NASA Technical Memorandum 85826

AN INVESTIGATION OF CHEMICALLY-INDUCED IMPROVEMENT IN SATURATION MOISTURE CHARACTERISTICS OF EPOXIES

JAG J. SINGH, TERRY L. ST. CLAIR, AND DIANE M. STOAKLEY

JUNE 1984

National Aeronautics and Space Administration

Langley Research Center
Hampton, Virginia 23665

ABSTRACT

MY-720/DDS epoxy samples were treated with three selected chemical compounds to render the active H-sites inactive for moisture absorption. Treating the epoxy castings with acetyl chloride and dichlorodimethyl silane leads only to surface changes indicating that these molecules are too large to penetrate the epoxy castings. Boron trifluoride, on the other hand, does penetrate the epoxy chain as is indicated by the formation of green domains in the interior of the castings. However, the process of saturating the specimens with moisture appears to leach out the chemical additives--thereby nullifying their possible ameliorative effects.

INTRODUCTION

Most epoxies are susceptible to moisture pickup because of the tendency of H on N or O atoms to interact with H in the H_2O molecule. It can thus be argued that it may be possible to reduce their moisture susceptibility if we can render active H sites in the epoxy chain inactive. With this goal in mind, tetraglycidyl methylene dianiline (TGMDA or MY-720) cured with 4, 4'-diamino diphenyl sulfone (DDS) was selected as the candidate epoxy. It is widely used in aerospace and electronic industries. The chemical additives selected for passivating the test epoxy were: (1) Acetyl chloride (CH_3COCl), (2) dimethyldichloro silane [$SiCl_2(CH_3)_2$] , and (3) Boron Trifluoride (BF_3). The saturation moisture characteristics of treated and untreated MY-720/DDS epoxy samples were measured. It was also planned to measure positron annihilation characteristics in the most promising moisture-proofed varieties in order to elucidate the mechanisms responsible for their hydrophobicity. The results of these studies are discussed in the following sections.

EXPERIMENTAL PROCEDURE AND RESULTS

The purpose of this study was to develop a technique that could render fully cured epoxy specimens less susceptible to moisture pickup. As indicated above, a highly cross-linked thermosetting resin (TGMDA/DDS) was selected for this study. Epoxy moldings in the form of 2" diameter x 0.1" discs were prepared. Some of these discs were chemically treated and their saturation moisture contents compared with those of the control (untreated) specimens(*). The results are discussed in the following sections.

(*) The saturation moisture contents were determined by comparing the weights of the specimens desiccated at 100°C with the weights of the specimens saturated with water at 90°C. (Notice that the specimens were actually immersed in water at 90°C for saturating them with water.)

Epoxy Preparation

Sixteen discs of MY-720/DDS epoxy were prepared in two batches. The first batch contained eight discs. The second batch, prepared 4 weeks later, also contained eight discs. All discs were prepared from an epoxy solution containing 49% by weight of tetraglycidyl methylene dianiline (TGMDA or MY-720), 14% by weight of 4, 4'-diaminodiphenyl sulfone (DDS) and 37% by weight of methyl ethyl ketone (MEK) solvent. The epoxy solution was poured into aluminum pans and degassed under vacuum at 120°C for 1 hour to remove the volatiles. Vacuum was then released, and the discs were cured by gradually heating from 120 → 150°C over a 3-hour period. The temperature was held at 150°C for 1 hour and then increased to 177°C for a 2-hour final cure. Figure 1 shows a structural diagram of the MY-720/DDS epoxy system[1].

The sample discs were treated with three different types of chemicals--acetyl chloride, dichlorodimethyl silane and boron trifluoride. These chemicals are expected to react with active hydrogens in the MY-720/DDS epoxy.

1. Acetylation Process: Four discs from the first batch were treated in the following manner:

i. The discs were left in contact with acetyl chloride vapors at room temperature for 4 days.

ii. They were then dried in a vacuum oven at 60-80°C for 24 hours.

iii. The discs were then soaked in liquid acetyl chloride at room temperature for 6 hours.

iv. They were next placed in boiling acetyl chloride at 40°C for 30 minutes.

v. Finally, the discs were washed in distilled water and wiped dry.

The discs changed from a yellow to a green color after initial treatment with acetyl chloride vapors. No further physical change was noted during the acetylation process. Figure 2 shows a structural diagram for acetylation of MY-720/DDS epoxy.

The remaining four discs were left untreated. The saturation moisture contents of the two sets of discs were then measured using the standard procedure (see page 1 footnote). It was noted that the treated discs had regained their original color/appearance after the saturation-desiccation cycle. The results are summarized in Table I. It is apparent from the data that acetylation makes no difference in the saturation moisture content of MY-720/DDS samples.

2. Silanization Process. The four untreated discs from the previous batch were silanized as follows:

i. The discs were immersed in a closed container of $SiCl_2(CH_3)_2$ at room temperature for 5 days.

ii. The samples were then washed in heptane.

iii. The samples were finally washed in distilled water and wiped dry.

It was noted that the silanized samples had acquired a dark green color. Figure 3 shows a structural diagram of silanized MY-720/DDS samples.

Since the acetylated samples from the previous test had regained their original state after saturation-desiccation cycle, they were treated as control samples for comparison with the silanized samples.

The saturation moisture contents of the silanized samples are summarized in Table II. During the saturation process, it was observed that the treated samples had recovered their original color after they had been in water for 65 hours.

It is apparent from the data shown in Table II that the silanized samples do pick up slightly less moisture than the untreated samples. It may be due to the fact that H in the original amine function of the epoxy has been replaced by a dimethyl chlorosilyl group which can react with water to form a slightly more hydrophobic dimethyl silanol group. However, the difference is rather small.

3. Boron Fluoridation Process. Four new discs from the second batch were subjected to boron trifluoride by placing them in a vessel containing a mixture of hexanes. Boron trifluoride gas was bubbled into the liquid and then the vessel was closed. This procedure was repeated twice daily for 4 days. At the end of this time, the samples were removed and examined. There was no appreciable weight gain. However, the amber-colored sample discs had developed green spots in their interiors. The samples were photographed and placed back into the BF_3/hexane bath over the weekend. Figure 4 shows a structural diagram of BF_3-treated MY-720/DDS samples.

The saturation moisture contents of BF_3-treated samples are summarized in Table III. During the saturation process, it was again noted that the BF_3-treated samples had recovered their original color after they had been in the hot water bath for about 3 days.

It is apparent from the data shown in Table III that the BF_3-treated samples pick up the same amount of water as the reference samples. However, the BF_3-treated samples took longer to lose their moisture content than the reference samples.

As seen in photographs 5 and 6, there were two different green spot patterns in the BF_3-treated discs before they were treated with water. In one case, the spots were larger in size but fewer in numbers. In the other case, the spots were finer but more numerous. Positron lifetime measurements were made in these BF_3-treated samples in order to explain the reasons for different spot size/distributions[2]. Results are summarized in Table IV.

DISCUSSION

The three chemical additives selected for passivating the epoxy samples are expected to react with active hydrogen atoms on N or O sites in the cross-linked TGMDA/DDS chains. (See figures 1-4.) During these reactions, they will generate acids of the general form HX which can subsequently react with amines present in the cured epoxy samples to form hydrochloride salts (see figure 7).

In the case of the acetyl chloride-treated epoxy moldings, a green color formed on the surface. The same phenomenon occurred in dichlorodimethyl silane treatment. This color change may be related to the formation of hydrochloride salts on the surface.

When boron trifluoride was used, green areas formed in the center of epoxy moldings. This again may be related to the formation of hydrochloride salts. However, in this case, the HF molecule was evidently small enough and polar enough to pentrate the molding. The green specks started out as small spots and grew with time.

In all cases, the effects of the chemical additives were reversed after the specimens had been in the hot-water bath for some time. This explains why the saturation moisture contents of the treated and untreated samples are essentially equal in all cases.

As indicated earlier, the distribution of the green spots in the interior of the samples subjected to BF_3 treatment followed two distinct patterns: Half of the samples had smaller but more numerous spots whereas the remaining samples had larger but fewer numbers of spots. Positron annihilation characteristics in these samples are different, as seen from the data in Table IV. The pickoff ortho-positronium annihilation rate in samples with smaller spots is larger, accompanied by a larger probability of Ps-atom formation. On the other hand, the pickoff annihilation rate in samples with larger spots is slower, accompanied by a lower probability of Ps-atom formation. These results indicate the presence of uncured regions in the samples where BF_3 appears to concentrate, thereby affecting the local free electron density and distribution.

CONCLUDING REMARKS

MY-720/DDS epoxy samples were treated with three selected chemical compounds to render active H sites inactive. Treating the epoxy castings with acetyl chloride and dichlorodimethyl silane leads only to surface changes indicating that these molecules--as well as the hydrogen chloride that forms--are too large to penetrate the epoxy castings. Boron trifluoride, on the other hand, does penetrate the epoxy chain as is indicated by the formation of green domains in the interior of the castings. However, the process of saturating the specimens with moisture appears to leach out the additives, thereby nullifying their possible ameliorative effects. Positron annihilation characteristics in the test epoxy samples indicate rather large free volume, thus attesting the appropriateness of MY-720/DDS epoxy as the test medium.

REFERENCES

1. Lynn S. Penn and T. T. Chiao: Epoxy Resins (Handbook of Composites, edited by George Lubin, Van Nostrand Reinhold Publishing Company, New York, 1982, pp. 57-88).

2. William H. Holt and Willis Mock, Jr.: Positron Lifetime Technique for Nondestructive Evaluation of Materials. NSWC-DL-TR-3573, U. S. Navy, December 1976. (Available from DTIC as AD A038305).

3. Jag J. Singh, Terry L. St. Clair, William H. Holt and Willis Mock, Jr.: Moisture Dependence of Positron Annihilation in Nylon-6. Nucl. Instr. and Methods, Vol. 221, 427, 1984.

Table I. Summary of Saturation Moisture Contents of Untreated and Acetylated MY-720/DDS Epoxy Samples

Untreated Samples		Treated Samples	
Sample No.	Saturation Moisture Content	Sample No.	Saturation Moisture Content
1	5.34 w/o	1	5.29 w/o
2	5.37 w/o	2	5.35 w/o
3	5.32 w/o	3	5.32 w/o
4	5.38 w/o	4	5.32 w/o
(Average)	(5.35±0.03) w/o	(Average)	(5.32±0.03) w/o

Table II. Summary of Saturation Moisture Contents of Silanized MY-720/DDS Epoxy Samples

Untreated Samples		Treated Samples	
Sample No.	Saturation Moisture Content	Sample No.	Saturation Moisture Content
1	5.16 w/o	1	4.94 w/o
2	5.28 w/o	2	5.01 w/o
3	5.09 w/o	3	4.90 w/o
-	5.17 w/o	4	5.07 w/o
Average)	(5.18±0.08 w/o)	(Average)	(4.98±0.08 w/o)

Table III. Summary of Saturation Moisture Contents of Untreated and BF_3-Treated MY-720/DDS Samples.

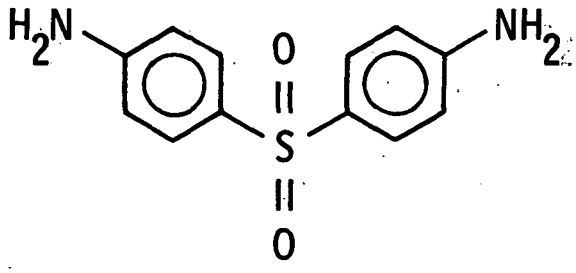
Sample No.	Saturation Moisture Content	Sample No.	Saturation Moisture Content
1	4.79 w/o	1 (larger spots)	4.83 w/o
2	4.90 w/o	2 (smaller) spots)	4.87 w/o
(Average)	(4.85±0.05) w/o	(Average)	(4.85±0.02) w/o

Table IV. Summary of Positron Lifetimes(*) in BF_3-Treated MY-720/DDS Samples (Dry)

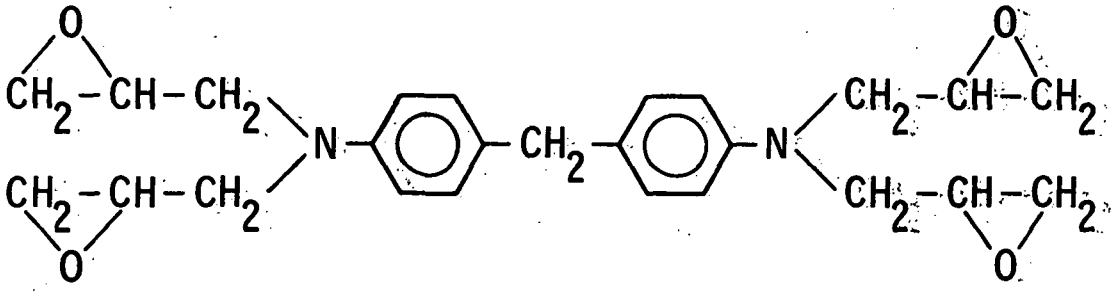
Parameter	Sample With Smaller Green Spots	Sample With Larger Green Spots
τ_1	366±17 ps	370±10 ps
τ_2	1521±68 ps	1596±43 ps
I_2	32.0±1.7%	26.4±1.0%

(*) τ_1 - Short Lifetime Component Lifetime
τ_2 - Long Lifetime Component Lifetime
I_2 - Long Lifetime Component Intensity

(Pick-off orthopositron lifetime (τ_2) is very sensitive to the atomic environment at the end of the range of the positrons injected into the target epoxies[3].)



DDS



MY-720

Figure-1. Structure of MY-720/DDS Epoxy.

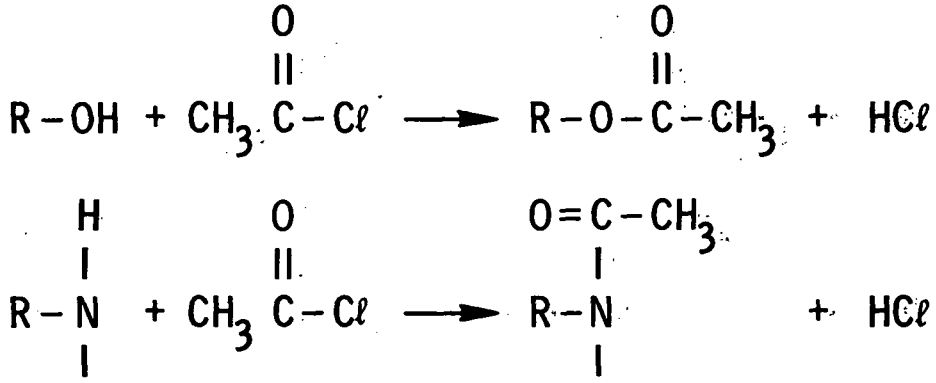


Figure-2. Structure of Acetylated MY-720/DDS Epoxy.

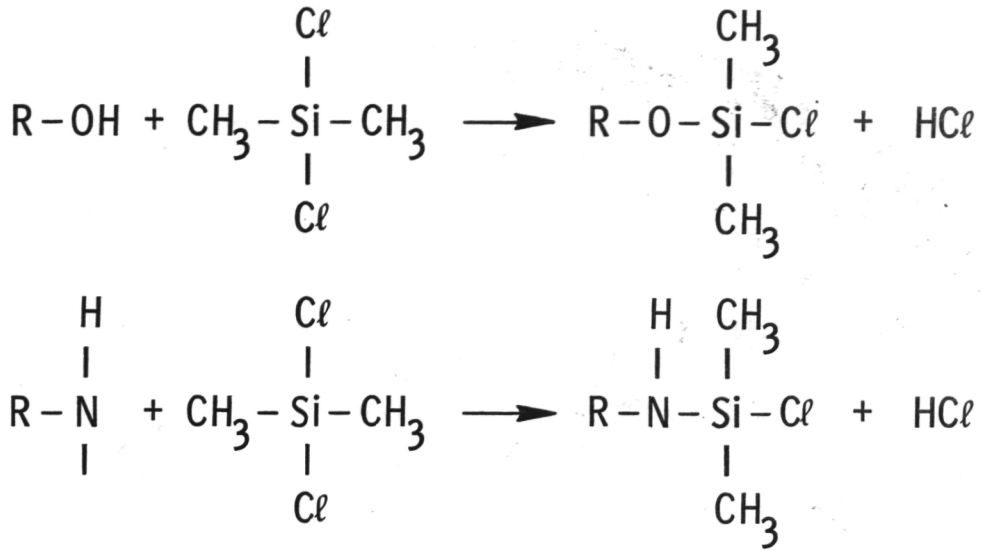


Figure-3. Structure of Silanized MY-720/DDS Epoxy.

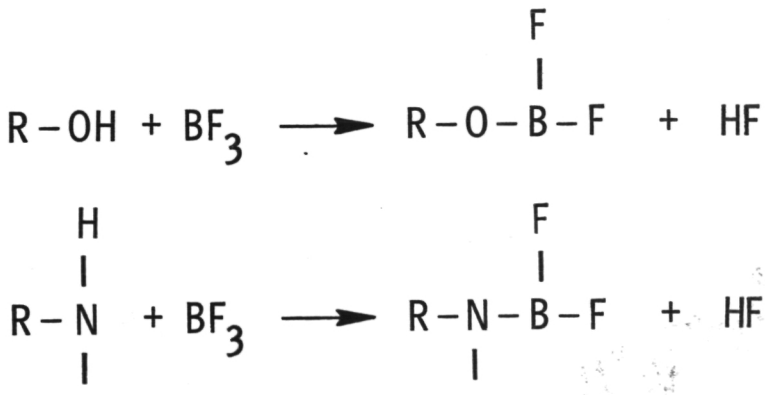


Figure-4. Structure of BF_3-treated MY-720/DDS Epoxy.

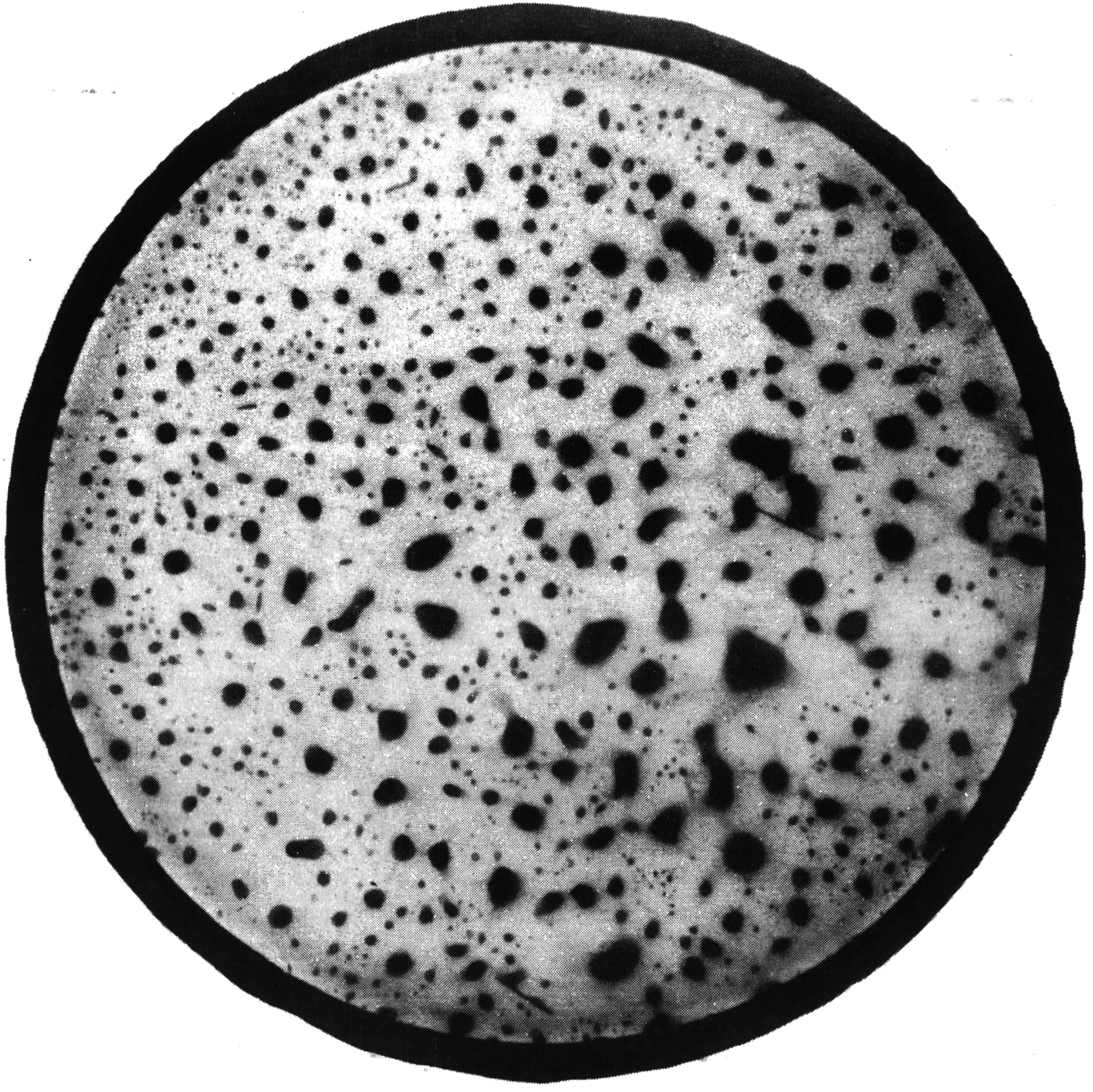


Figure-5. Photograph of BF_3-treated MY-720/DDS Epoxy (fine spots).

NASA
L-84-3253

Figure-6. Photograph of BF_3-treated MY-720/DDS Epoxy (coarse spots).

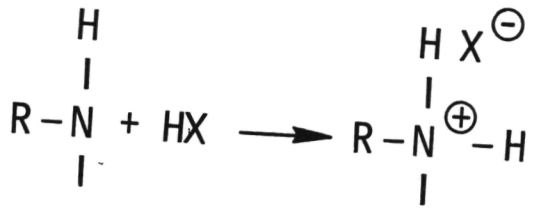


Figure-7. Effect of HX Acid on MY-720/DDS Epoxy.

1. Report No.	2. Government Accession No.	3. Recipient's Catalog No.
NASA TM-85826		

4. Title and Subtitle	5. Report Date
An Investigation of Chemically-Induced Improvement in Saturation Moisture Characteristics of Epoxies	June 1984
	6. Performing Organization Code 505-33-90-01
7. Author(s) Jag J. Singh, Terry L. St. Clair, and Diane M. Stoakley	8. Performing Organization Report No.
	10. Work Unit No.
9. Performing Organization Name and Address NASA Langley Research Center Hampton, VA 23665	11. Contract or Grant No.
	13. Type of Report and Period Covered Technical Memorandum
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, DC 20546	14. Sponsoring Agency Code

15. Supplementary Notes

16. Abstract

MY-720/DDS epoxy samples were treated with three selected chemical compounds to render the active H-sites inactive for moisture absorption. Treating the epoxy castings with acetyl chloride and dichlorodimethyl silane leads only to surface changes indicating that these molecules are too large to penetrate the epoxy castings. Boron trifluoride, on the other hand, does penetrate the epoxy chain as is indicated by the formation of green domains in the interior of the castings. However, the process of saturating the specimens with moisture appears to leach out the chemical additives--thereby nullifying their possible ameliorative effects.

17. Key Words (Suggested by Author(s))	18. Distribution Statement
Moisture-Resistant Epoxy, MY-720/DDS Epoxy, Acetyl Chloride, Dichlorodimethyl Silane, Boron Trifluoride, Surface Effects, Bulk/Interior Effects, Positron Lifetime	Unclassified - Unlimited Subject Category - 24

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price
Unclassified	Unclassified	13	A02

For sale by the National Technical Information Service, Springfield, Virginia 22161