

Technical Support Package

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'Stable Polyurethane Coatings for Electronic Circuits'

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Technical Support Package

For

STABLE POLYURETHANE COATINGS FOR ELECTRONIC CIRCUITS

MFS-25663

NASA Tech Briefs, Vol. 7, No. 1

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I. INTRODUCTION

One of the most severe deficiencies of polyurethanes as engineering materials for electrical applications has been their sensitivity to combined humidity and temperature environments. Gross failure by reversion of urethane connector potting materials has occurred under these conditions. This has resulted in both scrapping of expensive hardware and reduction in reliability in other instances.

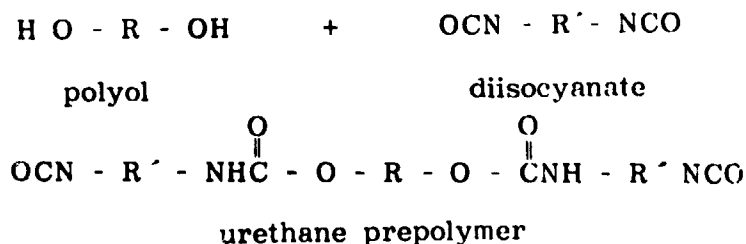
A basic objective of this study has been to gain a more complete understanding of the mechanisms and interactions of moisture in urethane systems to guide the development of reversion-resistant materials for connector potting and conformal coating applications in high humidity environments.

Basic polymer studies of molecular weight and distribution, polymer structure, and functionality were carried out to define those areas responsible for hydrolytic instability and to define polymer structural features conducive to optimum hydrolytic stability.

Polyurethanes are made essentially of three basic components:

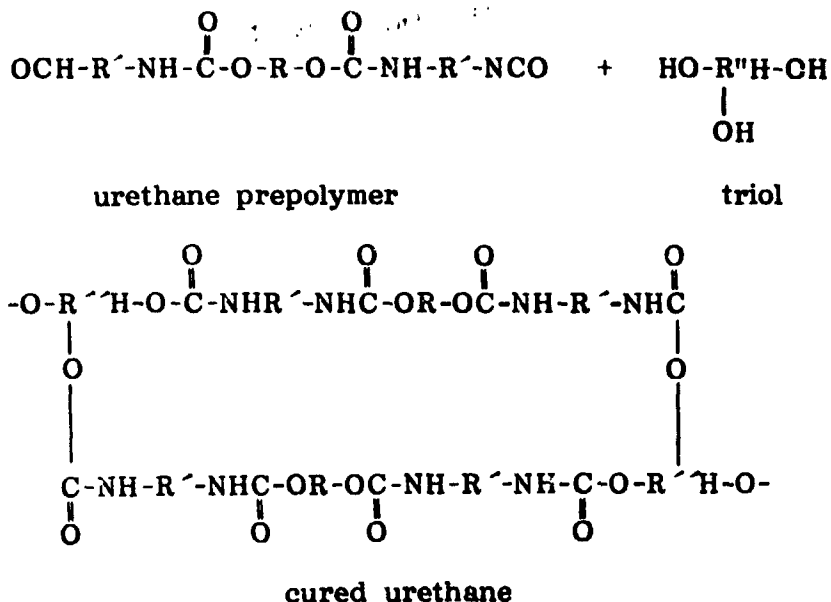
- 1) Polyols
- 2) Diisocyanates
- 3) Chain Extenders.

It is the interaction of these three components which produces the polyurethane:



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The urethane is cured with chain extenders which results in a crosslinked thermosetting material:



Four types of polyols considered in this report which are used to produce polyurethanes are:

- | | |
|------------------------------|---|
| 1) polyester | $\text{H-(OR-OC(=O)-R}'\text{-C(=O)-O)}_n\text{-OH}$ |
| 2) polyether | $\text{H-(O-R-O-R}''\text{)}_n\text{-OH}$ |
| 3) polybutadiene | $\text{HO-(R-CH=CH-R}''\text{)}_n\text{-OH}$ |
| 4) hydroxy-terminated alkane | $\text{HO-(R-CH}_2\text{CH}_2\text{-R}''\text{)}_n\text{-OH}$ |

Five polyether polyols, varying in molecular weight from 360 to 3000, were used for preparing polyurethanes to be used in this study. The first commercially available urethanes were based on polyester polyols. Conventional polyesters are made by reacting an organic acid with a diol. The polyester always contains some unreacted acid which acts as an initiator for hydrolytic degradation. Bond damage is a reversal of the acid-diol reaction at the ester linkage. Since urethanes prepared from polyethers are generally five to ten times more resistant to hydrolysis than those prepared from polyesters, ether-based urethanes have been

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used in this study. The ether group is the group most resistant to hydrolysis in the ether-based urethanes, and the rate of degradation depends upon the susceptibility of the carbamate, urea, and biuret groups, which are formed in addition to the basic urethane linkage.

Urethanes prepared from hydroxy-terminated polybutadiene are hydrolytically stable and have excellent dielectric properties. These polybutadiene-based urethanes are more hydrophobic than polyethers and the long polymer chain probably shields the hydrolytically sensitive carbamate linkage from moisture. However, these urethanes are oxidatively unstable. The material cracks severely in the presence of ozone. The unsaturation in the polybutadiene structure is believed responsible for this instability. Alkane polyols can be prepared by the hydrogenation of hydroxy-terminated polybutadiene. Urethanes prepared from these polyols should be oxidatively stable and at the same time retain the excellent hydrolytic stability of the polybutadiene-based urethanes. Five hydroxy-terminated alkanes, varying in molecular weight from 200 to 4000, were used for preparing polyurethanes to be used in this task. This study has been directed toward a comparison of the hydrolytic stability of ether-based urethanes with that of alkane-based urethanes.

Diisocyanates are the second group of components used in the manufacture of polyurethanes. These chemicals end-cap the polyols and supply the active sites necessary for cross-linking. The most commonly used and least expensive diisocyanate is 2,4-toluene diisocyanate (TDI) which was used in this study. No attempt was made to evaluate other diisocyanates for effects on physical properties. Since TDI was used in the preparation of all the test urethanes, it should not be a contributor to any differences in hydrolytic stability.

The final component of polyurethanes is the chain-extender or cross-linker. This component allows the urethane prepolymer to reach its final molecular weight and cures it. The chain extenders fall into two categories, diols and diamines.

The diol type was used in this study. A mixture of 2 ethyl-1, 3-hexane diol and triisopropanol amine was used. The most common diamine type is 4,4' methylene bis (2 chloroaniline), known under the DuPont trade name MOCA. This curing agent adds toughness to the urethane, but it was not used in this study because it is a carcinogen suspect.

The alkane and ether diols used were characterized for molecular weight, molecular weight distribution, and functionality. A method was developed for the preparation and purification of the urethane polymers. The urethanes were characterized for molecular weight, molecular weight distribution, and functionality. Cure techniques were developed. The urethanes were prepared, characterized, molded, and cured into configurations for testing. Test specimens were immersed in a tank of water at 160°F and monitored on a weekly basis. Four-inch discs were tested

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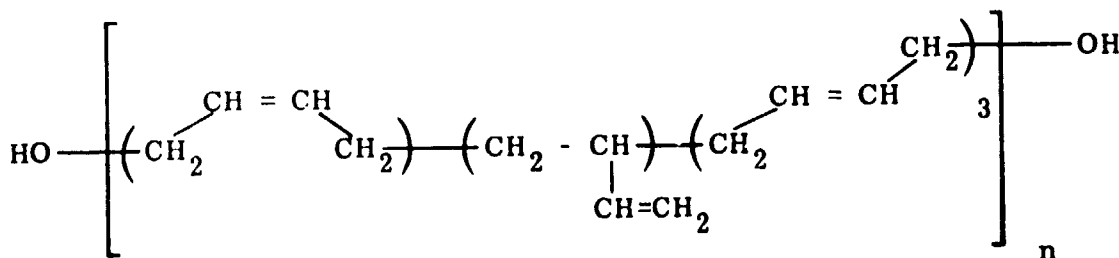
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for surface and volume resistivity and hardness. Two-inch discs were checked for dielectric constant, dissipation factor, and water absorption. Y-patterns were prepared, exposed in an environmental chamber at 160°F and 95 percent relative humidity, and tested for insulation resistance. Film was prepared from each urethane and used to determine moisture permeability.

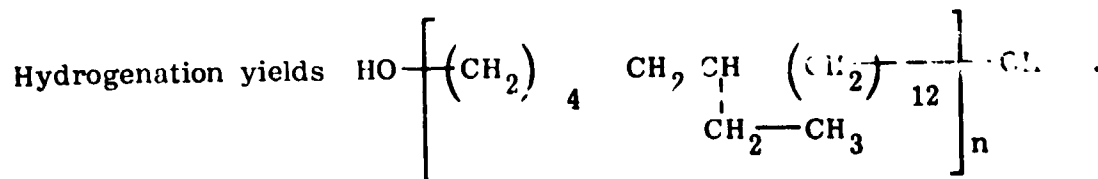
II. POLYMER DEVELOPMENT

A. Alkane Diols

Alkane diols are prepared by the hydrogenation of polybutadiene polyols. One typical commercially available hydroxy-terminated polybutadiene is:



The predominant configuration is Trans-1,4 (60 percent) with approximately 20 percent each Cis-1,4 and Vinyl-1,2. The terminal hydroxyl groups are primary and predominantly of the allylic type. The hydroxyl functionality is about 2.0 to 2.4.



General Tire and Rubber Company markets alkane diols of this type under the trade name Telagen-S. The alkane diols used in this study were:

- 1) 1, 12-Dodecanediol
- 2) Telagen-S A595-88
- 3) Telagen-S 3 HPL-185M
- 4) Telagen-S 3 HPL-186L.

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One alkane-based urethane, NBP 129001, a toluene-2,4-diisocyanate terminated Telagen-S prepared by Monsanto Research Corporation, was used in the comparative tests. Telagen-S A595-88 is a purified, primary hydroxyl-terminated alkane diol prepared by General Tire. This material is essentially difunctional with a narrow molecular weight distribution.

Telagen-S 3 HPL-185 is a mixture of hydroxyl-terminated alkane diols prepared by General Tire. Figure 1 shows a gel permeation chromatogram of this material. There are three principal molecular weight distributions in this mixture. The lower the molecular weight, the more soluble are these diols in a methylene chloride-methanol mixture. This principle was used for isolating the medium molecular weight fraction. It was designated Telagen-S 3 HPL-185M and used as one of the alkane diols in this study.

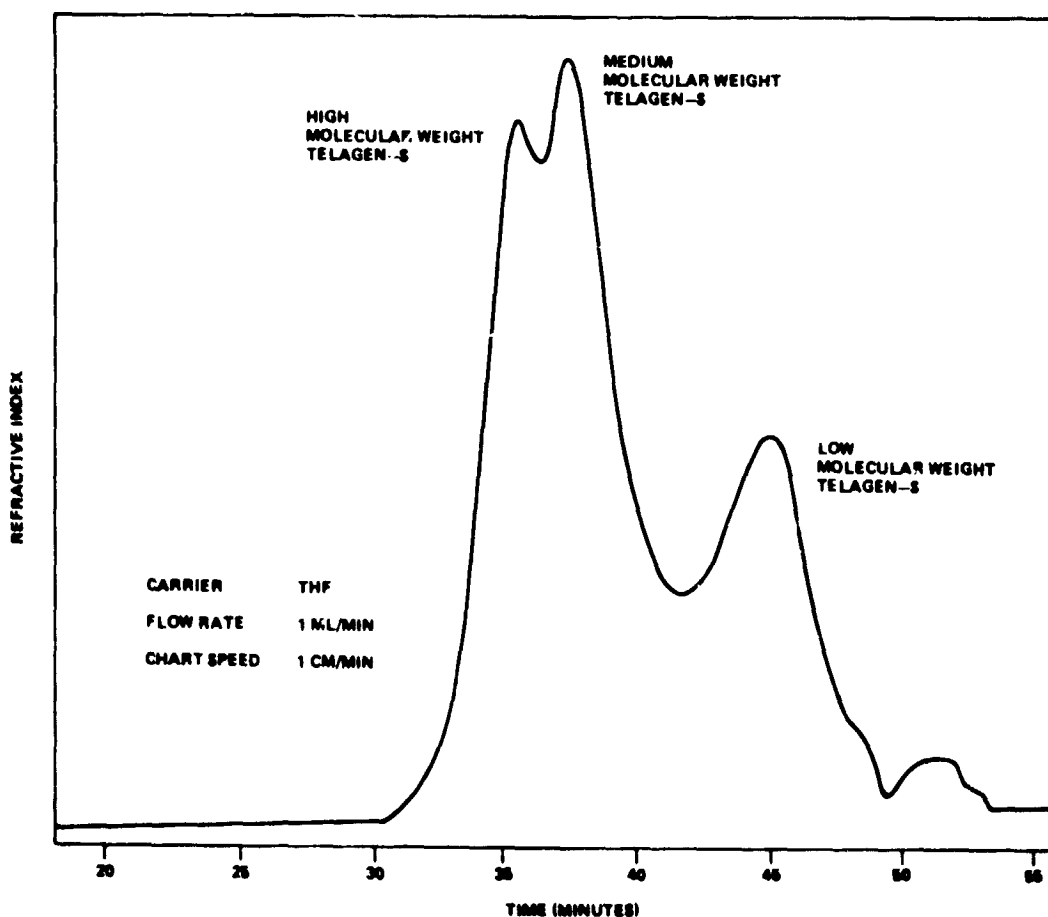


Figure 1. Gel permeation chromatogram for Telagen-S 3 HPL-185.

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A solution of the mixture was prepared by dissolving 300 grams of Telagen-S 3 HPL-185 in 3000 ml methylene chloride. When methanol was added to this solution, two phases separated - an oily layer on top and a methylene chloride-methanol solution on the bottom. Methanol was added in increments and the separation was monitored by GPC techniques. Figure 2 is a gel permeation chromatogram of the methylene chloride-methanol solution after the addition of 300 ml of methanol. The high molecular weight fraction had been removed from the solution. The methylene chloride-methanol solution was separated from the oily, high molecular weight fraction, and increments of methanol were again added to the solution. After 450 ml more methanol was added, the methylene chloride-methanol solution was discarded. The oily layer which contained the medium molecular weight fraction was retained. Its chromatogram is shown in Figure 3. Telagen-S 3 HPL-186L was prepared from Telagen-S 3 HPL-186 in a similar manner.

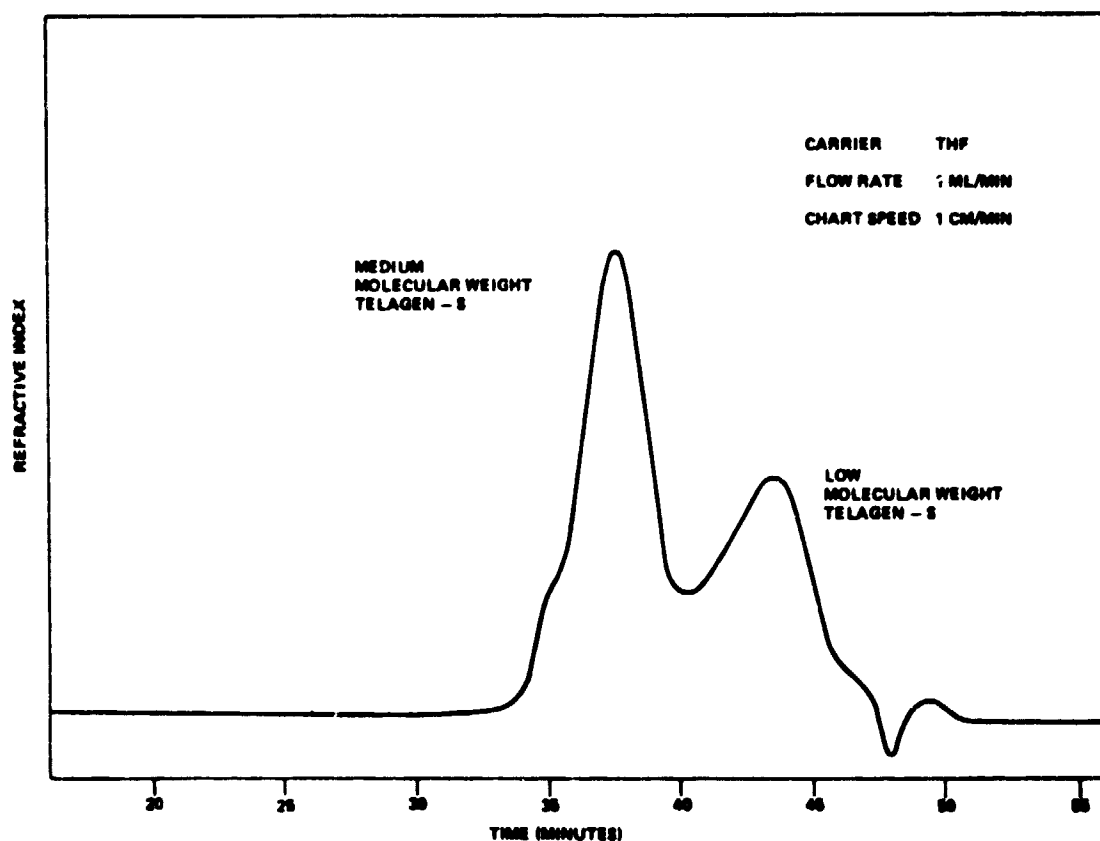


Figure 2. Gel permeation chromatogram for methylene chloride-methanol soluble portion of Telagen-S 3 HPL-185.

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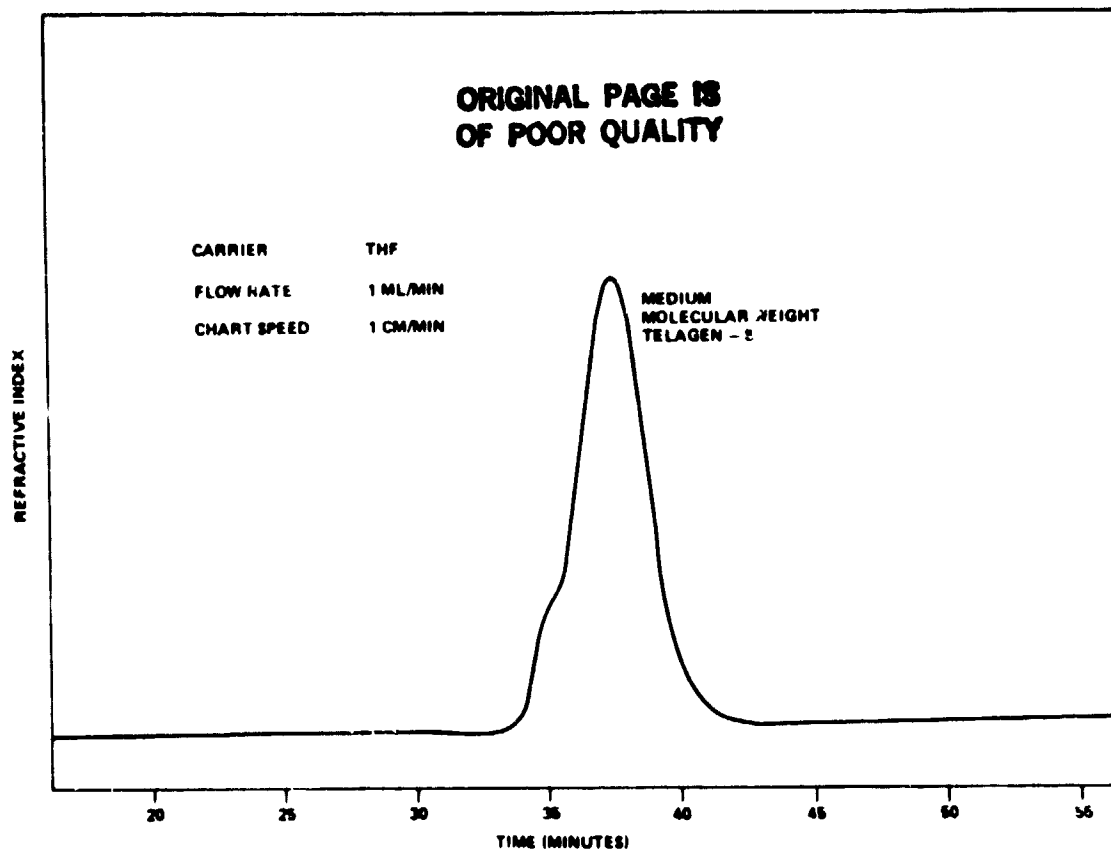


Figure 3. Gel permeation chromatogram for Telagen-S 3
HPL-185M.

B. Ether Diols

The ether-based urethanes tested in this study were prepared from polyethylene glycols (PEG). A general formula would be $H - (OCH_2CH_2)_n - OH$. PEG is available commercially in several molecular weights. The ether diols used in this study were:

- 1) Carbowax 400
- 2) Carbowax 600
- 3) Carbowax 1000
- 4) Carbowax 1540
- 5) Carbowax 4000.

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Carbowax is the Union Carbide Chemical Company trade name for PEG. The number corresponds to an approximate molecular weight. The Carbowax samples used were essentially one component with a narrow molecular weight distribution. This is illustrated in Figure 4, a gel permeation chromatogram of a typical Carbowax.

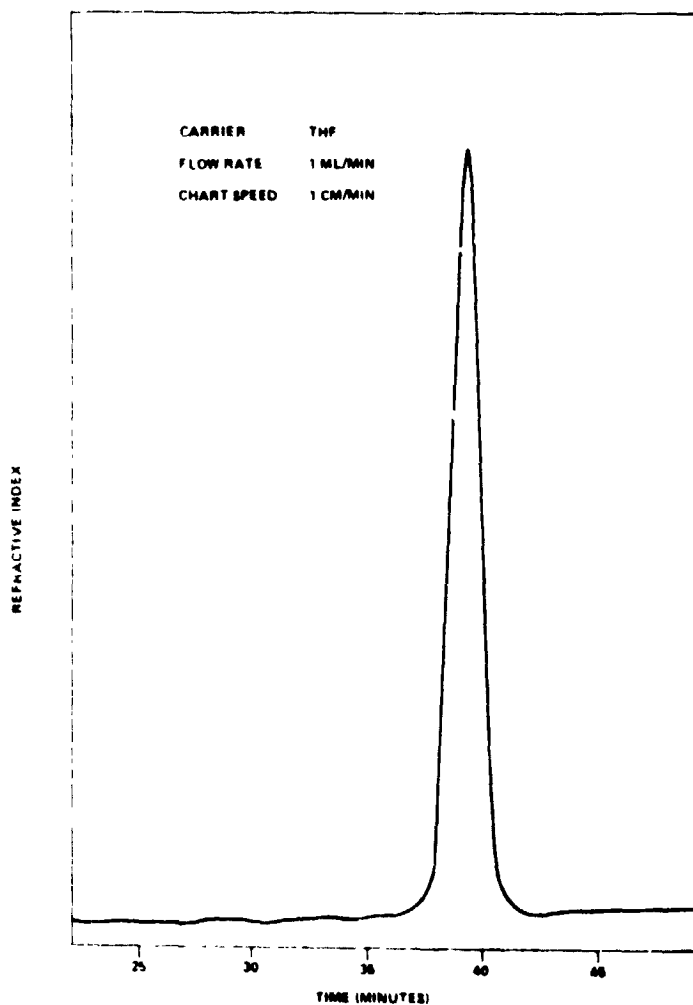


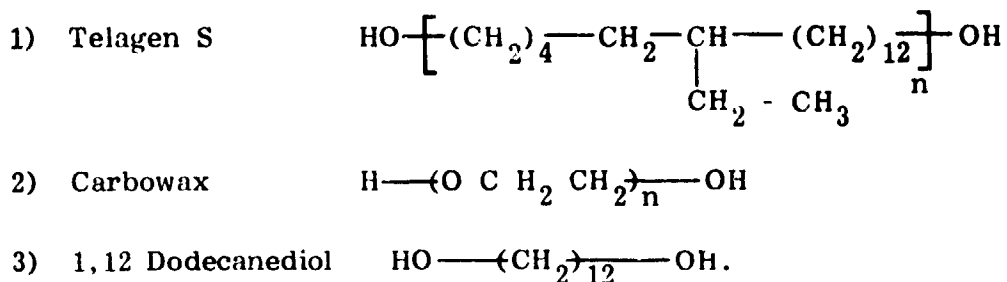
Figure 4. Gel permeation chromatogram for Carbowax 4000.

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C. Characterization of Prepolymers

No attempt was made to verify the structure of the polyols. However, the assumptions previously made were:



The diols were characterized for molecular weight, molecular weight distribution and functionality. Characterization of the prepolymers is shown in Table 1.

TABLE 1. CHARACTERIZATION OF PREPOLYMERS

Prepolymer	Molecular Weight			Functionality
	Number Average	Weight Average	Distribution	
1, 12-Dodecanediol ^a	202	207	1.02	2.00
Carbowax 300 ^b	318	387	1.22	2.15
Carbowax 400 ^b	361	426	1.18	1.84
Telagen S 3HPL-186L ^a	506	996	1.73	1.87
Carbowax 600 ^b	538	648	1.20	1.84
Carbowax 1000 ^b	977	1120	1.15	2.02
Carbowax 1540 ^b	1361	1506	1.11	1.94
Telagen S A595-88 ^a	1660	2129	1.28	2.12
Carbowax 4000 ^b	2989	3276	1.10	1.94
Telagen S 3HPL-185M ^a	3962	5769	1.46	1.93

a. Alkane Diol
b. Ether Diol

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Molecular weight and molecular weight distribution of the diols were determined using gel permeation chromatographic (GPC) techniques. The chromatography studies were carried out on a Waters Associates liquid chromatograph equipped with a Model 6000A solvent delivery system, Model 440 absorbance detector, and R 401 differential refractometer. A series of five columns packed with μ Styragel¹ (two 500 A, two 1000 A, and one 10,000 A) were used in this study. Tetrahydrofuran (THF) was used as the carrier. Numerical values for molecular weight, number and weight average, and molecular weight distribution were generated from GPC data. In GPC of polymers, $M[\eta]$ has been found to be a "Universal Calibration" parameter, where η is intrinsic viscosity and M is molecular weight. A calibration curve for low molecular weight polymers (300 to 20,000 M) using the universal calibration curve $\log M[\eta]$ versus elution volume was used in this study. Polymers used for this calibration included polystyrene, polypropylene glycol, and polyethylene glycol. The value of η was determined experimentally for each diol at 30°C in THF.

$$[\eta] = \lim_{C \rightarrow 0} \left[\frac{t/t_0 - 1}{C} \right]$$

where

t = effluent time of sample, sec.

t_0 = effluent time of THF, sec.

C = concentration, g/100 ml THF.

The value of the term $\frac{t/t_0 - 1}{C}$ is measured for several different concentrations of sample in THF and is plotted versus concentration. The value of the term when extrapolated to zero concentration is equal to $[\eta]$. Intrinsic viscosity is a measure of the hydrodynamic volume of the polymer particles. It is correlated with molecular weight by the Mark-Houwink equation:

$$[\eta] = KM_v^a$$

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1. A product of Waters Associates.

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where

M_v = viscosity average molecular weight

K = constant related to polymer solvent/temperature combination

α = Mark-Houwink exponent.

Viscosity average molecular weight is normally used for the universal calibration curve. However, number-average molecular weight, a good approximation for narrow molecular weight standards, was used in this work.

Weight-average and number-average molecular weight are then calculated from gel permeation chromatographic data using the following relationships:

$$M_w = \frac{\sum_{i=1}^n (H_i \times M_i)}{\sum_{i=1}^n (H_i)}$$

$$M_n = \frac{\sum_{i=1}^n (H_i)}{\sum_{i=1}^n (H_i/M_i)}$$

where

M_w = weight-average molecular weight

M_n = number-average molecular weight

H_i = height of the GPC at equally spaced intervals along the retention volume axis

M_i = molecular weight of species eluting from the GPC column at those points where H_i values are taken.

The number-average molecular weight of the diols used varied from 202 to 3962. This range would include the usual molecular weight, required in the preparation of polyurethanes for connector potting applications.

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Weight average molecular weight is equal to or greater than number-average molecular weight. The ratio M_w/M_n is used as a measure of the breadth of the molecular weight distribution.

Hydroxyl functionality was calculated from hydroxyl number and number-average molecular weight. Hydroxyl number is the milligrams of OH expressed as potassium hydroxide per gram of sample. The hydroxyl equivalent weight is $1000 \times \text{molecular weight of potassium hydroxide} / \text{hydroxyl number}$ or

$$\text{Hydroxyl equivalent weight} = \frac{56,100}{\text{Hydroxyl Number}}$$

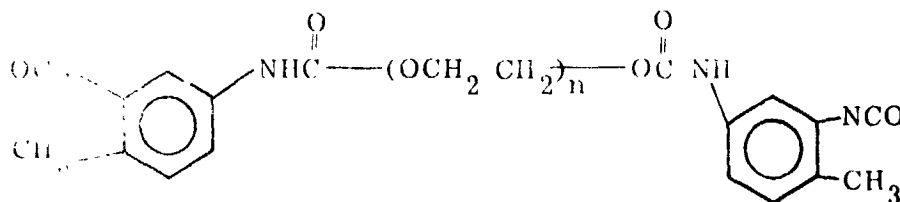
Functionality of the diol is the number-average molecular weight/hydroxyl equivalent weight or

$$\text{Functionality} = \frac{M_n \times \text{Hydroxyl Number}}{56,100}$$

A functionality of two indicates two hydroxyl groups per molecule. Monofunctional molecules would prevent chain extension and result in a lower molecular weight of the cured polymer. The functionality of the diols used in this study was very close to two considering variations due to experimental error.

D. Preparation of Polyurethanes

The alkane and ether-based polyurethanes were prepared by end-capping the respective diols with 2,4-toluene diisocyanate (TDI).



Two moles TDI were reacted with one mole diol to yield the TDI-terminated urethane. However, 25 percent excess TDI was used to insure complete reaction, and the excess was removed by extraction techniques. The para isocyanate group is the more reactive of the two isocyanate groups in the TDI molecule. This fact minimizes chain extension in the reaction by insuring that only one isocyanate group in the molecule will react with the diol. Chain extension can also be minimized by running the reaction cold and dry, and always maintaining an excess of TDI in the reaction flask. Figure 5 shows a gel permeation chromatograph of

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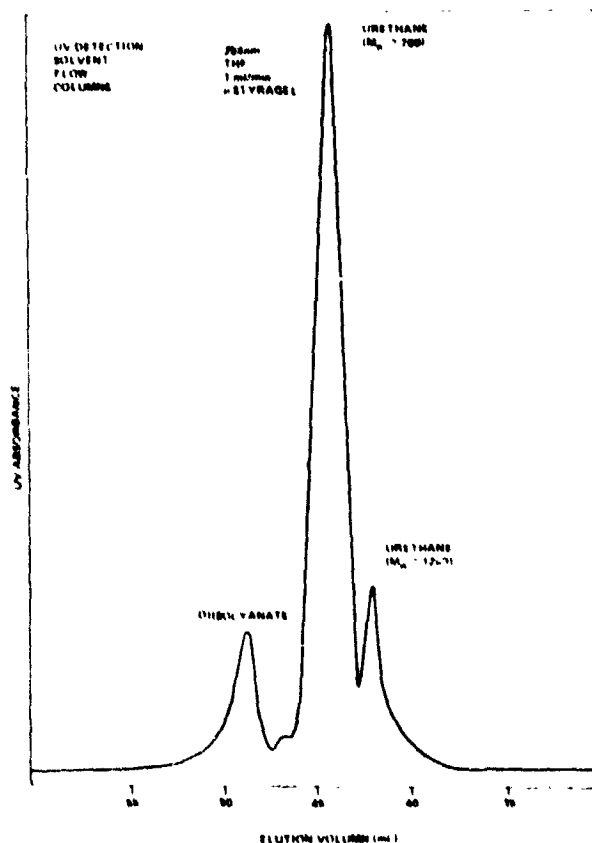


Figure 5. Gel permeation chromatogram of urethane prepared from Carbowax 400.

a urethane prepared from Carbowax 400. The major peak ($M_n = 700$) is a result of the 2 to 1 reaction of TDI and Carbowax 400. There is a small amount of chain extension ($M_n = 1250$) and some excess TDI. The excess TDI is removed by extraction with Freon TF.

A three neck, 1000-ml, round bottom flask was used as the reaction vessel. A drying tube packed with indicating Drierite was used as a breather. The Carbowax was added from a 250 ml dropping funnel. The reaction was agitated with a magnetic stirrer and an ice-water bath was used to maintain the reaction temperature at 20°C or less. This apparatus is shown in Figure 6. The apparatus was dried thoroughly, since TDI reacts readily with moisture, and precautions must be taken when using this material. A typical preparation would be the end-capping of Carbowax 1540. Thirty-two grams of TDI were weighed into the reaction flask. This was followed with 300 ml methylene chloride. One hundred grams of Carbowax 1540 were dissolved in 100 ml methylene chloride and transferred to the dropping funnel. The Carbowax solution was added dropwise to the reaction flask over a four hour period. The reaction mixture was maintained at 20°C or less and stirred vigorously. After the addition of the Carbowax was completed, the mixture was allowed to

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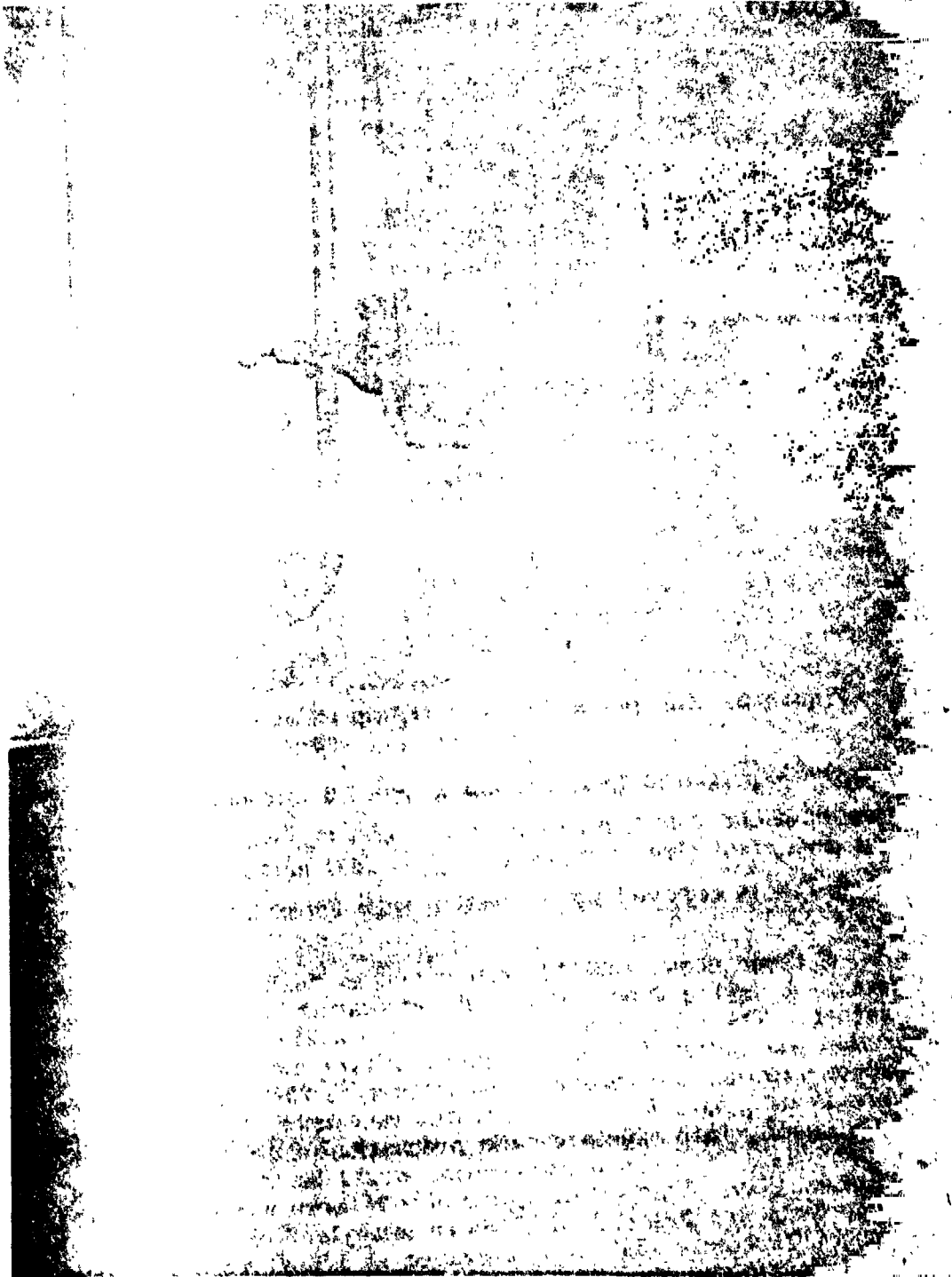


Fig. 6. Apparatus for the preparation of polyurethane.

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to stir overnight. The methylene chloride was removed by distilling under vacuum. The reaction product was slurried with Freon TF and transferred to a separatory funnel. The soluble portion containing excess TDI was drawn off and discarded. The reaction product was extracted 10 times with 50-ml portions of Freon TF in this manner. The product was transferred to sample bottles, dried under vacuum, and stored in a desiccator.

E. Characterization of Urethane Polymers

The polyurethanes were characterized for molecular weight, molecular weight distribution and functionality. Characterization of the polymers is shown in Table 2. Molecular weight, number and weight average, and molecular weight distribution of the urethanes were determined using gel permeation chromatographic techniques in the same manner as were the prepolymers shown in Table 1.

TABLE 2. CHARACTERIZATION OF URETHANE POLYMERS

Urethane Polymer	Molecular Weight			Functionality
	Number Average	Weight Average	Distribution	
1, 12-Dodecane-DI ^a	552	586	1.06	2.05
400 - DI ^b	729	1272	1.74	1.93
Telagen-S 3HPL-186L-DI ^a	765	1492	1.95	1.89
600 - DI ^b	881	1063	1.21	1.96
1000 - DI ^b	1322	1766	1.34	2.05
1540 - DI ^b	1799	2046	1.14	1.94
Telagen-S A595-88-DI ^a	2126	2802	1.32	2.09
NBP 129001 ^a	2737	3733	1.36	2.02
4000 - DI ^b	3347	4390	1.31	1.96
Telagen-S 3HPL-185M-DI ^a	4377	6547	1.50	1.97

- a. Alkane Based Urethane
- b. Ether Based Urethane

Isocyanate functionality was calculated from the percent NCO in the urethane and the number-average molecular weight of the urethane. The isocyanate equivalent weight is 4200/percent NCO. Functionality of the urethane is the number-average molecular weight/NCO equivalent weight or

$$\text{Functionality} = \frac{M_n \times \text{percent NCO}}{4200}$$

A functionality of two indicates two isocyanate groups per molecule. Monofunctional molecules would prevent chain extension and result in a lower molecular weight in the cured polymer.

The isocyanate content of the urethane was determined according to ASTM Standard D2572. A sample of the urethane was dissolved in toluene and treated with an excess of a standard di-n-butylamine solution. The excess amine was titrated with 0.1 N hydrochloric acid using bromophenol blue solution as the indicator.

F. Curing Agents

The urethanes were cured with a mixture of 2-ethyl-1, 3-hexanediol and triisopropanolamine. The diol extended the polymer while the triol provided the crosslinking necessary to obtain stability to flow at 160°F, the test temperature. In fact, the alkane-based urethane resin Telagen-S 3 HPL-185M-DI melted at test temperature even though it was cured entirely with triisopropanolamine. The amount of curing agent used for the various resins is shown in Table 3. The ratio diol/triol was varied according to the molecular weight of the urethane polymer. Stoichiometric amounts of curing agent were used for complete reaction with the isocyanate content of the resin. One gram equivalent of triol was used for each 2000 grams of resin. This provided one cross-link for each 2000 gram equivalent of resin. The diol was used for any additional curing agent required. The urethanes were cured at 160°F for 18 hours.

III. POLYMER EVALUATION

A. Water Absorption of Cured Urethane

The amount of water absorbed by a urethane is a good indication of the hydrophobic or hydrophilic properties of the material. If a urethane resin absorbs water, the urethane bond will be in closer and longer contact with the water and the bond will be more susceptible to cleavage. A hydrophobic backbone could actually protect the urethane bond from attack by water. The oxygen atom in the ether backbone of the ether-based urethane can interact with the protons of water to form some hydrogen bonding. Water would be absorbed and held by the urethane

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TABLE 3. CURING AGENTS FOR URETHANE POLYMERS

Urethane Polymer	Equivalent Weight	Curing Agents Conc., g./100 g Resin	
		Diol	Triol
1, 12-Dodecane-DI	269	23.5	3.3
400 - DI	377	15.7	3.3
Telagen-S 3HPL-186L-DI	405	14.4	3.3
600 - DI	450	12.6	3.3
1000 - DI	644	7.7	3.3
1540 - DI	925	4.3	3.3
Telagen-S A595-88-DI	1017	3.5	3.3
NBP 129001	1355	1.7	3.3
4000 - DI	1707	0.6	3.3
Telagen-S 3HPL-185M-DI	2222	0.0	3.3

molecule. Hydrocarbon molecules typical of the backbone of the alkane-based urethane would tend to interfere with hydrogen bonding between water molecules and the oxygen in the polymer and could offer in exchange, only the much weaker van der Waals forces. Very little water would be absorbed. On this basis the alkane-base urethanes should be hydrophobic. The ether-based urethanes should be hydrophilic to an extent depending upon the ether content of the polymer.

A 2-in. disc of each polymer was molded and cured for testing. The specimen was immersed in a tank of water maintained at 160°F. The sample was tested daily for the first week and once each week thereafter. The sample was removed from the water for testing, blotted with an absorbent towel, and weighed. The increase in weight was calculated as absorbed water.

$$\text{Water Absorption, \%} = \frac{\text{Weight gain, g.} \times 100}{\text{Weight of Sample, g}}$$

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The water absorbed by each resin is shown in Table 4. The amount of water absorbed by the urethanes appears to be a function of the calculated oxygen content of the resins. The calculation is based upon the molecular weight and an assumed structure of the polymer and the amount of curing agent given in Table 3. Figure 7 shows a plot of the oxygen content of the ether-based resins versus log of the percent water absorbed. According to this data the alkane-based urethane should absorb less than 0.1 percent water. The amount found experimentally varied from 0.0 to 0.9 percent. There is probably some experimental error due to incomplete removal of surface moisture from the test specimen. This error would be more significant for the alkane-based urethanes which absorb very little moisture.

TABLE 4. WATER ABSORPTION OF CURED URETHANE

Urethane Polymer	Molecular Weight	Oxygen Content (%)	Water Absorption, Max. (%)
1, 12-Dodecane DI ^a	552	18.4	0.0
400 - DI ^b	729	28.0	3.2
Telagen-S 3HPL-186L-DI ^a	765	14.0	0.9
600 - DI ^b	881	29.2	13.6
1000 - DI ^b	1322	31.4	30.7
1540 - DI ^b	1799	32.7	76.4
Telagen-S A 595 88-DI ^a	2126	5.7	0.5
NBP 129001 ^b	2737	4.5	0.0
4000 - DI ^b	3347	34.4	225.9
Telagen-S 3HPL-185M-DI ^a	4377	2.9	0.6

- a. Alkane Based Urethane
- b. Ether Based Urethane

The ether-based urethanes initially gain weight when immersed in water. The absorbed water promotes bond cleavage and degradation of the urethane. There is simultaneous gain in weight due to absorption of water and loss in weight due to degradation of the polymer. This is another source of experimental error in measuring absolute values for water absorption. However, the general trend of the absorption curve in Figure 7 would still be valid.

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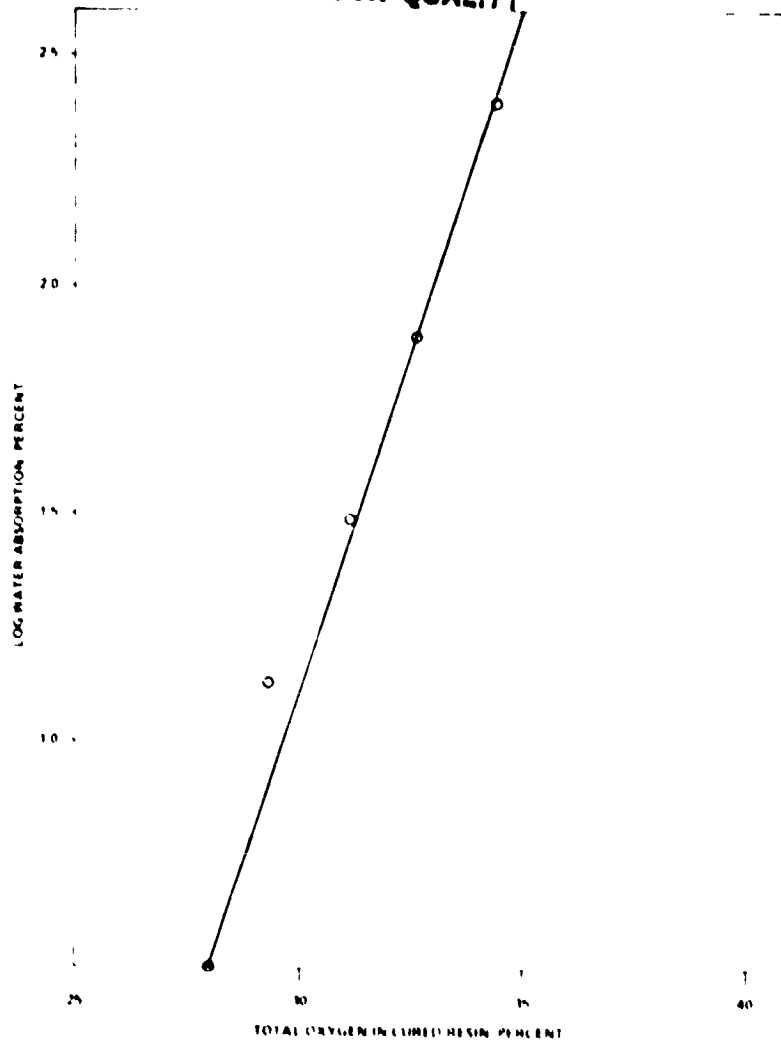


Figure 7. Oxygen content of urethane versus percent water absorbed.

B. Effect of Water on Hardness of Cured Urethanes

If the urethanes absorb water, the urethane bond will be more susceptible to cleavage. If the polymer bond is broken, the resin would become soft and tacky. Thus, hardness change can be used as an indication of hydrolytic attack.

A 4-in. disc of each polymer was molded and cured for testing. The specimen was immersed in a tank of water maintained at 160°F and tested on a weekly basis initially. The specimen was removed from the water and dried in a vacuum oven at 120°F for 24 hr. The sample was then cooled and the hardness was determined with a Shore Durometer, Hardness Type A-2 manufactured by the Shore Instrument Company.

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The more readily the urethane absorbs water (Table 4), the more susceptible the urethane bond should be to cleavage, and the more rapidly the resin should soften. This is shown in Table 5. The ether-based 4000-DI became too soft and tacky for a hardness measurement in 2 days, 1540-DI in 28 days, 1000-DI in 32 days, and 600-DI in 49 days. The resin 400-DI was not softened after being exposed to high temperature/humidity for 256 days when it was vacuum dried before testing. However, the hardness dropped from an initial hardness of 94A to 47A when the hardness was measured with only the surface moisture removed. This indicates the specimen was plasticized by some absorbed moisture. Table 4 shows that 400-DI absorbs the least water of the ether-based urethanes tested.

TABLE 5. EFFECT OF WATER ON HARDNESS OF CURED URETHANES

Urethane Polymer	Oxygen Content, Percent	Test Duration ^a , Days	Shore Hardness, Type A	
			Dry ^d	Wet ^e
1, 12 Dodecane DI ^a	18.4	0	91	
		240	93	92
Telagen S 3HPL 186I DI ^a	14.0	0	96	
		221	96	95
Telagen S A595 88 DI ^a	5.7	0	57	
		221	59	55
NBP 129004 ^a	4.5	0	52	
		256	54	50
Telagen S 3HPL 185 M DI ^a	2.9	0	53	
400 DI ^b	28.0	0	94	
		256	95	47
600 DI ^b	29.2	0	50	
		49	10	
1000 DI ^b	31.3	0	39	
		32	10	
1540 DI ^b	32.7	0	31	
		28	11	
4000 DI ^b	34.4	0	95	
		2	11	

- a. Alkane based urethanes
- b. Ether based urethane
- c. Sample immersed in water at 160°F
- d. Dried in vacuum oven for 24 hours at 120°F
- e. Surface moisture removed by blotting

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The alkane-based urethanes showed no significant drop in hardness after being immersed in water at 100%. Hardness measurements on the wet samples indicate very little plasticizing effects due to absorbed moisture. Hardness measurements show no deterioration of the alkane-based urethane due to high humidity. Teligen-S 3HPL-185-M-DI melted at test temperature and hardness measurements could not be made. The ether-based urethanes, with the exception of 400-DI, reverted to viscous liquids.

C. Water Vapor Transmission Rates

Urethane conformal coatings have been utilized for many years on printed circuitry as a seal against hostile environments, including moisture. However, accelerated testing at high humidity reveals corrosive effects on copper conductor patterns of coated test boards indicating that water permeates the polymeric film.

The water vapor transmission rate through polymeric materials occurs by three steps. First, the water "dissolves" in the permeable polymeric film on the side of high permeant concentration. It then diffuses slowly through the film toward the side of lower permeant concentration. Finally the permeant desorbs on the side of the lower concentration. The permeant transport rate through the film is an exponential function of temperature and is also influenced greatly by the chemical interaction between permeant and barrier material. The driving force for any permeant through a polymeric film is a concentration gradient of the permeant across the film. In the experimental measurements described in this report, mass transport was detected by weight change. The water transmission rate (R) carries the following dimensions:

$$R = \frac{MT}{tA}$$

where

M = mass of water transported, g

T = film thickness, mm

t = time interval, day

A = film area, cm².

The value of R is not a true constant for the polymer film, and it is used in this study for relative ranking.

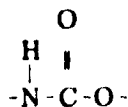
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The relative water transmission rates through film prepared from the urethane resins were determined using the Fisher-Payne permeability cup. This device consists of a shallow flanged cup with a matching flat ring. The cup was loaded by placing 10 ml distilled water in the reservoir. The test film was cut as a circle having the same diameter as the outer diameter of the flange. The film was placed on the flanged cup and the matching flat ring was set in place and secured to the cup flange by three equally spaced clamps. An initial weight of each loaded cup was obtained using an analytical balance, and the cup was placed in a desiccator containing indicating drierite, a very efficient desiccant. After a period of time the cup was reweighed. The loss in weight represented the mass of water transported through the film. The water transmission rate of the urethane was calculated according to the relationship given for R. All tests were conducted at 30°C.

Water vapor transmission rates for the cured urethane are given in Table 6. The resins that absorbed the greatest amount of water also had the highest transmission rates. This is an expected result since one of the steps in water transmission through film requires that the water "dissolve" in the polymeric film. The transmission rates for the ether-based urethanes are a function of the oxygen content of the resin. This is shown in Figure 8. These data indicate that the alkane-based urethanes should have a transmission rate less than 0.2 at 30°C. The rates found experimentally varied from 0.18 to 0.31. Factors other than oxygen content of the resin could contribute to the transmission rate. However, the protection of the circuitry from water by a urethane coating will depend upon the structure of the polymer. Best protection is offered by urethane with the lowest percent of ether oxygens.

D. Weight Loss of Cured Urethanes in Water

Urethanes are characterized by the carbamate linkage



which is subject to hydrolytic degradation. Urethane elastomers have been known to revert to liquids or semi-liquids upon exposure to a combination of high temperature and humidity. The rate of degradation depends upon the susceptibility of the carbamate group to hydrolytic attack. The ether group in the structure of the ether-based urethanes is resistant to hydrolysis. However, this group can interact with the protons of water to form hydrogen bonds. This hydrogen bonding of water to the urethane molecule makes the carbamate group more susceptible to hydrolytic attack, and cleavage of carbamate bonds results in the formation of low molecular weight liquids. These species are leached out of

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**TABLE 6. WATER VAPOR TRANSMISSION RATES THROUGH
CURED URETHANE FILM AT 30°C**

Urethane Polymer	Molecular Weight	Oxygen Content (%)	Transmission rate, g. xmm ² day xcm ²
1, 12-Dodecane-DI ^a	552	18.4	0.18
400-DI ^b	729	28.0	3.0
Telagen-S 3HPL-186L-DI ^a	765	14.0	0.25
600-DI ^b	881	29.2	9.8
1000-DI ^b	1322	31.4	73.8
1540-DI ^b	1799	32.7	294.
Telagen-S A595-88-DI ^a	2126	5.7	0.23
NBP 129001 ^a	2737	4.5	0.31
400-DI ^b	3347	34.4	c.
Telagen-S 3HPL-185-M-DI ^a	4377	2.9	0.23

- a. Alkane Based Urethane
- b. Ether Based Urethane
- c. Film Dissolved

the resin by water with a resulting loss in weight in the resin. Urethanes prepared from long chain, hydroxy-terminated saturated hydrocarbon prepolymers are non-polar, provide no hydrogen bonding, are more hydrophobic than polyethers, and should shield the hydrolytically sensitive carbamate linkage from moisture more readily.

Two and four-inch discs were molded of each material and cured for testing. The specimens were immersed in a tank of water maintained at 160°F and tested on a weekly basis initially. The samples were removed from the water and dried in a vacuum oven at 120°F for 24 hr. The samples were then cooled and weighed. The weight loss was expressed as a percent of the sample weight.

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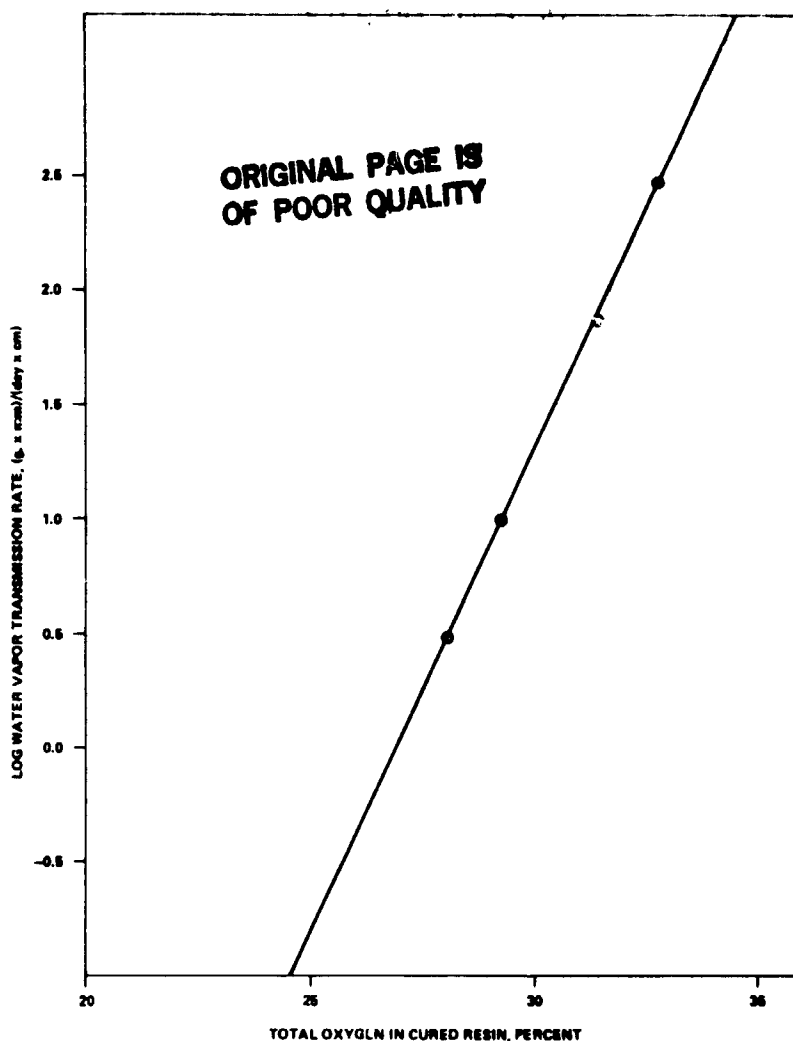


Figure 8. Oxygen content of urethane versus water vapor transmission rate.

Degradation of the ether-based urethanes is shown in Figure 9 and that of the alkane-based urethanes in Figure 10. After a sharp loss in weight the first 10 to 20 days of exposure, the specimens lost weight at a constant rate over the test period. This rate of weight loss is shown in Table 7. Five ether-based and five alkane-based urethanes were tested. The highest molecular weight ether-based urethane, 4000-DI, dissolved completely and rate data were not obtained. No weight loss was detected for the highest molecular weight alkane-based urethane, Telagen-S 3HPL-185M-DI. There was some lack of precision in measuring the very small rates for the alkane-based urethanes. However, considering these limitations, Figure 11 indicates that the rate of weight loss by the urethanes in water at 160°F is a function of the oxygen content of the resins. The ether-based urethanes, especially the higher molecular weight resins containing the greater percent of ether oxygens, were degraded severely. The alkane-based urethanes showed very good resistance to hydrolytic degradation.

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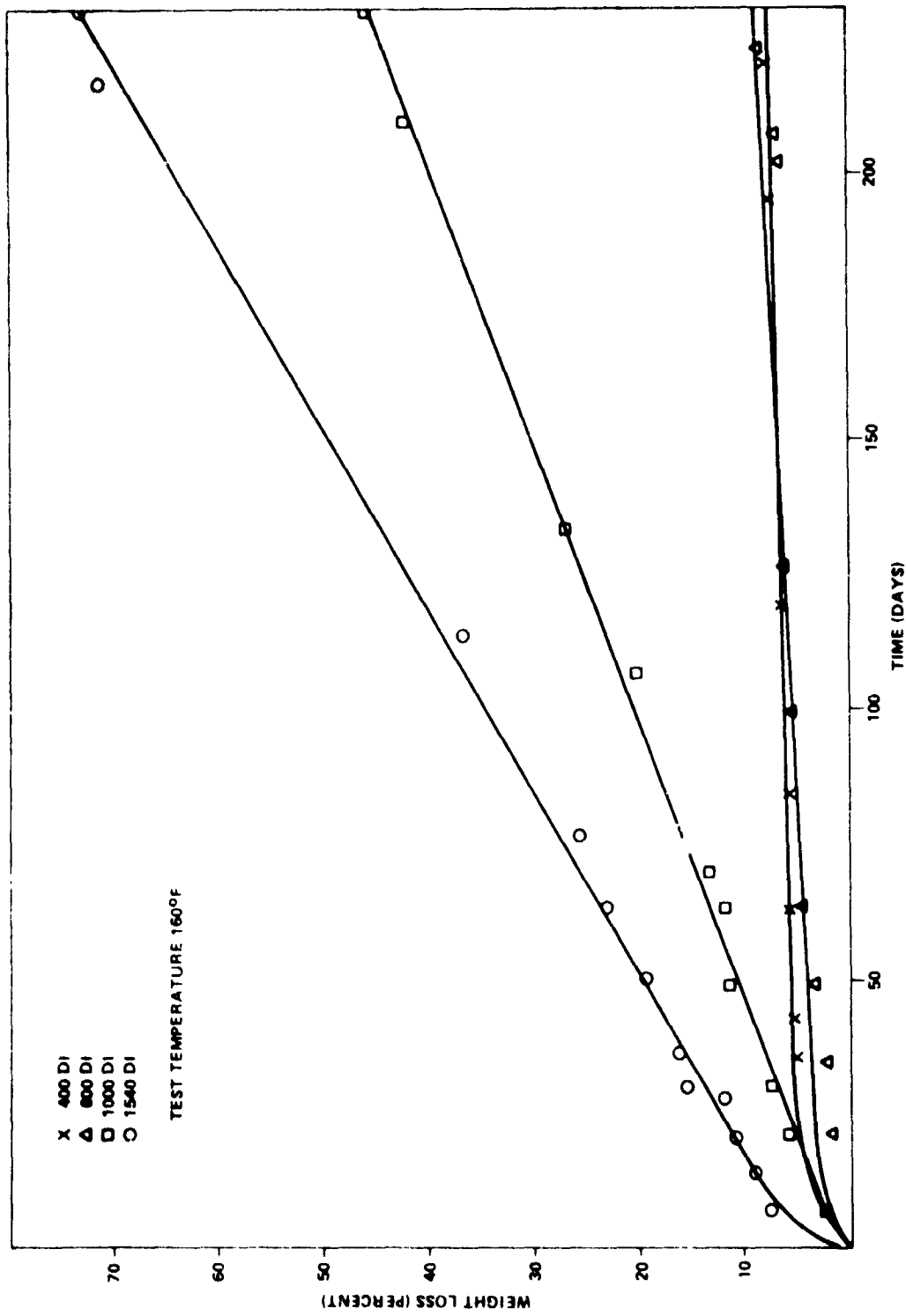


Figure 9. Weight loss of ether-based urethanes in water versus time.

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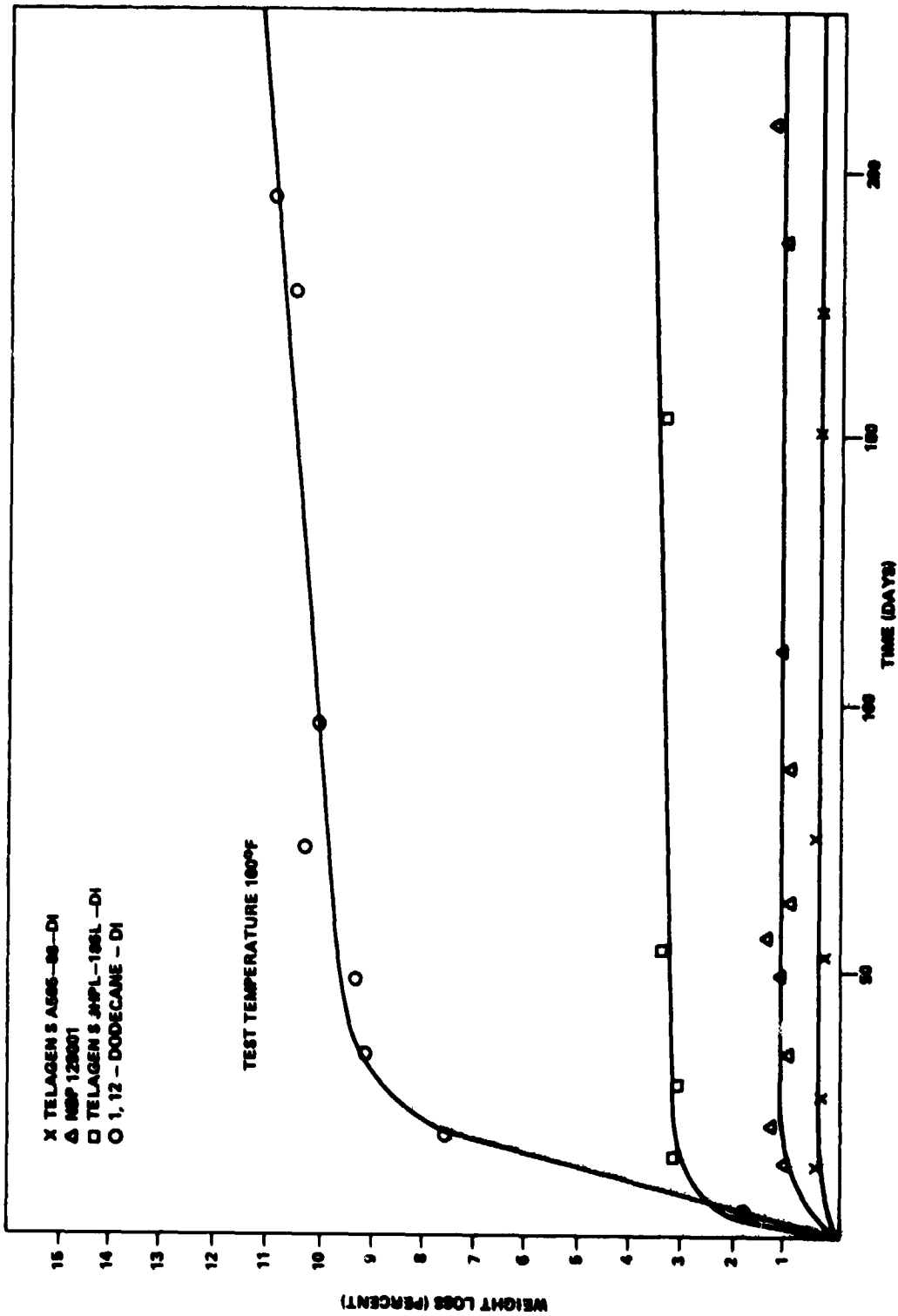


Figure 10. Weight loss of alkane-based urethanes in water versus time.

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TABLE 7. RATE OF WEIGHT LOSS OF URETHANES IN WATER
AT 160°F

Urethane Polymer	Molecular Weight	Oxygen Content (%)	Rate Of Weight Loss (%/day)
1, 12-Dodecane-DI ^a	552	18.4	0.00803
400-DI ^b	729	28.0	0.0132
Telagen-S 3HPL-186L-DI ^a	765	14.0	0.00235
600-DI ^b	881	29.2	0.0227
1000-DI ^b	1322	31.4	0.195
1540-DI ^b	1799	32.7	0.297
Telagen-S A595-88-DI ^a	2126	5.7	0.000167
NBP 129001 ^a	2737	4.5	0.000277
4000-DI ^b	3347	34.4	c
Telagen-S 3HPL 185M-DI ^a	4377	2.9	d

- a. Alkane-Based Urethane
- b. Ether Based Urethane
- c. Sample Dissolved
- d. No Weight Loss Detected

E. Dielectric Properties of Urethanes

Polyurethanes are used as connector potting materials and in formulating conformal coatings for printed circuit boards. A major requirement for these materials is good dielectric properties (low dielectric constant and dissipation factor). MSFC SPEC-515, a specification for urethane molding and potting material, requires a dielectric constant of 5.0 or less and a maximum dissipation factor of 0.09.

2-in. discs, approximately 1/8-in. thick, were molded and cured for testing the experimental materials. The specimens were immersed in a tank of water maintained at 160°F and were initially tested on a weekly basis. The samples were removed from the water and dried in a vacuum oven at 120°F for 24 hr. Dielectric properties were determined at 25°C and 50 percent relative humidity using a General Radio Model 716C Capacitance Bridge, Type 1214M IMC Unit Oscillator, Type 1212 PZ IMC Filter, Type 1203B Power Supply, Type 1212A Null Detector, and Type 1690 Dielectric Sample Holder.

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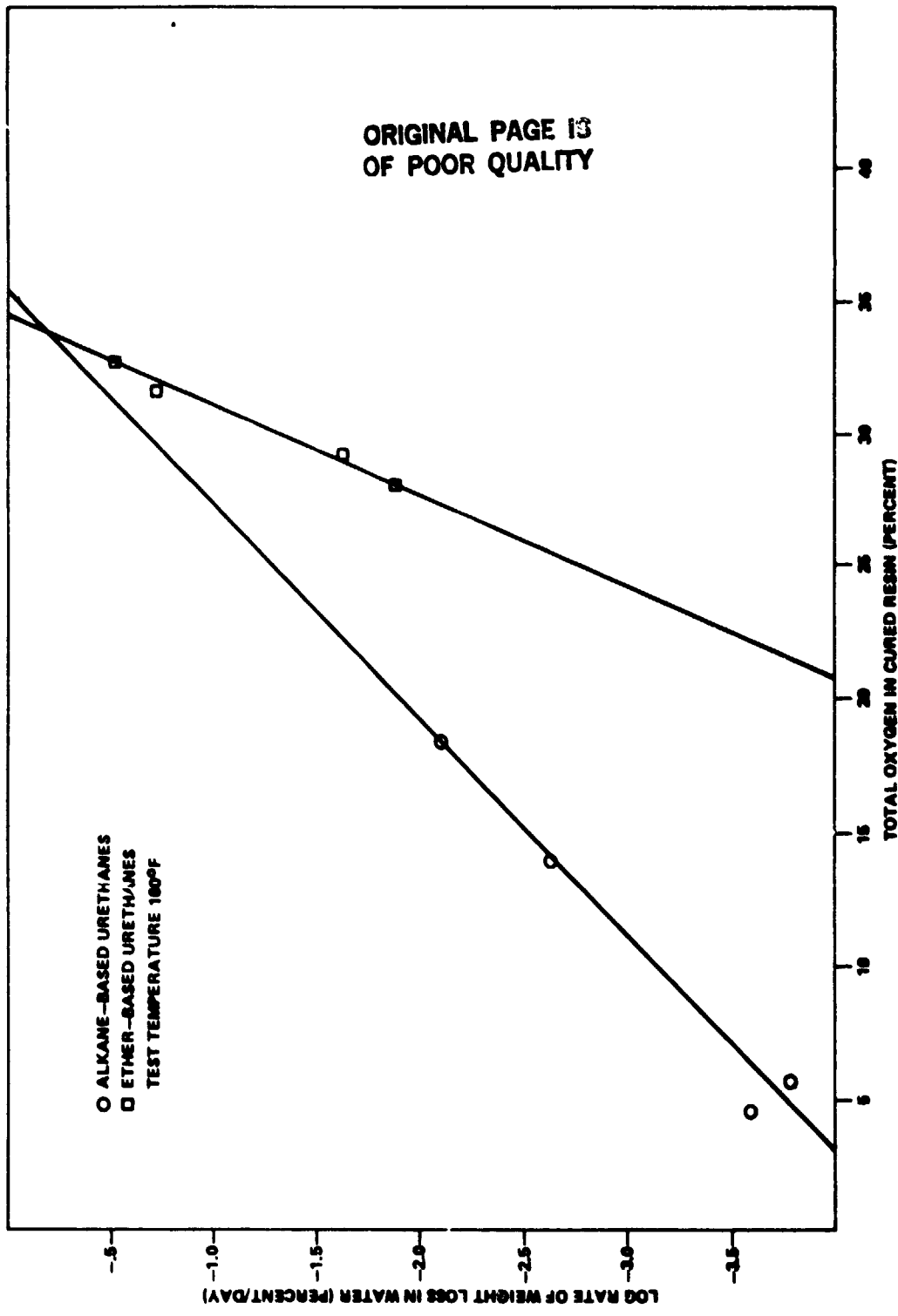


Figure 11. Oxygen content of urethane versus rate of weight loss in water.

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Test results are shown in Table 8. The ether-based urethanes were degraded by hot water at different rates. As the samples became soft and tacky, they were removed from the test cycle. The specimen prepared from the alkane-based urethane, Telagen S 3HPL-185M-DI, was melted and distorted by the hot water. Because of these complications, the duration of the tests varied for the different samples. However, no direct relationship is apparent in Table 8 between the length of time the urethane was immersed in the water and the final dielectric properties of the urethane.

The initial dielectric properties of the alkane-based urethanes are very good and are well within the requirements of MSFC-SPEC-515. The values found were all within a very narrow range and do not appear to be a function of any obvious variation in molecular structure, such as oxygen content or molecular weight. There was no deterioration of the dielectric properties of these samples during the test period except for an unexplained change in the dissipation factor for 1, 12 dodecane-DI.

The initial dielectric properties of the ether based urethanes are poor. Only 400-DI met the requirement of MSFC-SPEC-515. The dielectric constants ranged from 2.9 to 6.9 for these urethanes and varied in loose proportion to the oxygen content of the resin. This relationship, however, indicates that an oxygen content below 20 percent would have little effect. There was some deterioration of the dielectric properties during the test period. However, there is no correlation between the amount of deterioration and the structure of the urethane.

F. Insulation Resistance of Urethane Film

The directions taken in recent years by circuit designers have given rise to new requirements in high resistance materials. Printed circuit board materials and their resistance to environmental conditions, such as humidity and elevated temperatures, can be critical to high-impedance solid-state circuits. MSFC-SPEC-507, a specification for conformal coating materials for printed boards, requires a minimum insulation resistance of 1×10^{12} ohms.

A 30 percent solution of the urethane was prepared in toluene. Y-shaped test patterns were dip-coated to produce a film thickness of 2 to 4 mils and cured. The test patterns were fabricated from 2 oz, single-sided, copper-clad, glass-epoxy laminate and were prepared according to the design requirements of MSFC-SPEC-507. The coated specimens were placed in an environmental chamber maintained at 160°F and 95 percent relative humidity and were initially tested on a weekly basis. Prior to each measurement the samples were removed from the environmental chamber and dried in a vacuum oven at 25°C for 3 hr. Insulation resistance measurements were made using the Hewlett Packard 4329A High Resistance meter shown in Figure 12. In these tests, the test voltage was 500 V and the charge time was 1 min.

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TABLE 8. DIELECTRIC PROPERTIES OF CURED URETHANES

Urethane Polymer	Oxygen Content (%)	Test Duration ^c (Days)	Dielectric Constant 1 Mhz		Dissipation Factor 1 Mhz	
			Initial	Final	Initial	Final
1,12-Dodecane-DI ^a	18.4	194	2.1	1.7	0.06	0.10
Telagen-S 3HPL-186L-DI ^a	14.0	175	2.3	2.2	0.07	0.07
Telagen-S A595-88-DI ^a	5.7	173	2.0	2.0	0.05	0.03
NBP 129001 ^a	4.5	209	2.2	2.2	0.05	0.03
Telagen-S 3HPL-185M-DI ^a	2.9	27	2.0	1.5	0.04	0.06
400-DI ^b	28.0	218	2.9	3.4	0.08	0.06
600-DI ^b	29.2	64	4.7	7.8	0.07	0.14
1000-DI ^b	31.4	25	5.9	5.7	0.11	0.10
1540-DI ^b	32.7	55	6.9	6.2	0.10	0.10
4000-DI ^b	34.4	d	6.9	d	0.08	d
MSFC-SPEC-515 Requirement			5.0 (max.)		0.09 (max.)	

- a. Alkane based urethanes.
- b. Ether based urethanes.
- c. Sample immersed in water at 160°F.
- d. Sample dissolved.

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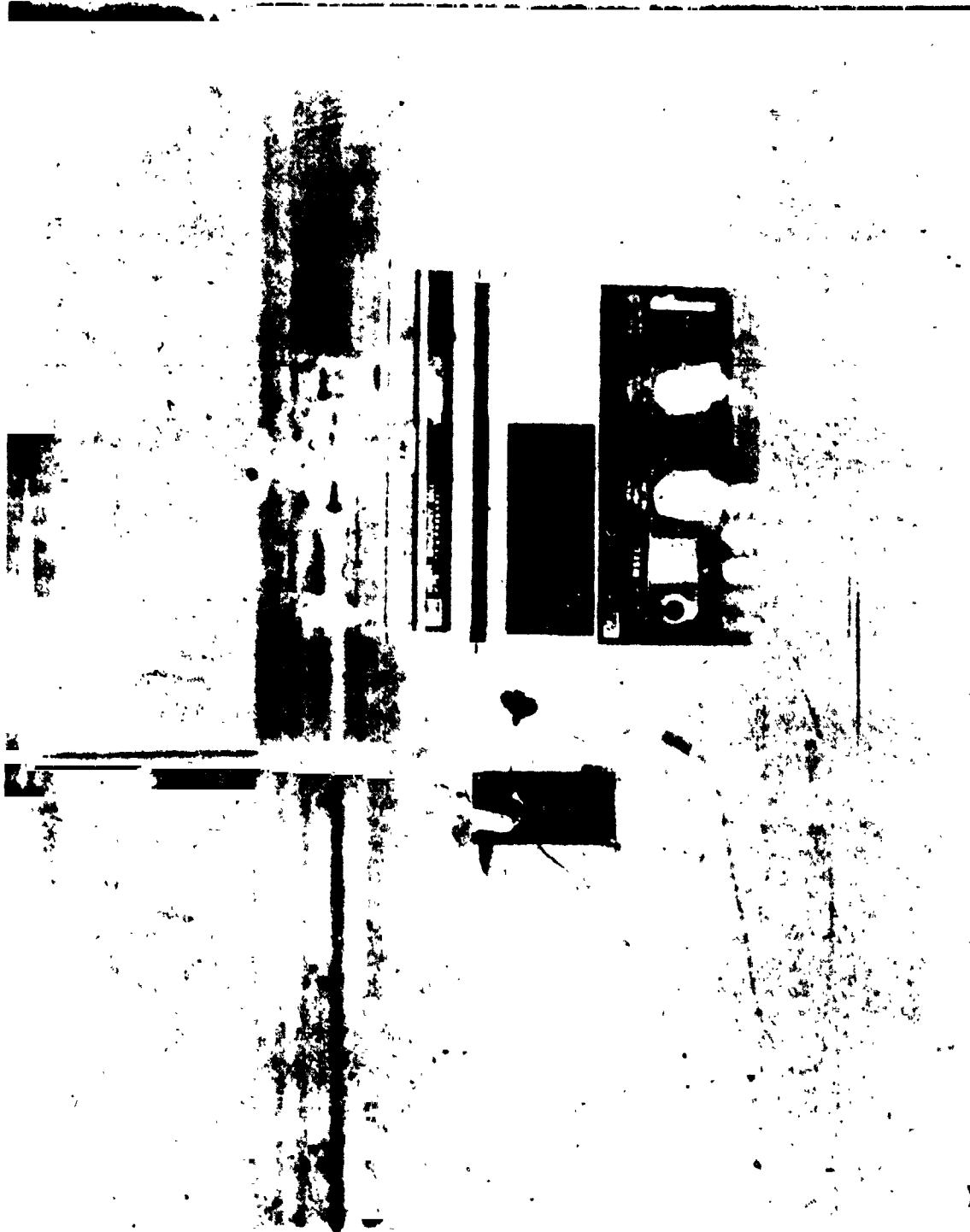


Figure 12. Measurement of insulation resistance of urethane conformal coating material.

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Moisture permeates the urethane film, as shown in Figure 13. The test pattern coated with the ether-based urethane was kept in the environmental test chamber for 153 days at 160°F and 95 percent relative humidity as compared to 159 days for the alkane-based urethane. The copper Y-pattern coated with the ether-based urethane is severely corroded while the one coated with the alkane-based urethane is only slightly damaged. The alkane-based urethane coating would offer much better protection for a printed circuit board in a high humidity/temperature environment.

Insulation resistance values for the two resin types are shown in Table 9. The initial values for the alkane-based urethanes are very good. The initial insulation resistance of the ether-based urethanes, as a group, was lower and would not meet the requirements of MSFC-SPEC-507.

Their resistance varied from 9.0×10^{12} ohms for 400-DI (28 percent oxygen) to 3.8×10^9 ohm for 4000 DI (34.4 percent oxygen), but this relationship (resistance versus oxygen content) was not consistent or well defined. After the specimens were exposed to the high temperature/humidity conditions for 60 days, there was no significant difference between the insulation resistance of the two groups.

G. Surface and Volume Resistivity of Urethane Polymers

Resistivity (per unit area or volume) measurements occupy a specialized place in the field of insulation testing. Strict requirements are necessary to prevent problems in solid state circuit design. MSFC-SPEC-515, a specification for urethane molding and potting material, requires a minimum surface resistivity of 1×10^{12} ohms and a minimum volume resistivity of 1×10^{12} ohm-cm.

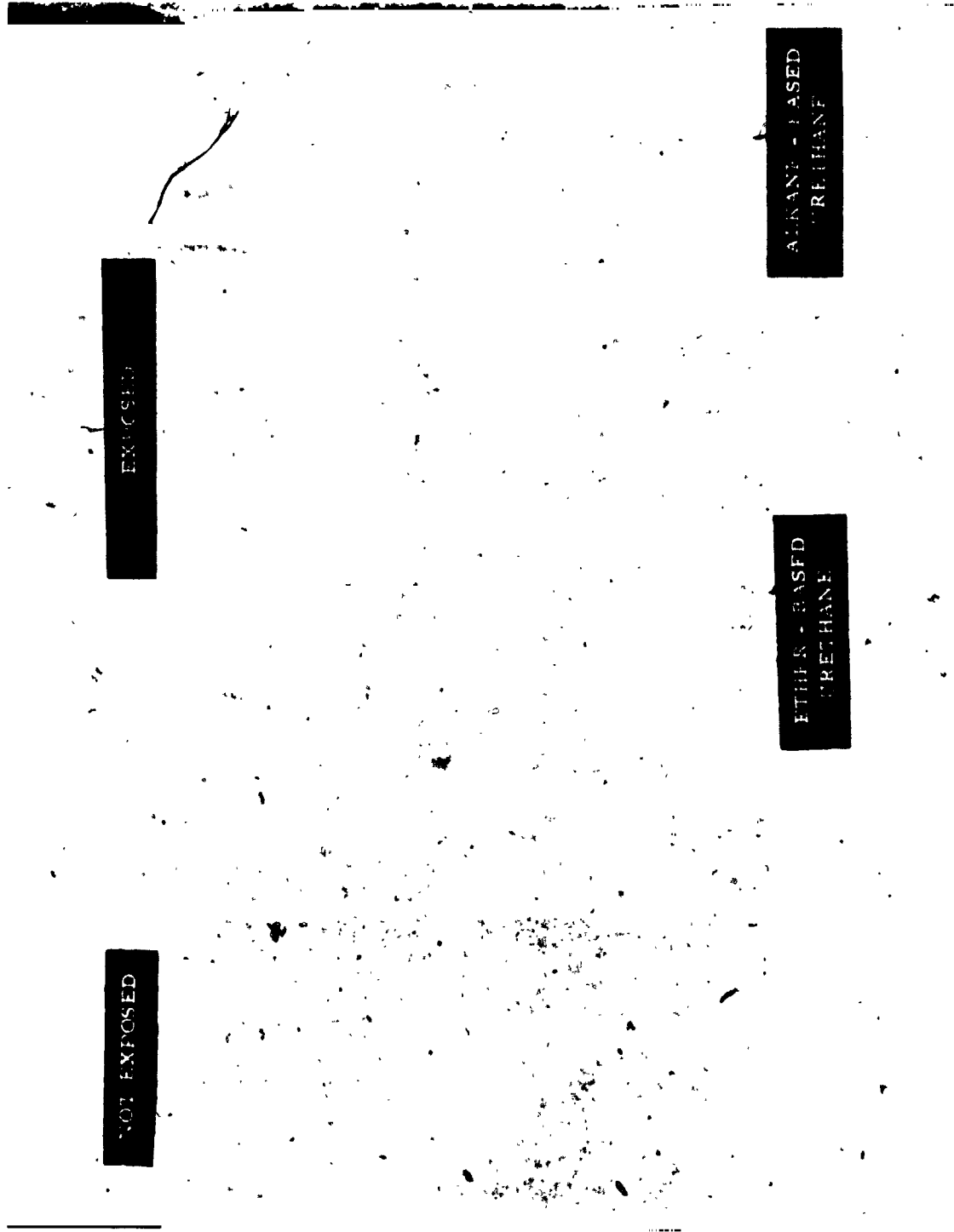
4-in. discs, approximately 1/8-in. thick, were molded and cured for testing each material. The specimens were immersed in a tank of water maintained at 160°F and were initially tested on a weekly basis. The samples were removed from the water and dried in a vacuum oven at 120°F for 24 hr. Surface and volume resistivity measurements were made using the Hewlett Packard 4329A High Resistance meter and 16008A Resistivity Cell shown in Figure 12. In these tests, the test voltage was 500 V and the charge time was 1 min.

The test technique is to apply the test voltage to the sample in such a way as to distribute the potential over both sides (volume) or one side (surface) of sheet samples of the urethanes. Resistivity values are calculated from the size of the electrode and the dimensions of the sample.

Surface resistivity is defined as the ratio of potential gradient parallel to the current along a surface to the current per unit width of the surface. The 4329A meter readings are converted to resistivity quantities using the following expression (derived from the dimensions of the 16008A electrodes):

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NOT EXPOSED

EXPOSED

ETHER-BASED
URETHANE

ALKANE-BASED
URETHANE

Figure 13. Corrosion of urethane coated copper test patterns in high temperature/
humidity environments.

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TABLE 9. INSULATION RESISTANCE OF URETHANE FILM

Urethane Polymer	Oxygen Content (%)	Insulation Resistance (Ohms)	
		Initial	After 60 days ^c
1,12 - Dodecane - DI ⁱⁱ	18.4	8.1×10^{14}	1.7×10^8
Telagen S 3HPL- 186L - DI ⁱⁱ	14.0	1.8×10^{13}	3.5×10^8
Telagen S A595 - 88 - DI ⁱⁱ	5.7	9.0×10^{14}	3.9×10^8
NBP 129001 ⁱⁱ	4.5	9.0×10^{13}	1.9×10^9
Telagen-S 3HPL - 185 M - DI ⁱⁱ	2.9	1.7×10^{12}	1.0×10^9
400 - DI ^b	28.0	9.0×10^{12}	5.7×10^9
600 - DI ^b	29.2	3.8×10^{11}	1.6×10^{10}
1000 - DI ^b	31.4	6.9×10^9	3.0×10^8
1540 - DI ^b	32.7	5.0×10^9	3.2×10^8
4000 - DI ^b	34.4	3.8×10^9	4.4×10^8
MSFC - SPEC - 507 Requirement		1×10^{12} (min.)	

- a. Alkane based urethane.
- b. Ether based urethane.
- c. Immersed in water at 160°F.

$$\sigma = 18.8 R_g$$

where

σ = surface resistivity in ohms

R_g = indicated surface resistance in ohms.

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Volume resistivity is defined as the ratio of the potential gradient parallel to the current in the material to the current density. Thus, calculation of volume resistivity figures was done with the following formula:

$$\rho = \frac{19.6}{t} R_v$$

where

ρ = volume resistivity in ohm-cm

t = sample thickness in cms

R_v = indicated volume resistance in ohms.

Test results are shown in Table 10. The ether-based urethanes were degraded by hot water at different rates. As the samples became soft and tacky, they were removed from the test cycle. The specimen prepared from the alkane-based urethane, Telagen-S 3HPL-185M-DI, was melted and distorted by the hot water. Consequently, not all of the samples were tested for the 150-day maximum.

The initial resistivity of the alkane-based urethanes was excellent and exceeded the requirements of MSFC-SPEC-515. Volume resistivity dropped about a decade and surface resistivity dropped from 1 to 3 decades over a 150-day test period. However, the values still exceeded those required by MSFC-SPEC-515.

The initial resistivity of the ether-based urethanes varied from 10^{11} to 16^{16} ohms and 10^{10} to 10^{15} ohm-cm. Generally, the urethane with the lesser oxygen content had better resistivity values, but this relationship was not consistent or well defined. Deterioration of the resistivity of the ether-based materials after exposure to high humidity/temperature conditions was not significantly greater than that of the alkane-based materials.

It was concluded that the alkane-based urethanes have excellent surface and volume resistivity, and retain these good properties after exposure to the high humidity/temperature conditions.

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SURFACE AND VOLUME RESISTIVITY OF
URETHANE POLYMERS

Sample No.	Dry-ness Content (%)	Test Duration ¹ (Days)	Resistivity	
			Surface (ohm-cm)	Volume (ohm-cm)
101	18.4	0	8.1×10^{11}	2.3×10^{16}
		10	5.8×10^{15}	3.1×10^{16}
		20	8.0×10^{15}	1.1×10^{16}
		150	9.4×10^{11}	1.1×10^{15}
102	11.9	0	1.1×10^{17}	1.9×10^{16}
		10	8.7×10^{16}	1.6×10^{16}
		20	8.1×10^{16}	1.1×10^{16}
		150	1.7×10^{15}	6.6×10^{15}
103	6.4	0	4.5×10^{16}	2.7×10^{16}
		10	2.7×10^{16}	2.1×10^{16}
		20	1.7×10^{15}	1.6×10^{16}
		150	7.1×10^{13}	2.1×10^{15}
104	1.5	0	3.8×10^{16}	1.9×10^{16}
		10	1.3×10^{15}	1.2×10^{16}
		20	1.6×10^{15}	1.0×10^{16}
		150	7.0×10^{13}	1.5×10^{16}
105	1.9	0	6.6×10^{16}	1.8×10^{16}
		10	2.4×10^{16}	8.5×10^{15}
		20	5.6×10^{16}	2.9×10^{16}
		150	7.3×10^{16}	2.3×10^{16}
106	28.0	0	2.4×10^{16}	8.5×10^{15}
		10	5.6×10^{16}	2.9×10^{16}
		20	7.3×10^{16}	2.3×10^{16}
		150	7.2×10^{11}	1.1×10^{16}
107	20.2	0	1.0×10^{13}	9.4×10^{11}
		10	6.7×10^{12}	3.6×10^{13}
		20	1.2×10^{11}	5.9×10^{13}
108	31.1	0	2.6×10^{11}	1.8×10^{11}
		10	3.7×10^{11}	2.2×10^{11}
109	33.4	0	6.8×10^{11}	1.1×10^{10}
		10	5.1×10^{11}	3.8×10^{10}
		20	9.1×10^{11}	8.2×10^{10}
110	31.1	0	2.4×10^{12}	8.5×10^{12}
		10	1.0×10^{12} (corr.)	1.0×10^{12} (corr.)

H. Ozone Resistance

Urethanes prepared from polybutadiene are known to have excellent dielectric properties and are hydrolytically stable. However, when these materials are placed under stress and exposed to ozone, they deteriorate because ozone attacks the double bond in the butadiene structure and severs the polymer chain. Ether-based urethanes are oxidatively stable but are not hydrolytically stable and do not have the excellent dielectric properties of the butadiene-based urethanes. The alkane-based urethanes are prepared from hydrogenated polybutadiene prepolymers. Since the double bond has been removed from the polymer chain, there is no point of attack for the ozone. The saturated alkane-based urethanes should be oxidatively stable while retaining hydrolytic stability and excellent dielectric properties.

All test specimens and a commercially available butadiene-based urethane were tested for resistance to ozone. Dumbbell specimens were molded from each type of urethane. These specimens were mounted in a frame under stress. The frame and specimens were exposed for 7 days to an ozone concentration of 50 parts per 100 million parts air at 38°C. At the end of the exposure time the specimens were examined for cracks. Figure 14 compares an unexposed dumbbell of each type of urethane with one that has been exposed to ozone. The butadiene-based urethane which was exposed to ozone was cracked and severely deteriorated. The ether and alkane-based urethanes were not damaged. Both the ether-based and the alkane based urethanes are oxidatively stable.

IV. CONCLUSIONS

Because of the non-polar nature of the hydrocarbon backbone in the prepolymer, alkane based urethanes were found to be superior to their ether counterparts with respect to hydrolytic stability and electrical properties. Commercially available urethanes are usually based on some type of polyether.

High temperature/humidity conditions had very little effect on the physical properties of the alkane based urethanes. Water vapor transmission rates through film prepared from the urethane were very low as compared to that for the ether based urethanes. The alkane based materials absorbed little or no water, and showed very little weight loss in water at 160°F.

The hydrophilic ether based urethanes swell and absorb water and their films have relatively high water vapor transmission rates. The materials lost weight when immersed in water at 160°F. The highest molecular weight (greatest number of ether oxygens) resin dissolved completely in water. Four of five specimens reverted to a liquid or semi-solid. The resistance to water of the ether-based urethanes varied from fair for the resin lowest in ether oxygen content to poor for the one highest in ether oxygen content.

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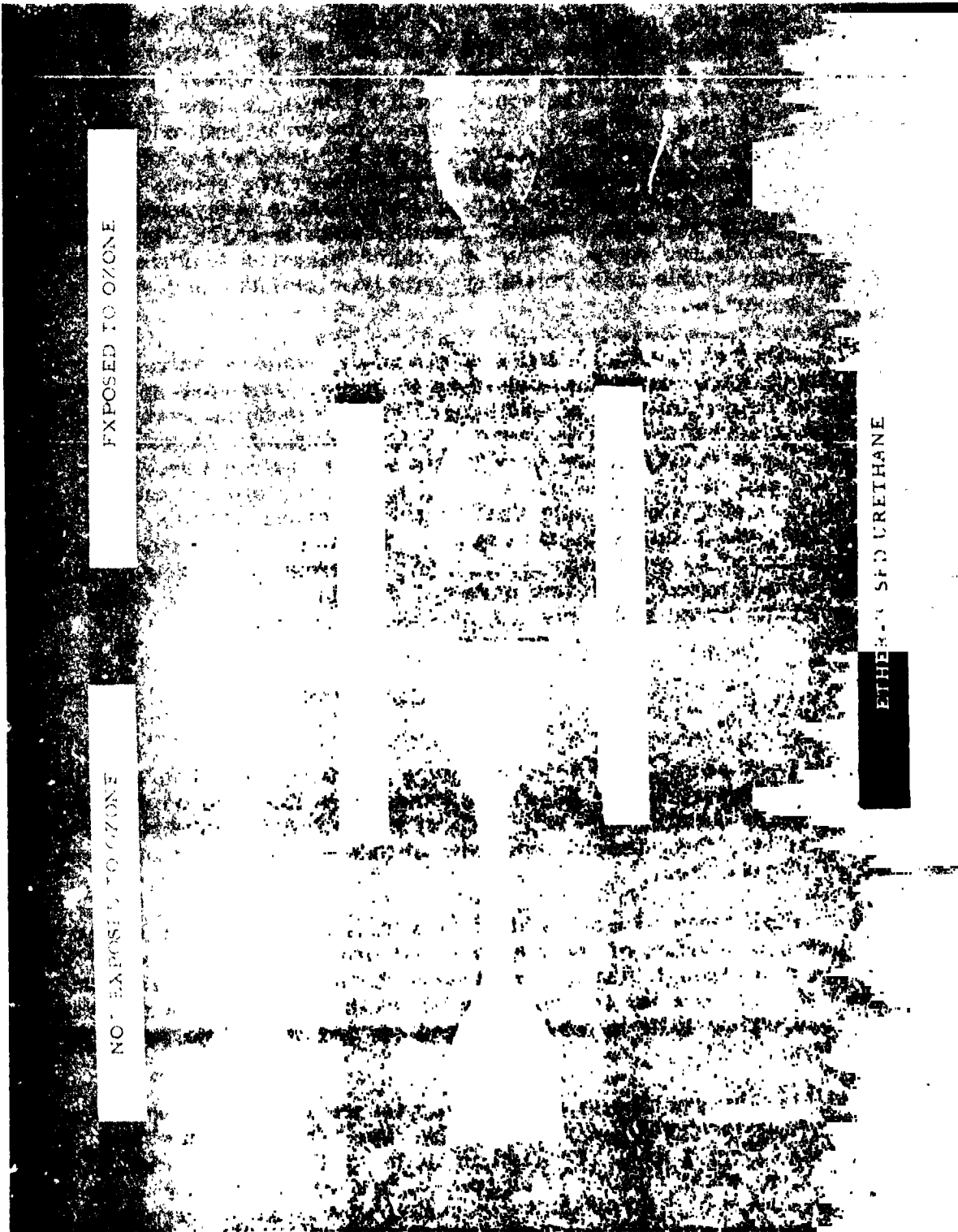


Figure 14. Resistance of urethanes to ozone.

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The initial electrical and dielectric properties of the alkane-based urethanes were very good. In all instances, for those properties tested, the values exceeded the requirements of current MSFC specifications for potting compounds and conformal coatings. Except for insulation resistance (for conformal coatings), the properties were still very good after the specimens had been immersed in water at 160°F for as many as 200 days. The dielectric properties of the ether-based urethanes varied from poor for the high molecular weight urethanes to good for the low molecular weight resins. Generally there was greater deterioration of the dielectric properties of the ether-based urethanes after exposure to hot-humid conditions than for the alkane-based urethanes.

The alkane-based urethanes were found to be oxidatively stable in contrast to the commercially available urethanes based on polybutadiene. Butadiene-based urethanes have excellent dielectric properties. The alkane-based urethanes have retained these excellent dielectric properties of the butadiene-based urethanes, but do not suffer from the oxidative instability common to the latter. The hydrolytic stability of the alkane-based urethanes is also superior to that of the ether-based materials.

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