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# SPECIFIC PERMEABILITY OF EPOXY RESIN SYSTEMS

by

James L. Parham

14 June 1971



U.S. ARMY MISSILE COMMAND
Redstone Arsenal, Alabama

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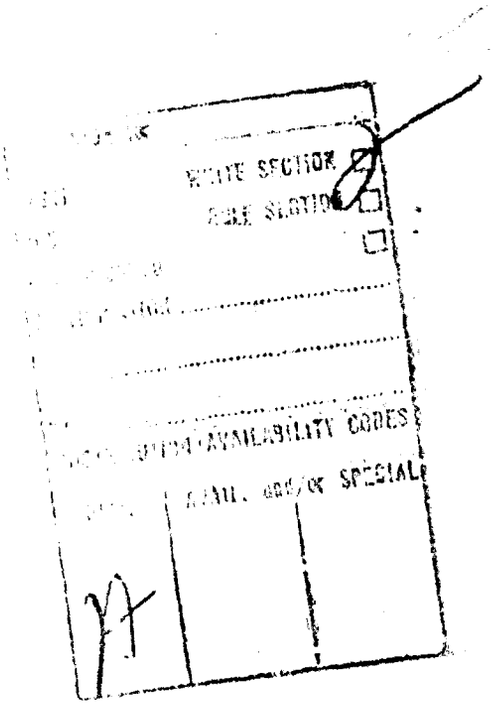

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13. ABSTRACT

Several types of coatings and filler materials were evaluated for their effectiveness in reducing moisture permeability of epoxy resins. Only the metallic coatings gave significant reductions. The specific permeability of a number of epoxy resin systems is given at room temperature and 140°F. Data is presented on the effects of post cure, curing agent concentration, and specimen thickness on specific permeability.

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Several types of coatings and filler materials were evaluated for their effectiveness in reducing moisture permeability of epoxy resins. Only the metallic coatings gave significant reductions. The specific permeability of a number of epoxy resin systems is given at room temperature and 140°F. Data is presented on the effects of post cure, curing agent concentration, and specimen thickness on specific permeability.

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## 1. INTRODUCTION:

It has been well established that fiberglass composites are highly susceptible to environmental degradation. In fact, severe degradation has been observed in composites exposed to high relative humidity conditions at moderate temperatures. Many observers believe this degradation is caused by entrance of moisture and subsequent corrosion of the reinforcement and degradation of the glass-resin interfacial bond. This moisture may enter through cracks or pinholes in the resin and diffuse through the resin and penetrate the interface between resin and glass.

Various techniques have been tried in efforts to inhibit this degradation from moisture. These include the utilization of glass coupling agents to lessen the bonds' susceptibility to degradation, the selection of low-permeability binder systems and fillers, and the use of coatings as barrier materials to prevent entrance of moisture into the composite. Unfortunately, no detailed study has been made of the effectiveness of many of these processes and treatments.

In the study reported here, an attempt was made to measure the effectiveness of several types of barrier materials and to study several variables affecting moisture transmission through the epoxy resin. These include curing agent concentration, post cure, and temperature.

## 2. EXPERIMENTAL METHODS:

### a. Resin Systems

The epoxy resin used in this study was a standard commercial resin composed of a diglycidyl ether of bisphenol A of molecular weight approximately 380. The curing agents used in these tests were representative of several different types. They are described in Table I.

### b. Test Methods

In this study, moisture transmission was measured by the rate of weight loss from a Payne peremability cup (Figure 1). This cup is a small, hemispherical cup over which a diaphragm of the test material is tightly clamped. Water is placed in the cup and the test specimen clamped and sealed on the cup. The cup is weighed and placed in a desiccator. Subsequent weighings determine weight loss, reflecting moisture transmission through the resin.

In order to compare results from specimens of different thicknesses, all raw data was reduced to transmission of a one-square-centimeter by one-millimeter-thick sample in a 24-hour period. Data in this form is called specific permeability and is expressed in milligrams of water loss per square centimeter of exposed area per millimeter of specimen thickness per 24 hours ($Mg/Cm^2/MM/24$ hrs).

The test specimens, except where intentionally varied, averaged about 0.010 inch thick with a range of 0.007 to 0.015 inch. Such variations were caused by different resin viscosities and cure rates.

Preliminary tests indicated that the daily rate of moisture transmission by the specimens varied considerably. This is believed to be caused by several factors. For example, changes in atmospheric pressure and laboratory temperature fluctuations probably caused most of the inconsistencies. Other influences include the minor variations in resin composition and their post cure. To lessen the impact of these variables, measurements of moisture transmission were carried out over a two- or three-week period to average out daily variations. A control was also included with each set of tests.

c. Formation of Metallic Coating

The metallic coatings on the resin specimens were applied in three ways; vapor deposition, electroless plating, and electroplating.

In the first method, as recommended for metallized coatings, a baking varnish base was first applied to the resin specimens and cured. The varnished specimens were then placed in a vacuum metallizing chamber and the appropriate metal vaporized to form the coating on the specimens. A thin topcoat of the varnish was then applied to the thin metal coating.

For electroless plating, the resin specimens were first mechanically roughened with sandpaper. The specimens were then sensitized in solutions of stannous chloride and palladium chloride. Immediately after sensitizing, the specimens were transferred to an electroless plating bath where the plating proceeded spontaneously. Specimens were removed from the bath after the desired metal thickness was obtained.

For electroplating, a thin electroless copper flash was first applied to the specimens. Plating of the appropriate metal then proceeded according to standard electroplating methods.

## 3. DISCUSSION OF RESULTS:

### a. Effect of Various Curing Agents on Specific Permeability

As Table II shows, the type of curing agent used has an important effect on the specific permeability of the resin. The aromatic types had relatively low transmission rates, the anhydrides had high rates, and the aliphatic types varied from high to low.

Unfortunately, no obviously direct relationship can be shown between specific premeability at room temperature and the environmental degradation rates of composites composed of these same resin systems. Degradation rates of these composites are given in references 1 and 2. The aromatic polyamines, a popular type of curing agent for resins used in composites, exhibited low specific permeability and were relatively resistant to environmental degradation. The aliphatic polyamines and polyamides, on the other hand. varied from high to low specific permeability but are all highly susceptible to degradation.

It can also be seen from the table that temperature has a distinct effect on specific permeability. At 140°F, the specific permeabilities of the resins were 10 to 20 times the permeability at room temperature. This may be one cause of the large increase in moisture-induced degradation of composites as the temperature is raised above room temperature. In fact, at the higher temperature, there is some reordering of the position of some of the resins in the table, which more closely correspond to the relative degradation rates of the composites. However, there are still too many variations between the two to declare a definite relationship.

Although the data is inconclusive, it is almost certain that moisture permeability plays an important role in composite degradation. Without permeability in some form or other there could be no moisture degradation of the interface or the reinforcement. The problem is to determine if the small differences in resin permeability account for the differences in rates of degradation of the composites. The data indicates a possible relation between the two, but cannot be considered firm.

The results of the study by R. F. Register of du Pont should be noted here (reference 3). He found a direct relationship between water permeation of the laminate at various temperatures and the laminate's retention of flexural strength. The decrease in flexural strength depended upon the amount of water passing through the laminate, and was independent of the time of exposure.

b. Effect of Curing Agent Concentration on Specific Permeability

Curing agent variations apparently can have a significant effect on specific permeability (Figure 2). The effects were different, however, for the two systems used. The A cured specimens showed a continuing upward trend in moisture transmission as the amount of curing agent was increased. The MDA cured specimens, on the other hand, showed a maximum at the 100 percent level. This corresponds to the stoichiometric amount of curing agent and resin.

The A curing agent was an aliphatic polyamine used in a concentration of 6 Phr. The MDA curing agent, however, is used in a concentration of 30 Phr. It can be seen, therefore, that although the percent variations in amounts of curing agent were much higher with the A cured system, the actual amount of variation was nearly the same in both cases.

From the limited amount of data available, the only conclusion that can be drawn is that specific permeability can be affected by curing agent concentration.

c. Effect of Fillers and Barrier Materials on Specific Permeability

Table III shows that inorganic fillers in small quantities have very little effect on the specific permeability of the resin. Fiberglass cloth reinforcement appeared to reduce specific permeability somewhat, but this result was probably colored by a reduction in the effective exposure area of the specimen. Paper reinforcement increased the specific permeability considerably.

The metallic coatings were partially effective in reducing specific permeability. Very thin plates, such as the vapor-deposited metal and the flash coats were only marginally effective. The thicker coats, up to a mil thickness, reduced the specific permeability to very low levels. However, moisture transmission was not completely stopped in any specimens.

d. Effect of Sample Thickness on Specific Permeability

Figure III indicates that variations in specimen thickness have only minor effects on specific permeability. There was a small increase in specific permeability with increasing thickness in both systems, however. It should be noted that although thickness does not severely affect specific permeability, it does affect, in inverse ratio, water vapor transmission rates.

e. Effect of Post Cure on Specific Permeability

The effect of post cure on specific permeability apparently depends upon the particular system (Figures 4 and 5). There was a small decrease in specific permeability with the MDA cured system during extended post cure. There was a significant increase, however, with the A cured system and the anhydride cured systems. The significance of these differences is unknown.

4. CONCLUSIONS:

a. The type of curing agent significantly affects the specific permeability of epoxy resin systems.

b. The anhydride systems were relatively high in specific permeability and the aromatic polyamines were low. The aliphatic polyamines and polyamides varied from high to low.

c. Higher temperatures increased specific permeability drastically.

d. The data indicates a possible relationship between the moisture degradation of composites and the specific permeability of the resins.

e. Small amounts of filler materials do not significantly reduce specific permeability of the resin system.

f. Glass reinforcement does appear to reduce specific permeability, probably by decreasing the effective exposure area.

g. Metallic coatings can reduce specific permeability to near zero, depending upon type and thickness.

h. Specimen thickness has only minor effects on specific permeability.

i. Post cure and curing agent concentration can significantly affect specific permeability.

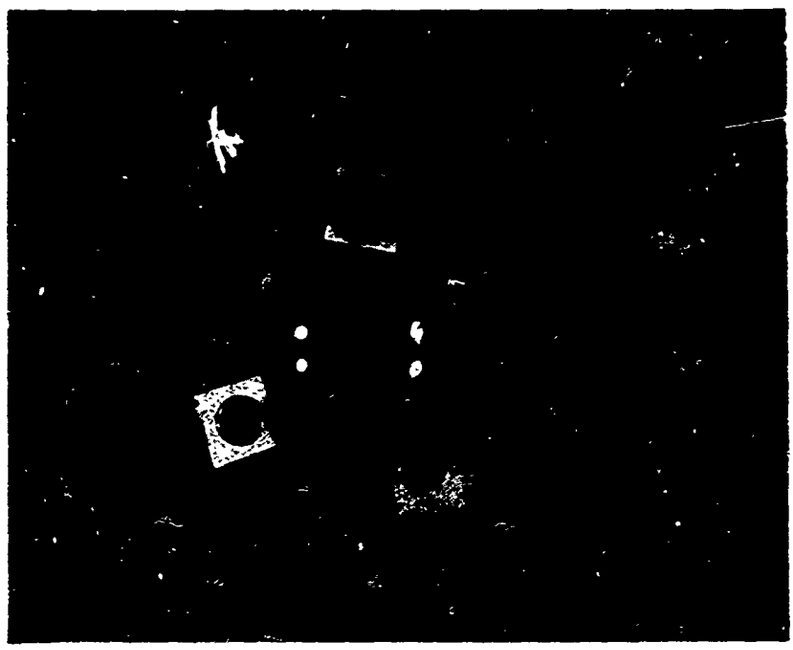

Figure 1. Payne permeability cup.

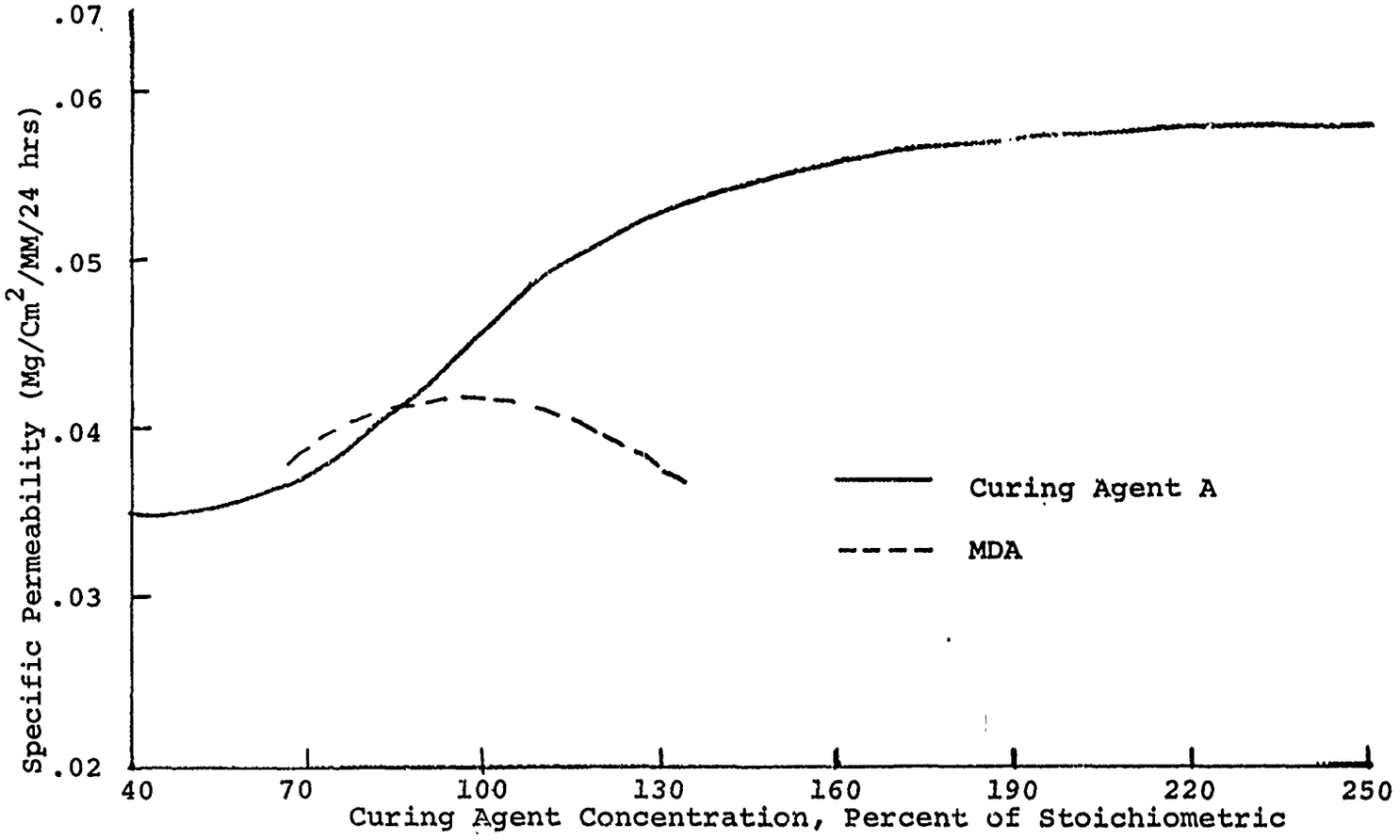


Figure 2. Specific Permeability Versus Curing Agent Concentration

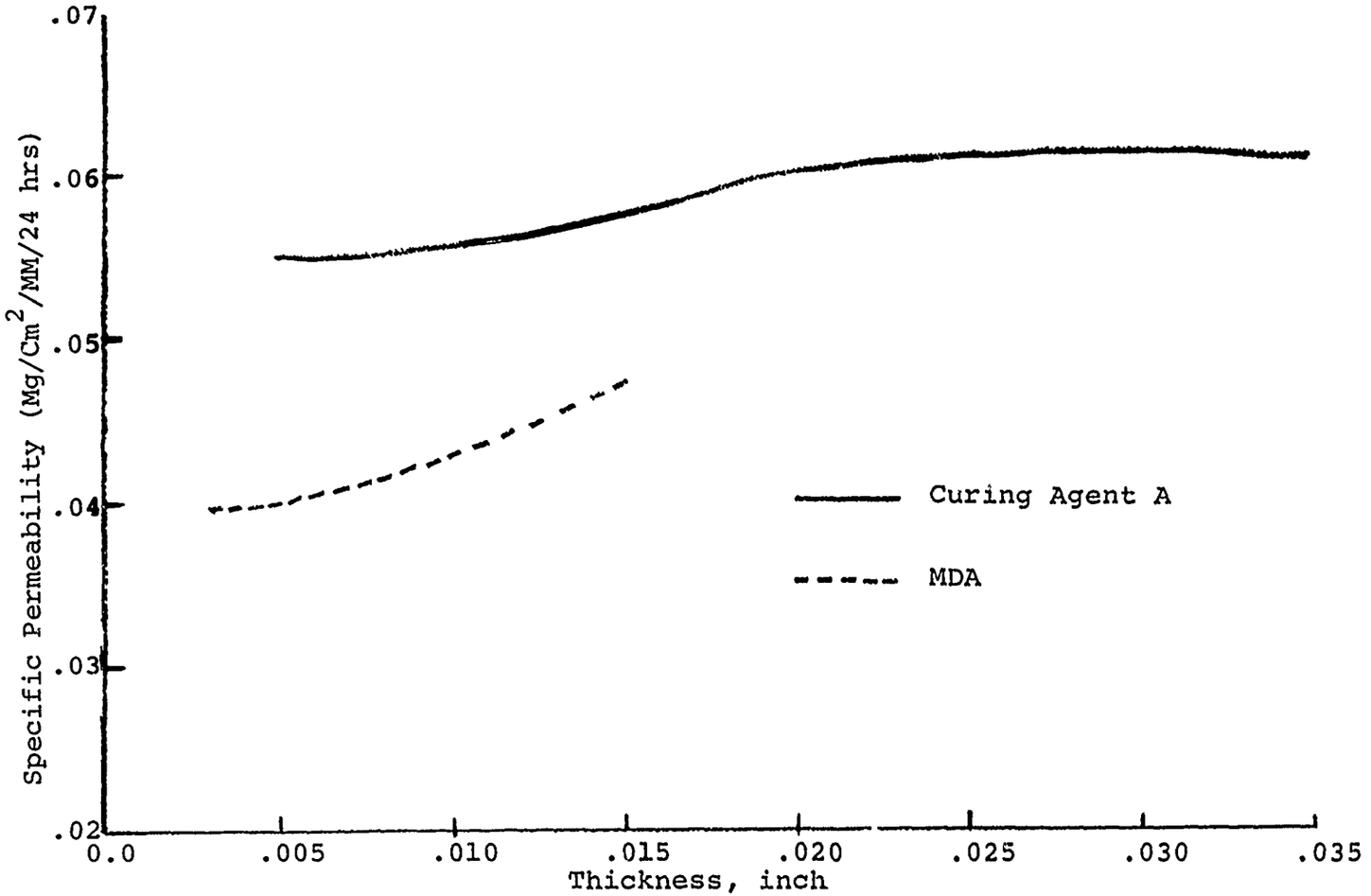


Figure 3. Specific Permeability Versus Thickness

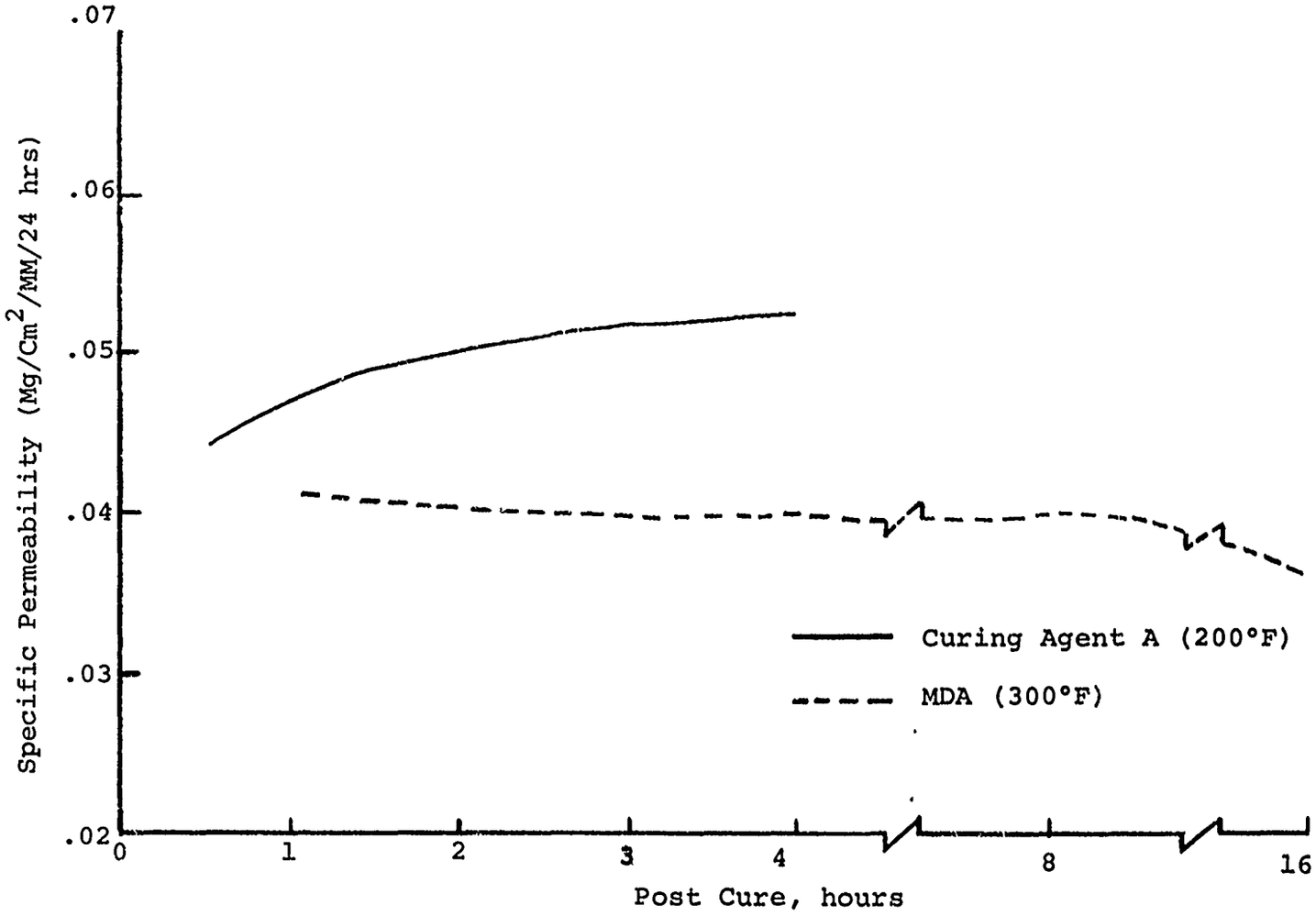


Figure 4. Specific Permeability Versus Post Cure

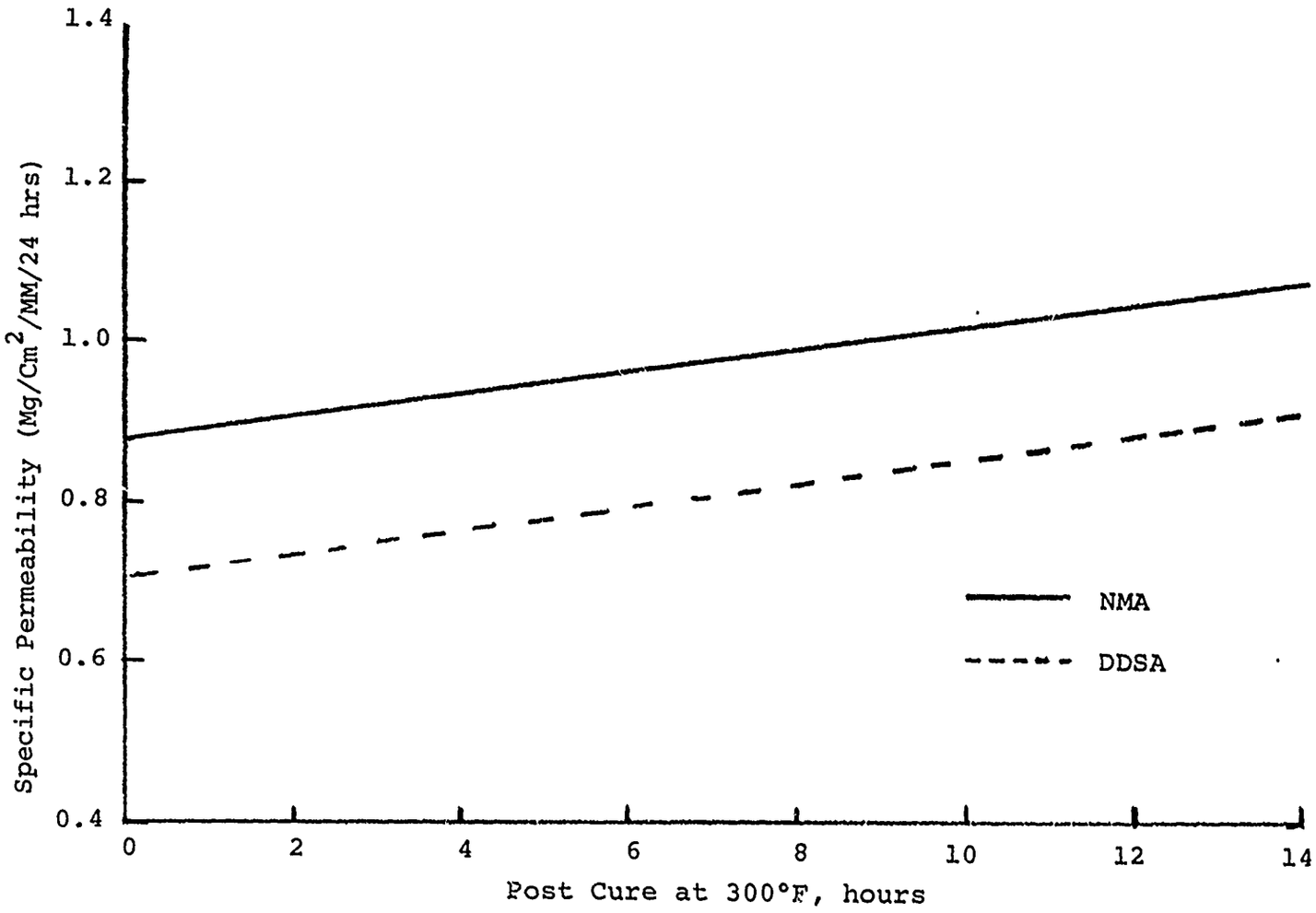


Figure 5. Specific Permeability Versus Post Cure

TABLE I

Data on Curing Agents Used in the Tests

| Curing Agents | Type | (PHR) Concentration | Cure Schedule |
|---|---|---|---|
| MDA | Aromatic Polyamine | 30 | Gel at RT + 2 hrs 300°F |
| MPDA | Aromatic Polyamine | 14 | " " " |
| Z | Aromatic Polyamine | 20 | " " " |
| DDS | Aromatic Polyamine | 25 | " " " |
| DDSA* | Anhydride | 135 | 2 hrs at 200°F + 2 hrs 300°F |
| NMA* | Anhydride | 90 | " " " |
| V-115 | Aliphatic Polyamide | 100 | RT Gel + 1 hr at 200°F |
| V-125 | Aliphatic Polyamide | 55 | " " " |
| V-140 | Aliphatic Polyamide | 33 | " " " |
| A | Aliphatic Polyamine | 6 | " " " |
| DETA | Aliphatic Polyamine | 10 | " " " |
| DMP-30 | Aliphatic Polyamine | 6 | " " " |

*0.5% benzyldimethylamine added as an accelerator.

TABLE II

Specific Permeability of Various Epoxy Resin Systems

| No. | Curing Agent | Specific Permeability ($Mg/Cm^2/MM/24$ hrs) | |
|---|---|---|---|
| | | 75°F | 140°F |
| 1 | DETA | .030 | .36 |
| 2 | V-12S | .037 | .60 |
| 3 | V-140 | .038 | .53 |
| 4 | Z | .040 | .46 |
| 5 | MPDA | .040 | .47 |
| 6 | MDA | .040 | .50 |
| 7 | DDS | .049 | -- |
| 8 | A | .050 | .63 |
| 9 | V-115 | .050 | .95 |
| 10 | DMP-30 | .055 | .63 |
| 11 | DDSA | .070 | 1.35 |
| 12 | NMA | .085 | -- |

TABLE III

Specific Permeability of An Epoxy Resin System* With Various Coatings and Fillers

| No. | Coating or Filler | Specific Permeability ($Mg/Cm^2/MM/24$ hrs) |
|---|---|---|
| 1 | Fiberglass Cloth | .030 |
| 2 | Filter Paper | .120 |
| 3 | Electroless Nickel Flash | .045 |
| 4 | Electroless Nickel (.0005") | .015 |
| 5 | Electroless Nickel (.001") | .010 |
| 6 | Vapor Deposited Aluminum | .025 - .040 |
| 7 | Electroless Copper Flash | .045 |
| 8 | Electroless Copper (.001") | .010 |
| 9 | Electro-Copper (.001") | .015 |
| 10 | Vapor Deposited Tin | .035 |
| 11 | Premetallizing Varnish | .060 - .080 |
| 12 | Electro-Cadmium (.001") | .005 - .025 |
| 13 | Electro-Brass (.001") | .020 |
| 14 | Electro-Zinc (.001") | .020 - .035 |
| 15 | Electro-Tin (.001") | .005 - .035 |
| 16 | Calcium Carbonate (20%) | .045 - .055 |
| 17 | Z-6040 Coupling Agent (3%) | .060 - .070 |
| 18 | Kaolin (2%) | .050 |
| 19 | Cabosil (3%) | .050 |
| 20 | Carbon Black (20%) | .045 - .060 |
| 21 | Control | .050 |

*Epoxy resin plus 6 Phr curing agent A.

## REFERENCES


1. J. Lynn Paraham and E. A. Verchct, "Environmental Compatibility of Glass Reinforced Plastics," Report No. RS-TR-67-6, Army Missile Command, Redstone Arsenal, Alabama.

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3. R. F. Register, "Behavior of Fiber Reinforced Plastic Materials in Chemical Service," Corrosion, volume 25, number 4, pg 157, April 1969.