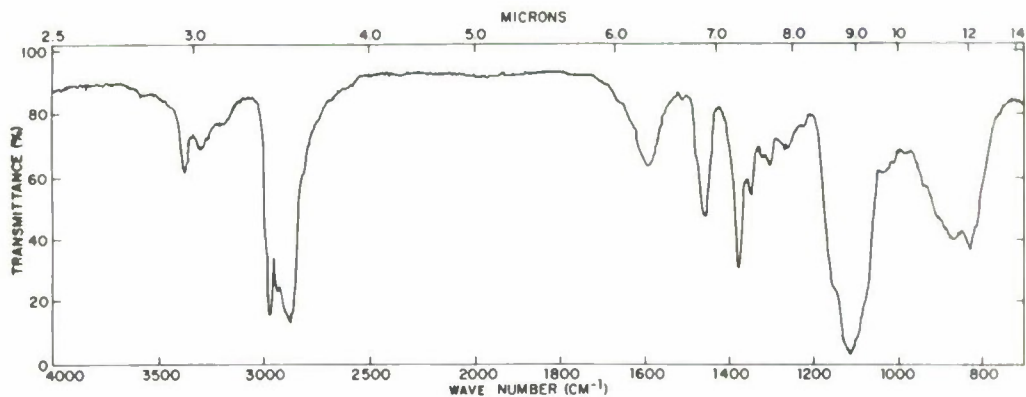


Figure A-3. Hardener Jeffamine D230.

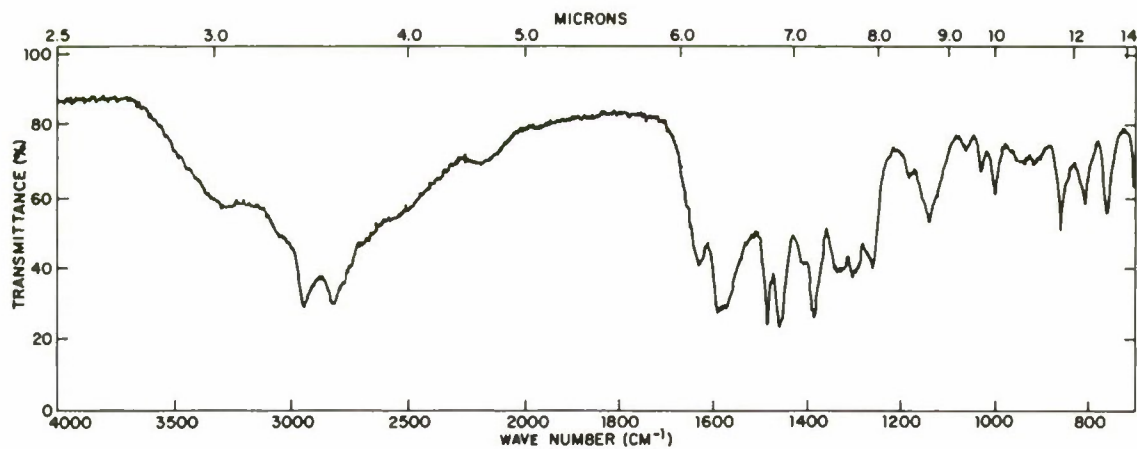


Figure A-4. Jefferson's accelerator 298.

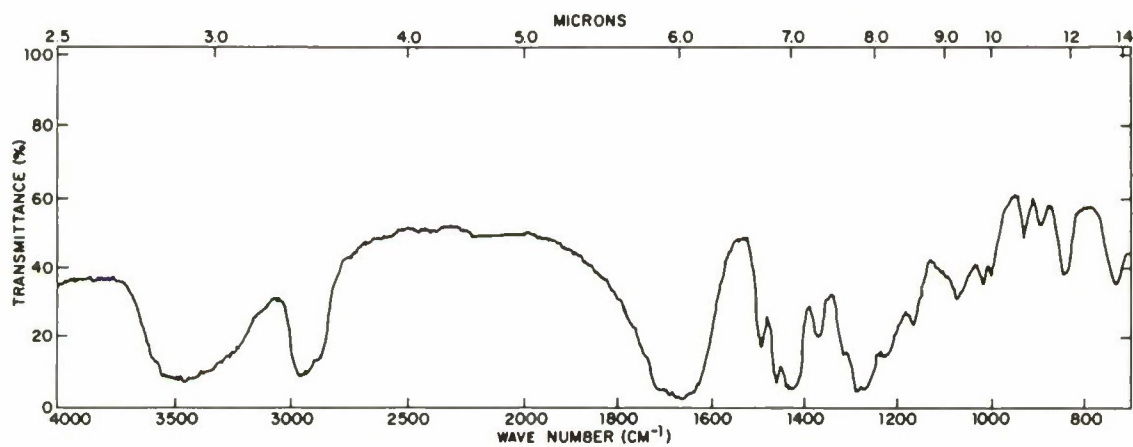


Figure A-5. Poly(N-vinyl-2-pyrrolidone) K15.

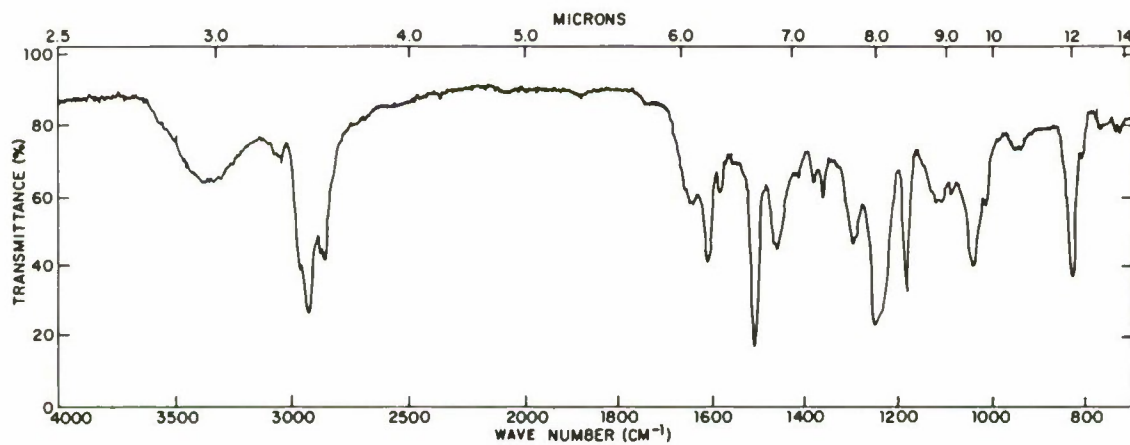


Figure A-6. Epoxy PC-17M cured.

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