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DEVELOPMENT OF IMPROVED STERILIZABLE POTTING COMPOUNDS AND CONFORMAL COATINGS FOR SPACE APPLICATIONS

NORMAN BILOW

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FOREWORD

This summary report was prepared by the Hughes Aircraft Company under the National Aeronautics and Space Administration Contract NAS 8-5499. The program was administered by the Materials Division, Propulsion and Vehicle Engineering Laboratory, George C. Marshall Space Flight Center. Mr. William J. Patterson served as the contracting officer's Technical Representative.

Dr. Norman Bilow, Hughes Senior Staff Chemist and Head of the Chemical Synthesis Group, was the principal investigator. He was closely assisted by Dr. Stuart B. Eglin, Mr. Raymond E. Lawrence, Mr. Kenneth Rose, and Mr. Raymond F. Murphy in Materials Synthesis. Dielectric properties data were obtained from the Hughes Components Department, Components and Materials Laboratory, and from Mr. Philip Crepeau. Dr. Charles Escoffery, utilizing the Hughes Computer Center, provided microwave test results. Physical test data was provided by Mr. James Cowan and ethylene oxide sterilization measurements by Mrs. Diana Fraser.

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INTRODUCTION

The purpose of this program was to develop sterilizable electronic embedment materials and conformal coatings suitable for use in an aerospace environment. Many materials which are appropriate for use on earth are virtually useless in outer space. Reasons for this are numerous. Often the materials outgas seriously under the high vacuum of space. This may be accompanied by matrix embrittlement as well as by recondensation of volatilized gases on other spacecraft components, thus causing them to fail. Condensation type polymers are especially susceptible to this type of problem. In some cases, commercial prepolymers may be pretreated under high vacuum to remove their volatile fractions; however, this treatment often leaves the materials too viscous to process easily.

Potentially wide temperature variations in space coupled with the need for heat sterilization capability also limit the selection of candidate materials. An appropriate use temperature range appears to be -60°C to 150°C. At the lower temperature many polymeric materials become brittle due to their high glass transition temperatures, whereas at the upper temperature many polymers tend to degrade, both physically and chemically. This is especially true of the completely aliphatic polymers which, incidently, tend to have the best dielectric properties.

The program covered herein includes both the synthesis of new polymers and their evaluation. Commercial materials were not evaluated to any degree during the current program since they were very extensively screened during a prior year's work. However, commercial products such as Epon X24 (an epoxy prepolymer) and Adiprene L315 (an isocyanate prepolymer) were used extensively as standards in the evaluation of newly synthesized amines or polyols, respectively.

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SUMMARY AND CONCLUSIONS

Synthesis procedures have been developed for the preparation of 1,3-bis(p-epoxypropylphenyl)tetramethyldisiloxane, the meta isomer of this compound, and various analogous diepoxy compounds of higher molecular weight. Cured epoxysilicones of this type show considerable promise as both potting compounds and conformal coatings useful over a wide temperature range. The most difficult phase of this investigation was the development of epoxidation procedures capable of providing good yields of fully epoxidized compounds having a high degree of purity. This objective was attained through the development of a trifluoroperacetic acid epoxidation process. Temperatures and stoichiometry for the epoxidations are, however, highly critical.

Trifunctional silazanes such as phenyltris(ethylamino)silane, vinyltris(hexylamino)silane and other homologous compounds have been found to be excellent curing agents for epoxy resins. Such resins have excellent dielectric properties below 100°C. The extremely low viscosities of these curing agents enable them to be formulated with epoxy resins and fillers to provide easily cast composites. Silica microballoon filled composites have also been found to outgas very little (1 percent maximum) in high vacuum; furthermore, the outgas products were found to be noncondensable at ambient temperature. Moisture resistance of the cured resins was excellent at ambient temperature although at 100°C only those cured with silazanes having long aliphatic groups were excellent. Cured resins of this type also had excellent physical properties.

N-Methylaniline formaldehyde condensation products have also been found to be excellent curing agents for epoxy resins. The dielectric performance of these resins depends greatly upon the molar ratio of N-methylaniline to formaldehyde used in the aniline formaldehyde preparation. Ratios of 2:1 through 1.30:1 respectively have been studied. The highest ratios are of little value but the lower ratios provide curing agents which yield cured epoxides with stable dielectric properties between 25°C and 150°C. Dielectric constants have varied

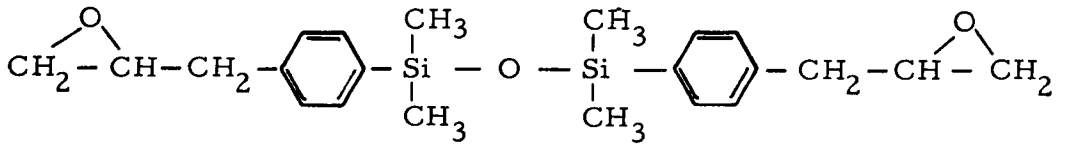
from 4.0 to 4.2 in this temperature range while dissipation factors varied from 0.005 to 0.007. The cured resins also have excellent physical properties, are easily sterilized with ethylene oxide-Freon mixture, and outgas very little (0.1 percent) in high vacuum (10^{-6} torr). Filled resins are rather viscous, however, and are preferably cast using vacuum impregnation techniques.

Various types of siloxypolyols have been made by the condensation of either trimethylolpropane or 1,4-bis(hydroxymethyl)diphenyloxide with diphenyldiethoxysilane, methylphenyldiethoxysilane, or phenyltriethoxysilane. Siloxyurethanes derived from these siloxypolyols often were tough elastomers or strong resins. Their dielectric properties were, however, never sufficiently good to meet the objectives of this program.

1. EPOXYSILICONES

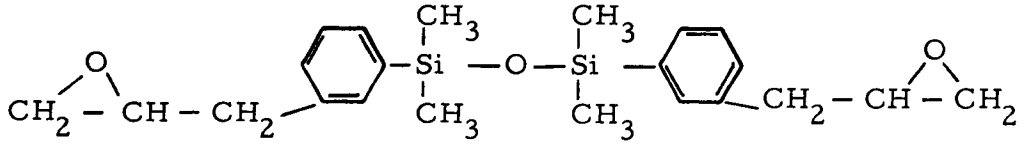
DISCUSSION

Efforts made to develop epoxysilicones suitable for conformal coating applications were directed toward the synthesis of 1,3-bis-[p-(2,3-epoxypropyl)phenyl]tetramethyldisiloxane, the homologous meta isomer, and several analogous higher molecular weight siloxanes. Structures of these various compounds are shown below:



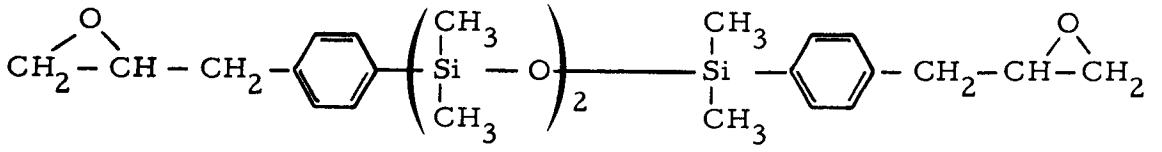
1,3-bis[p-(2,3-epoxypropyl)phenyl]tetramethyldisiloxane

I



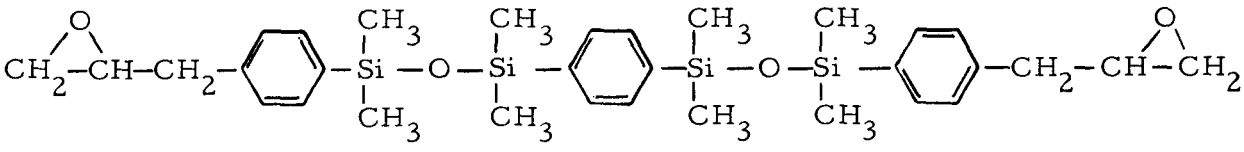
1,3-bis[m-(2,3-epoxypropyl)phenyl]tetramethyldisiloxane

II



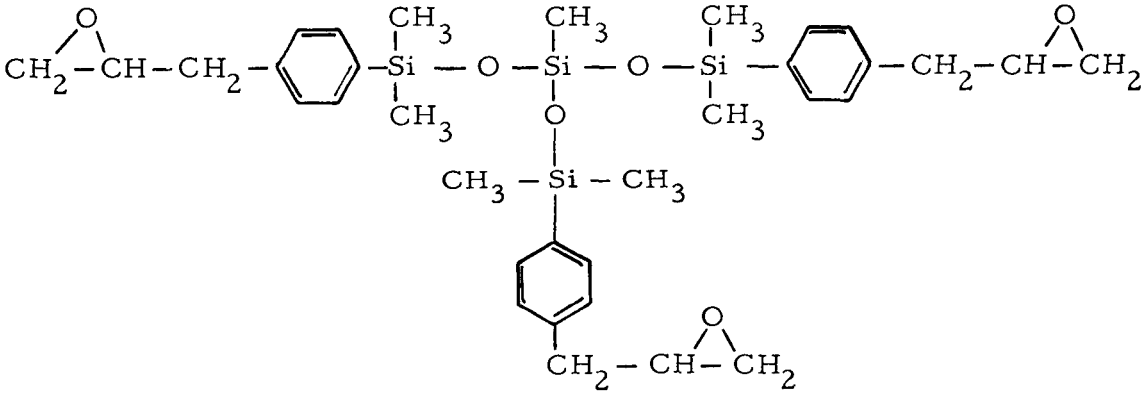
1,5-bis[p-(2,3-epoxypropyl)phenyl]hexamethyltrisiloxane

III



1,4-bis[(p-epoxypropylphenyldimethylsiloxy)dimethylsilyl]benzene

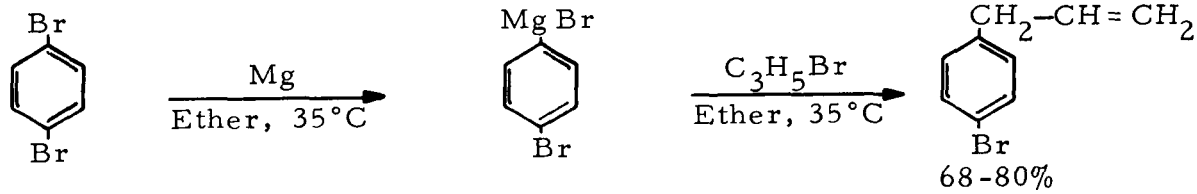
IV



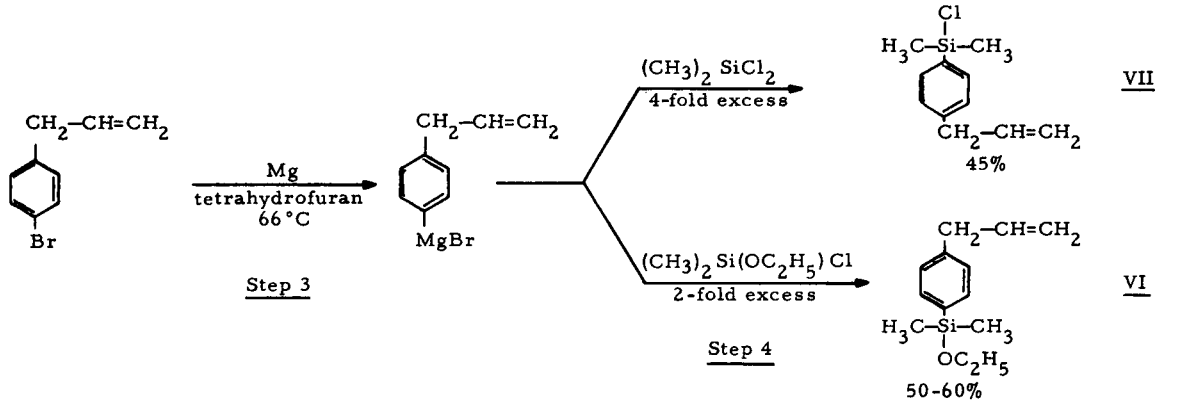
Methyltris[p-2,3-epoxypropyl)phenydimethylsiloxy]silane

V

Several key intermediates were common to each of these epoxysilicones and consequently synthesis procedures developed for these intermediates were of general utility. Undoubtedly, the most important of these intermediates were p-allylphenyldimethylethoxysilane (VI), the analogous chlorosilane (VII) and the meta isomers of these compounds. Their structures and methods of synthesis are illustrated below:



Step 1 Step 2



In the first step of this process, either meta- or para-dibromobenzene may be used. The meta isomer has an advantage over the para isomer in that it is a liquid readily soluble in ether and thus is more convenient to monitor into the reaction mixture. Low solubility of the para isomer in ether renders it less convenient to use, particularly in large scale preparations; however, it can be added in small portions in the solid state. Yields from these reactions have generally been about 70 ± 10 percent, although lower yields were observed when difficulties were encountered in keeping the reactions under control due to excessively rapid addition rates. The refractive index of the para-allylbromobenzene $\left(n_D^{23}\right)$ was 1.5522 and the boiling point was 62°C at 3 torr, 80°C at 5-6 torr, 96°C at 14 torr, and 117°C at 35 torr. Infrared spectra of the meta and para isomers are shown in Figures 1-1 and 1-2 respectively.

Conversion of the allylbromobenzene to allylphenylmagnesium bromide (step 3) was generally carried out in tetrahydrofuran because the reaction is rather sluggish and gives much poorer yields in ethyl ether. After preparation, the Grignard reagents were added dropwise

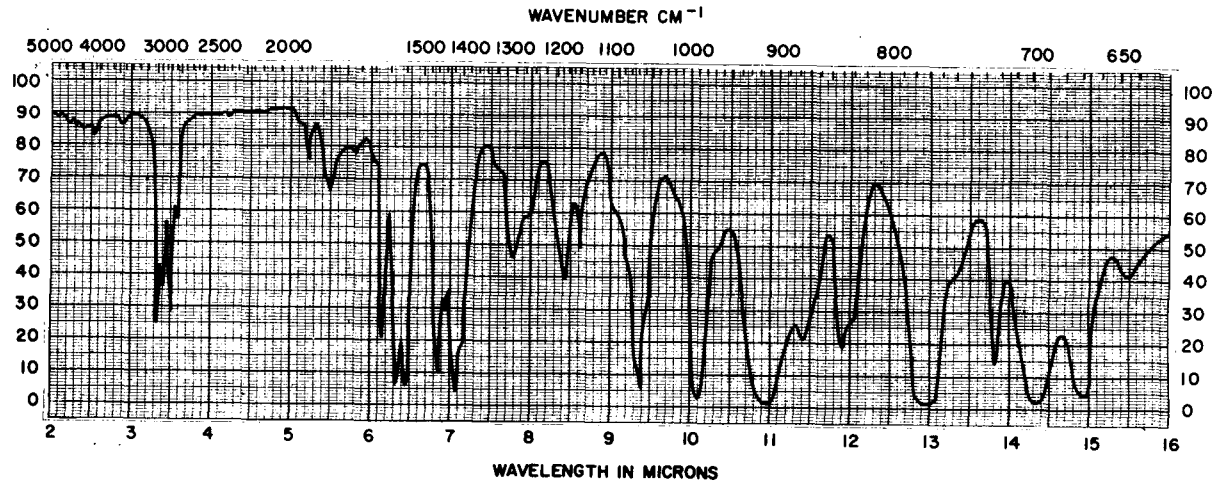


Figure 1-1. Infrared spectrum of m-bromoallylbenzene.

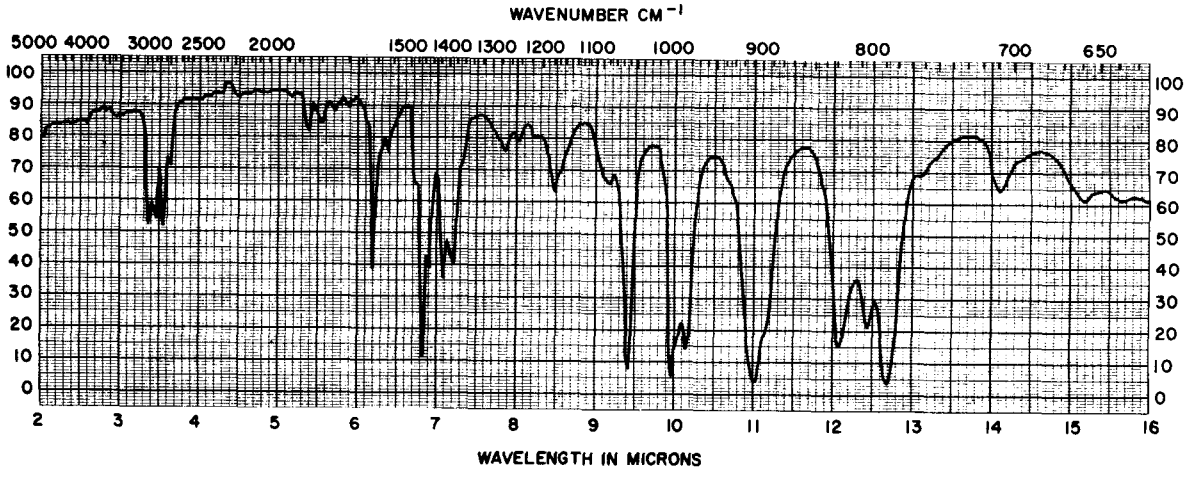


Figure 1-2. Infrared spectrum of p-bromoallylbenzene.

to excess quantities of either dimethyldichlorosilane or dimethylchloroethoxysilane. With a fourfold molar excess of dimethyldichlorosilane a yield of 43 percent of allylphenyldimethylchlorosilane was obtained, whereas with the dimethylchloroethoxysilane yields of 50 to 60 percent were obtained when the ethoxy compound was used in a twofold excess. The use of the ethoxy compound does, however, have a disadvantage in that its purification is difficult. It is generally contaminated with both the dichlorosilane from which it is made and with dimethyl diethoxysilane. Furthermore, its synthesis by the partial ethanolysis of dimethyldichlorosilane as illustrated below

$$(CH_3)_2\,SiCl_2 + C_2H_5OH \longrightarrow (CH_3)_2\,Si(OC_2H_5)Cl$$

is wasteful, since yields were about 40 percent when a 3°C boiling range was collected, 50 percent when a 12°C boiling range was collected, and 67 percent when a 20°C boiling range was collected. The apparent boiling point of the pure compound is about 90°C at atmospheric pressure.

m-Allylphenyldimethylethoxysilane prepared from dimethylchloroethoxysilane distills at 95 ± 5°C at five torr. Its refractive index varied between 1.49 and 1.50 at ambient temperature, due to the variation in the amount of m-allylphenyldimethylchlorosilane which it contains, since the chlorosilane has a refractive index $\left(n_D^{23}\right)$ of 1.5139. This contamination is, of course, of little concern since both compounds hydrolyze to the same disiloxane. It has been noted that when the ethoxysilane was treated with ethanol prior to distillation, the chlorosilane therein was esterified and the foaming problem, which was always encountered during distillation, was drastically reduced. Infrared spectra of both the meta- and para-allylphenyldimethylethoxysilanes are shown in Figures 1-3 and 1-4 respectively.

An elemental analysis which was carried out on a sample of m-allylphenyldimethylethoxysilane with a refractive index $\left(n_D^{23}\right)$ of 1.4919 gave the following results:

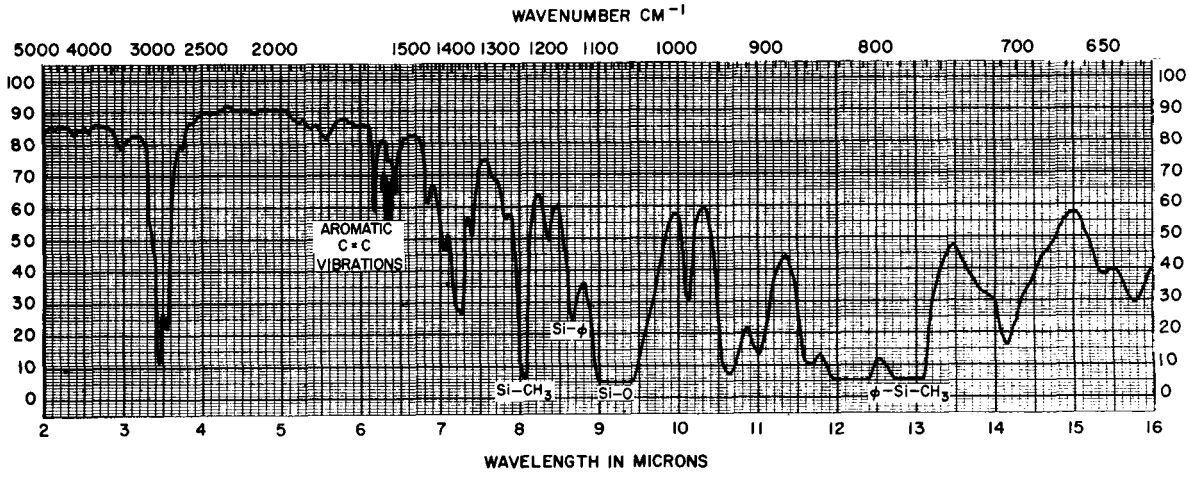


Figure 1-3. Infrared spectrum of m-allylphenyldimethylethoxysilane.

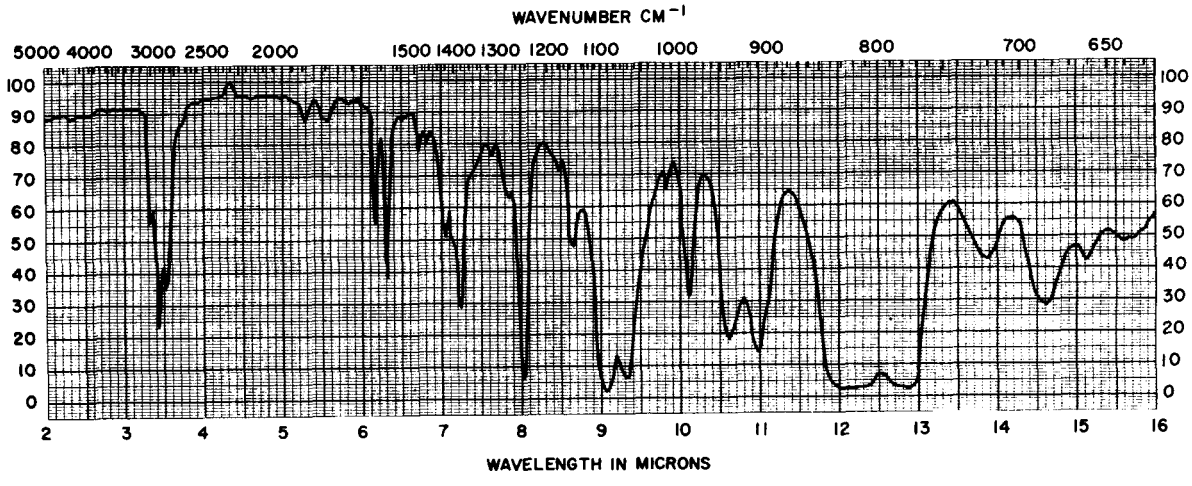
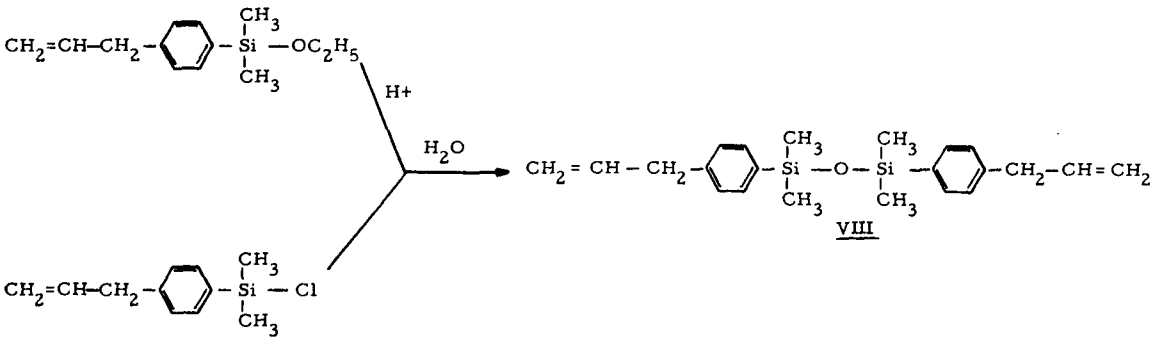


Figure 1-4. Infrared spectrum of p-allylphenyldimethylethoxysilane.

	Percent C	Percent H	Percent Si
Observed	68.55	9.07	12.19
Calculated	70.96	9.16	12.77

A sample of the homologous para isomer free of halosilane boiled at about 100°C at 9 torr or 70-75°C at 0.2 torr and had a refractive index $\left(n_D^{23}\right)$ of 1.4965.

Both allylphenyldimethylchlorosilane and allylphenyldimethylethoxysilane are suitable for the preparation of di- and poly-siloxanes. Hydrolysis of either compound produces dimer as shown below:



Both the meta and para substituted disiloxanes can be distilled under high vacuum. The meta isomer has been collected at 130°C at 0.003 torr and at 150-155°C at 1.3 torr, whereas para isomer has been collected at 130-140°C at 0.010 ± 0.006 torr and at 120-130°C at 0.002 torr. The refractive index of the meta isomer $\left(n_D^{23}\right)$ was always 1.5208 ± 0.0009 and that of the para isomer was 1.5206 ± 0.0006. At least three independent values, from different preparations, were obtained on each of these compounds. Infrared spectra of both isomeric disiloxanes are shown in Figures 1-5 and 1-6.

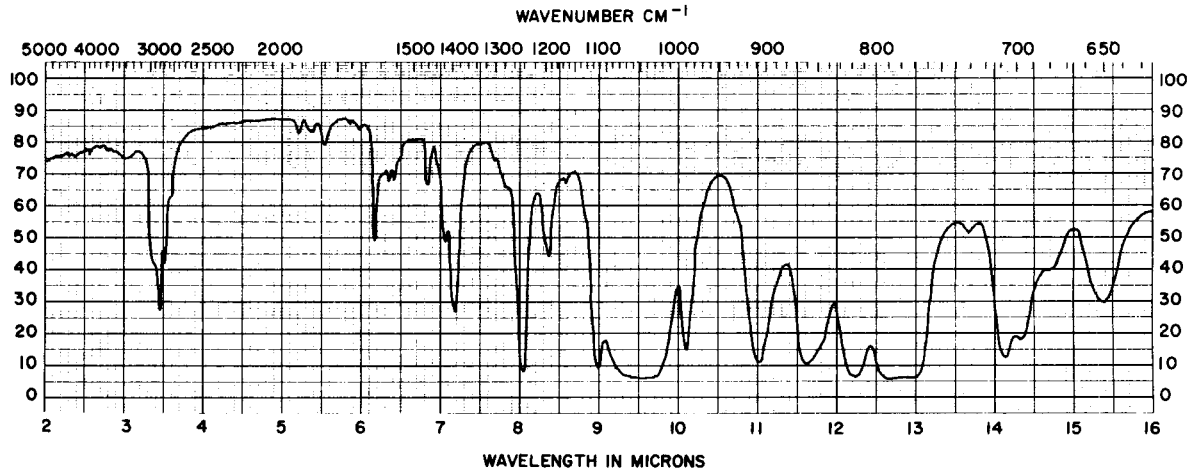


Figure 1-5. Infrared spectrum of 1, 3-bis(m-allylphenyl)-tetramethyldisiloxane.

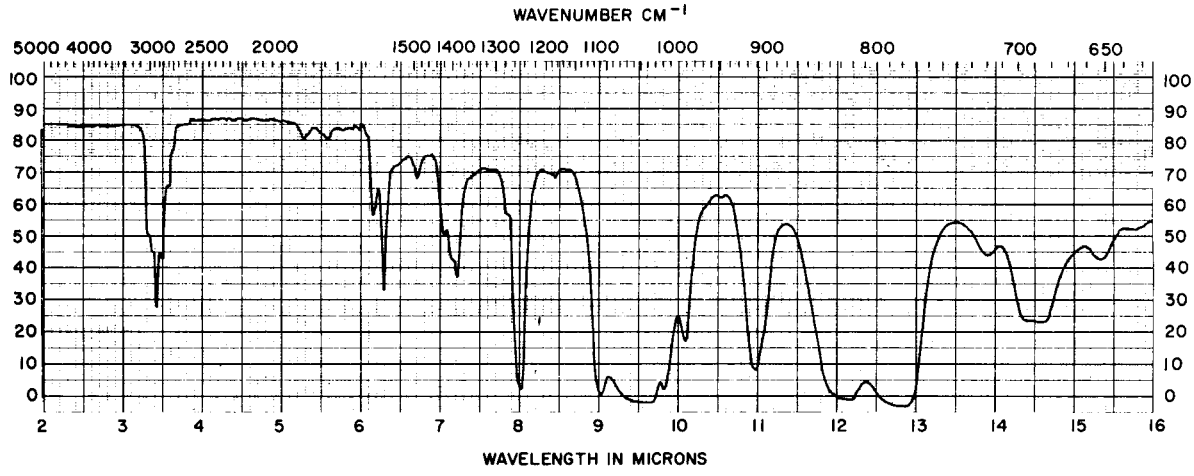
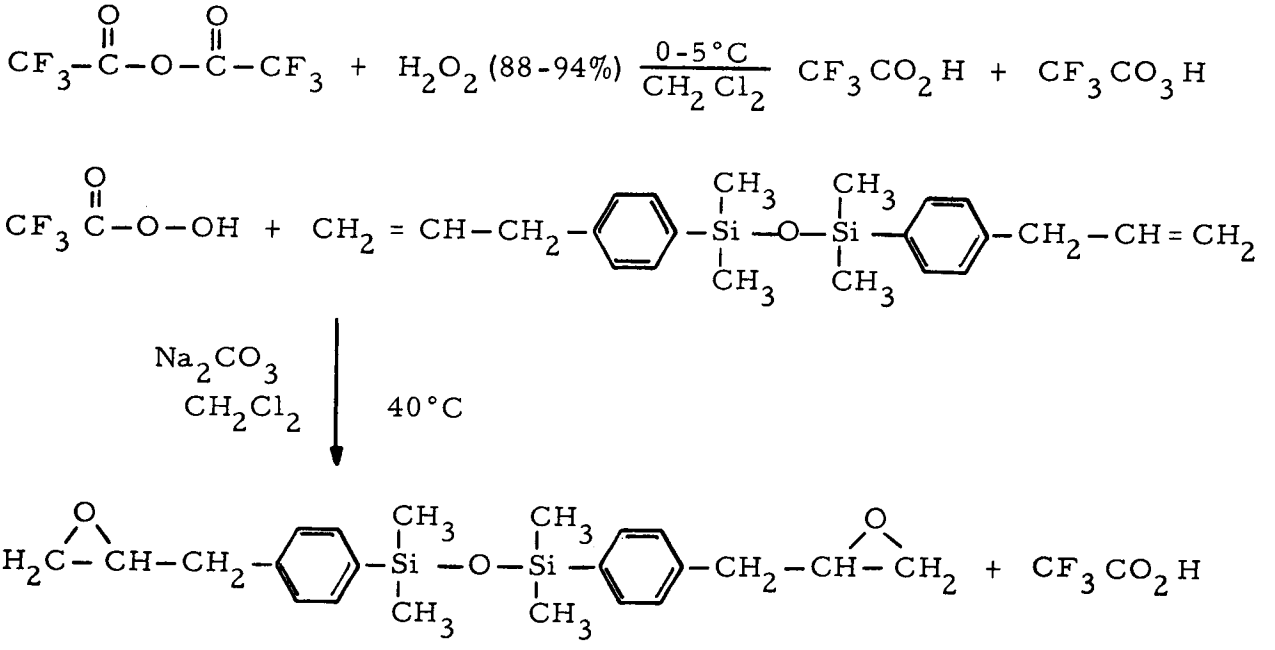


Figure 1-6. Infrared spectrum of 1, 3-bis(p-allylphenyl)-tetramethyldisiloxane.

Elemental analyses carried out on two independently synthesized samples of the meta substituted disiloxane supported the proposed structure. The results of these analyses were as follows:

	Percent C	Percent H	Percent Si
C1961-68F1	72.43	8.14	13.48
C1961-42B	71.14	8.14	15.22
Theoretical	72.20	8.26	15.35

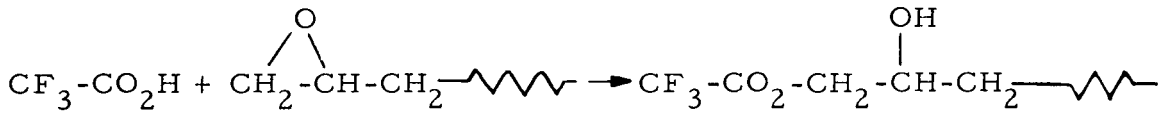
Epoxidation of the bis(allylphenyl)tetramethyldisiloxanes was carried out with freshly prepared trifluoroperacetic acid as illustrated below:



IX

A considerable number of epoxidation experiments which were carried out at 0-8°C proved partly unsuccessful in that the bis epoxy

compounds which were obtained were always contaminated with fluorinated esters resulting from the addition of trifluoroacetic acid to the epoxy compound as shown below:



These esters could not be removed readily by vacuum distillation.

Evidence for this reaction came from infrared spectroscopy. Absorption peaks observed in many of the epoxysilicones at 1170 cm^{-1} and 1200 cm^{-1} can be attributed to C-F absorptions and this was verified by the deliberate addition of trifluoroacetic acid to a sample of the epoxy silicone. Absorption at 1770 cm^{-1} is attributed to the carbonyl groups and absorption at 3300 cm^{-1} is attributed to the hydroxyl group (see Figure 1-7). All of these absorptions are absent when the epoxidations are carried out in refluxing methylene chloride (40°C). The deliberate addition of trifluoroacetic acid to the epoxysilicone also verified the assignment of absorptions at 965 cm^{-1} and 752 cm^{-1} to the epoxy groups. These absorptions virtually disappeared as a result of the addition even though only part of the epoxy groups were being destroyed. This observation was very important because all of the generally recognized epoxy group absorptions were masked by Si-O, Si-ϕ, Si-CH_3 and other groups.

Contamination by fluoroester was considered serious because its removal by molecular distillation was not readily accomplished. Furthermore, epoxy silicones containing fluoroester often polymerized into viscous fluids during attempted distillation. This was attributed to the liberation of trifluoroacetic acid which acted as a polymerization catalyst at the elevated temperatures. Epoxidations carried out in methylene chloride below 8°C tended to yield solutions which were acidic to dry wide range indicator paper. This proved to be an excellent test technique. Oddly enough, moist indicator paper did not necessarily show this acidity. Problems encountered with low temperature epoxidations were thus attributed to the failure of the suspended carbonates to absorb spent acids in the reaction mixture at a sufficiently high rate.

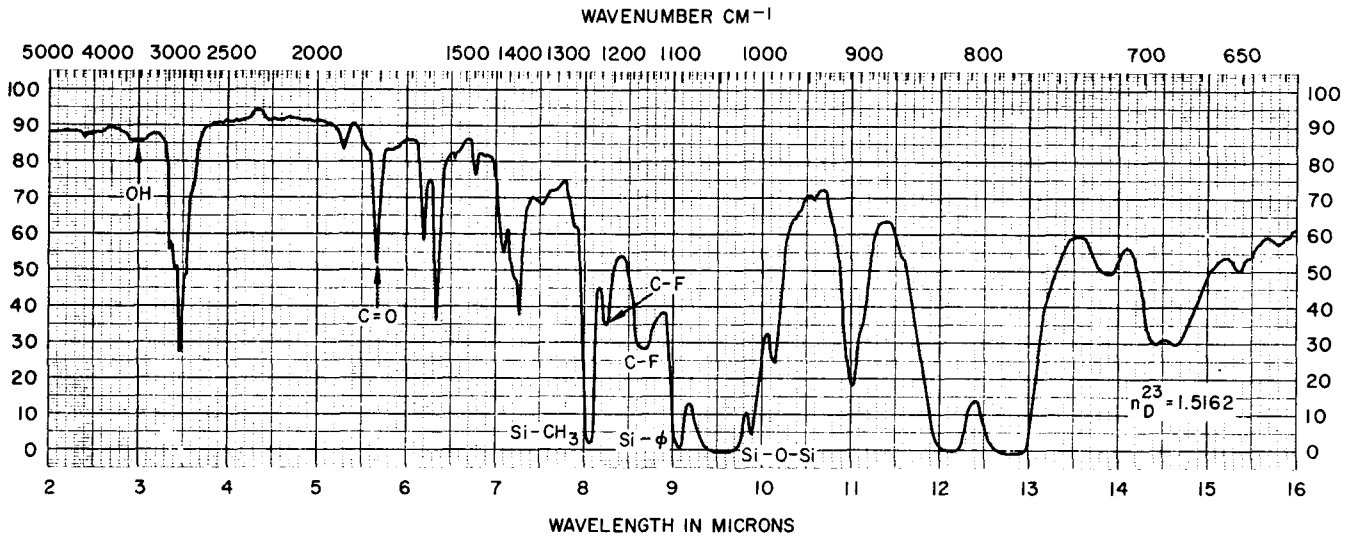


Figure 1-7. Infrared spectrum of impure bis(p-epoxypropylphenyl)-tetramethyldisiloxane. (C2425-54F-2).

Epoxidations carried out at 40°C were always free of C-F, C=O, and OH absorptions. Furthermore, the use of excess trifluoroperacetic acid was necessary at the elevated temperature as long as sufficient carbonate was present, whereas in the lower temperature epoxidations excess peracid was always very detrimental.

Elemental analyses carried out on a distilled sample of bis(m-epoxypropylphenyl)tetramethyldisiloxane gave the following results:

	Percent C	Percent H	Percent Si
Observed on C1961-71F2	66.57	7.59	14.15
Theoretical for $C_{22}H_{30}Si_2O_3$	66.38	7.60	14.11

This fraction was molecularly distilled at about 90 ± 10°C at 10^{-3} torr and had a refractive index $\left(n_D^{23}\right)$ of 1.5251. The best fraction of para isomer isolated from a low temperature epoxidation had the following analysis:

	Percent C	Percent H	Percent Si
Observed on C2425-54F2	68.29	7.87	15.36
Theoretical for $C_{22}H_{30}Si_2O_3$	66.38	7.60	14.11

This fraction was distilled at 100-125°C at 5×10^{-4} torr and had a refractive index $\left(n_D^{23}\right)$ of 1.5162.

An undistilled sample of bis(p-epoxypropylphenyl)tetramethyldisiloxane isolated from an epoxidation which was carried out at 40°C and in which the theoretical amount of peracid was used had the following analysis:

Observed on C1961-97B	14.86 percent Si
Calculated for $C_{22}H_{30}Si_2O_2$	14.73 percent (50 percent epoxidized)
Calculated for $C_{22}H_{30}Si_2O_3$	14.11 percent (100 percent epoxidized)

An infrared spectrum of this product showed that it was free of C-F, C=O, and OH groups. Its equivalent weight was found to be 401 rather than 200 as calculated and thus it appeared to have only 50 percent of its allyl groups epoxidized. This was supported by the elemental analysis. It was thus concluded that, whereas epoxidations carried out at 40°C produce epoxy compounds with virtually no fluoroester contamination, they must be carried out in the presence of a significant excess of peracid to achieve complete epoxidation. Such a peracid excess could not be tolerated below 10°C.

Epoxidations at 40°C have subsequently been carried with 50 percent and 100 percent theoretical excess of peracid without producing products contaminated with trifluoroacetic acid-epoxy addition compounds. Reactions which produced the most complete epoxidation were those containing 100 percent excess peracid and a sodium carbonate/trifluoroacetic anhydride ratio of about 1.5. Results of several typical epoxidations are the following:

Experiment Number	Theoretical Excess Peracid, percent	Carbonate/Anhydride Mole Ratio	Product		
			Eq.* Wt.	Yield, percent	n_D^{23}
C1961-97	0	3.0	440	69	1.5245
C1961-97B	0	3.2	401	100	1.5245
D1516-4	50	3.0	367	72	1.5248
C1961-98	50	3.0	333		
D1516-5	100	3.0	295	57	1.5260
D1516-6	100	2.0	232	67	1.5270
D1516-7	100	1.5	217	85	1.5268

*theoretical value 200

An infrared spectrum of the bis(p-epoxypropylphenyl)tetramethyldisiloxane (D1516-6) is shown in Figure 1-8.

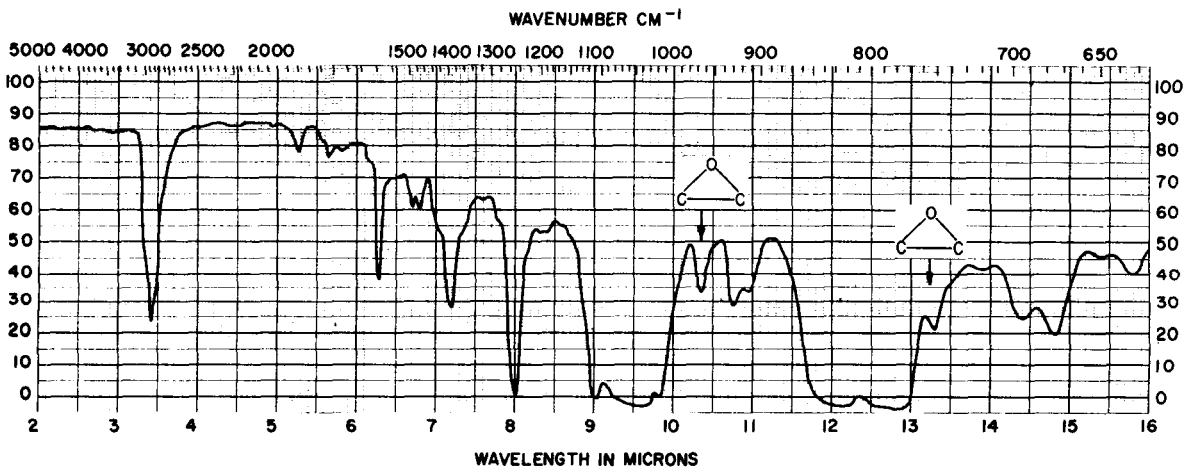


Figure 1-8. Infrared spectrum of 1,3-bis(p-epoxypropylphenyl)-tetramethyldisiloxane.

Dielectric properties of amine cured samples of both meta- and para-bis(epoxypropylphenyl)tetramethyldisiloxane have been measured. The first set of tests (C1961-76 and 77) were on epoxy compounds for

which the equivalent weights were unknown and which consequently were assumed to have the theoretical value although they undoubtedly had higher values. Elemental analyses were acceptable on these materials. However, due to the structural similarity of the diallyl and the diepoxy compounds, these analyses were not a sufficiently good indicator of the actual degree of epoxidation. The only samples in this first series which cured completely were those which also contained a fraction of 2, 2-bis(p-epoxypropoxyphenyl)propane (Shell Chemical Co. – Epon X-24). In subsequent experiments, analyzed equivalent weights were used in most cases, except for comparative purposes (series C2425-70 and 80). The composition of these cured epoxysilicones are presented in Table 1-1 and their dielectric properties are listed in Table 1-2.

Specimen Number	Epoxysilicone Number	Isomer‡‡	Epoxy Silicone		Epon X-24		Filler‡	Amine		Cure	Comments
			Weight (grams)	Eq.	Weight (grams)	Eq.	Weight (grams)	Weight (grams)	Eq.		
C1961-76-3	C1961-75	M	5.0	0.025*	4.2	0.025		5.7A	0.050	24 hours at 100°C	Hard, softened some when hot
-4	-75	M	5.0	0.025*	2.1	0.0125		4.3A	0.0375	24 hours at 100°C	Tough rubber
-5	-75	M	3.0	0.015*	2.52	0.015		3.45A	0.030	24 hours at 100°C	Hard, tough, softened some when hot
-6	C2425-54	P	5.0	0.025*	4.2	0.025		5.70A	0.050	24 hours at 100°C	Hard-dark film on top
-7	-54	P	5.0	0.025*	2.1	0.0125		4.30A	0.0375	24 hours at 100°C	Hard-dark film on top
-8	-54	P	2.00*	0.010*	3.40	0.020		0.81B	0.030	16 hours at 80°C-N_2 then 3-1/2 hours at 100°	Hard opaque solid
C2425-70-2	C1961-86	P	3.82	0.019*		–	1.40	0.47B	0.019	17 hours at 85°C 4 hours at 100°C in N_2	Crumbly, too much filler
-70-1	-86	P	4.0	0.014**				0.50B	0.02	60 hours at 85°C 3.5 hours at 100°C in N_2	Rigid tan
-80-1	C1961-91	P	5.02	0.018**				0.49B	0.018	16 hours at 80°C 8 hours at 100°C in N_2	Clear amber flexible disc
-80-2	-91	P	5.02	0.018**			0.97	0.49B	0.018	16 hours at 80°C 8 hours at 100°C in N_2	Light tan rigid disc
-80-3	-91	P	3.07	0.011**	1.87	0.011		0.59B	0.022	16 hours at 80°C 8 hours at 100°C in N_2	Cured sample not completely homogeneous
-80-4	-91	P	3.07	0.011**	1.87	0.011	0.98	0.59B	0.022	16 hours at 80°C 8 hours at 100°C in N_2	Only 50 percent filled due to flotation
-79-4	C1961-90		4.67	0.010**				0.27B	0.010	16 hours at 85°C 4 hours at 100°C in N_2	Flexible disc

*Based on theoretical equivalent weights.

‡Silica microballoons – Eccospheres SI dried at 250°C.

**Based on analyzed equivalent weights.

‡‡M or P designate meta or para isomer of bis(epoxypropylphenyl)tetramethyldisiloxane. Not applicable to 79-4.

A = N-methylaniline formaldehyde.

B = m-phenylenediamine.

Table 1-1. Composition of various cured epoxysilicones.

Specimen Number	Isomer*	Dielectric Constant at 1 kc			Dielectric Constant at 100 kc	Dissipation Factor, Percent at 1 kc			Dissipation Factor, Percent at 100 kc	Volume Resistivity, megohm-cm at 500 VDC				Epoxysilicone to Epon X-24 Ratio**
		25° C	50° C	100° C	25° C	25° C	50° C	100° C	25° C	25° C	50° C	100° C	25° C †	
C1961-76-6	P	3.2		5.4	3.0	0.7		7.5	2.3	1.72×10^{8}		1×10^{6}	2×10^{8}	1:1
-76-7	P	3.9			3.5	8.5			2.6	2.63×10^{5}		$<7 \times 10^{1}$	3×10^{5}	2:1
-76-8	P	4.0			3.8	2.8			2.2	1.22×10^{8}		5×10^{5}	1×10^{8}	1:2
-76-3	M	3.2		3.9	3.1	0.7		5.7	1.0	7.0×10^{7}		2×10^{5}	7×10^{7}	1:1
-76-4	M	3.3		4.9	3.2	2.0		61.8	1.6	7.0×10^{7}		4×10^{5}	7×10^{7}	2:1
-77-5	M	3.6			3.4	5.5			1.8	2.98×10^{7}		1×10^{2}	3×10^{7}	1:1
C2425-80-1	P	3.8	3.9	6.7		2.7	2.7	6.3		4×10^{7}	2×10^{6}	3×10^{4}		
-80-2	P	2.3	3.0	3.2		2.0	4.6	10.9		3×10^{7}	1×10^{6}	7×10^{3}		
-80-4	P	2.5	2.9	4.0		1.3	2.9	14.8		2×10^{7}	3×10^{6}	2×10^{4}		
-79-4	P	3.2	3.6	6.3		3.9	6.8	14.5		3×10^{7}	2×10^{6}	7×10^{3}		
-70-1	P	3.4	3.8	4.4		1.0	1.7	3.8		2×10^{8}	2×10^{6}	4×10^{3}		

*P refers to the para isomer of bis(epoxypropylphenyl)tetramethyldisiloxane, whereas M refers to the meta isomer.

**All epoxies were formulated on stoichiometrically equivalent basis with the various amines.

†Reevaluated after the elevated temperature tests were complete.

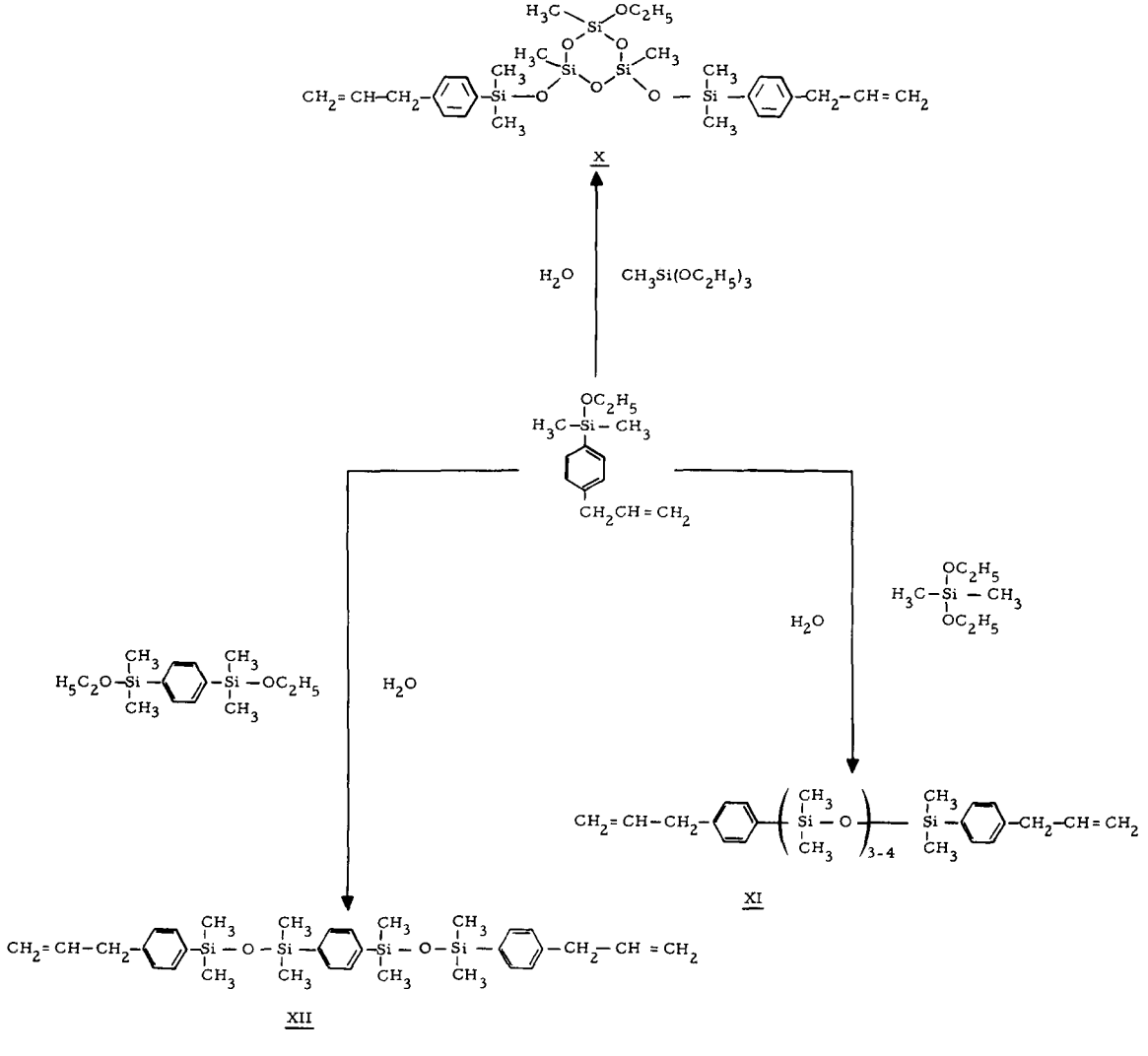
Table 1-2. Dielectric properties of various epoxysilicone Hartshorn type specimens.

It is most important to note here that the epoxidation process had not been optimized at the time most of the dielectric test data was obtained. Thus, although relatively good distilled fractions of epoxy compounds were studied, the dielectric test data probably does not represent the optimum dielectric potential of these materials.

An examination of this dielectric property data shows that the best sample of cured bis(epoxypropylphenyl)tetramethyldisiloxane was C2425-70-1. Its dielectric constant at 1 kc varied from 3.4 to 4.4 in the 25°-100° C temperature range while its dissipation factor varied from 1 to 3.8 percent. Analogous resin filled with 15 percent by weight of silica microballoons (Eccospheres SI) (C2425-80-2) had dielectric constants which varied from 2.3 to 3.2 between 25° and 100° C and dissipation factors which varied from 2.0 to 10.9 percent within this temperature range or from 2.0 to 4.6 percent between 25° and 50° C. It is the firm belief of this investigator that significant reductions in dissipation factors would be noted on epoxysilicones with equivalent weights closer to their theoretical values. Such materials can be made by procedures described herein.

Siloxane Copolymers

Allylphenyldimethylchlorosilane and allylphenyldimethylethoxysilanes are also useful in cohydrolysis reactions with other chloro- or ethoxysilanes. Such cohydrolyses may be used to produce various types of higher molecular weight allylphenylsiloxanes. Three such reactions which were carried out in the Hughes laboratories include the cohydrolysis of p-allylphenyldimethylethoxysilane with methyltriethoxysilane, with dimethyldiethoxysilane, and with 1, 4-bis(dimethylethoxysilyl)benzene. These reactions are illustrated below:



Cohydrolysis reactions do not, of course, yield single compounds as products, but rather yield mixtures of allylphenylsiloxanes. Each reaction product contained bis(allylphenyl)tetramethyldisiloxane and lower boiling cyclosiloxanes as well as the desired cohydrolysis products. For the purpose of this program, only the lower boiling cyclosiloxanes needed to be removed prior to epoxidation and polymerization. Studies were made nevertheless to determine the structure of high boilers after removal of the bis(allylphenyl)tetramethyldisiloxane. Analysis of the bis(allylphenyl) polydimethylsiloxane (after epoxidation) showed that the "non-volatile" cohydrolysis product XI contained on the average a little more than three dimethylsiloxy repeating units. The results were as follows:

	Percent Si	M. W.
Calculated for $C_{28}H_{48}Si_5O_{4.5}$*	23.52	597
Observed	21.96	572
Calculated for $C_{26}H_{42}Si_4O_{3.5}$*	21.48	523

The equivalent weight of this epoxy compound was found to be 1089 and thus it turned out to have only 25 percent of its allyl groups epoxidized. Due to termination of the program, however, the reaction could not be studied further. A significant portion of the dimethyldiethoxysilane used in this cohydrolysis ended up as cyclosiloxane and was removed by vacuum distillation.

In the cohydrolysis of p-allylphenyl-dimethylethoxysilane with methyltriethoxysilane the "non-volatile" siloxane which was isolated appeared to be primarily an incompletely hydrolyzed trisiloxane X. Analysis of this undistilled high boiling fraction gave the following results:

*Fractional units are used here because the compound was incompletely epoxidized.

	Observed (undistilled product) Fraction 85P	Calculated for $C_{27}H_{44}Si_5O_6$	Observed Distilled Fraction 85F4
% Carbon	53.03	53.59	55.45
% Hydrogen	7.64	7.33	7.68
% Silicon	23.34	23.21	

The presence of unreacted ethoxy groups in the product was not expected although the hydrolysis was carried out under very weakly acidic conditions. The reaction thus warrants re-examination using more vigorous hydrolysis conditions. The major portion of the reaction product distilled at about 165° C at 10^{-4} torr, had a refractive index $\left(n_D^{23}\right)$ of 1.4943 and was primarily the bis(p-allylphenyl)tetramethyldisiloxane.

In the cohydrolysis of p-allylphenyldimethylethoxysilane with 1,4-bis(dimethylethoxysilyl)benzene a non-volatile siloxane was obtained which after epoxidation had an equivalent weight of 491. The theoretical value is 287. Elemental analyses could not be obtained as a result of the termination of the program. Apparently, the epoxidation was only 58 percent complete. Nevertheless, when the epoxy compound was reacted with an equivalent amount of m-phenylenediamine, it cured to a flexible tough elastomer when heated at 100° C in nitrogen for two days, then in air for 2-1/2 days. A simple flexibility test carried out at about -70° C showed the elastomer to be tough and nonbrittle at this temperature.

Optimum epoxidation processes had not been developed at the time the three previously described copolymers were epoxidized. The process ultimately developed for the epoxidation of the bis(allylphenyl)tetramethyldisiloxanes, namely, the use of 100 percent excess peracid, epoxidation temperatures of 40° C, and sodium carbonate/trifluoracetic anhydride molar ratios below 2, would currently be recommended.

EXPERIMENTAL

Synthesis of p-Bromoallylbenzene (D1151-28)

To a slurry of dry magnesium (245 g., 10 moles) in anhydrous ether (6.4 l) was gradually added, in small portions, solid p-dibromobenzene (2360 g., 10 moles) after the reaction was initiated with a small amount of ethylmagnesium iodide. The reaction flask was cooled in an ice water bath throughout the reaction to maintain control; however, reflux was maintained by carefully monitoring the rate of dibromobenzene addition. In this manner, the addition was completed within 2-1/2 hours. Reflux was then continued for one hour by an auxiliary heat source.

Allyl bromide (1295 g., 10.7 moles) in anhydrous ether (1 l) was then added slowly to the Grignard reagent at a rate which permitted controlled reflux. Upon completion of this reaction the reaction mixture was cautiously poured over acidified ice. The ether phase was then separated and the aqueous phase was washed with fresh ether. Combined ether layers were then distilled. The p-allylbromobenzene (1534 g., 78 percent) was collected at 60-63° C and three torr.

Synthesis of m-Bromoallylbenzene (C2425-48)

A solution of m-dibromobenzene (571 g., 2.42 moles) in absolute ether (200 ml) was gradually added to a slurry of magnesium (60 g., 2.5 moles) in absolute ether (200 ml) after initiating the reaction with iodine and ethyl iodide. After the exothermic phase of the reaction was over the mixture was heated at reflux for 1 hour using an auxiliary heat source. Allyl bromide (300 g., 2.5 moles) was then added dropwise to the reaction mixture at such a rate as to maintain control. When the addition was completed, heating was maintained for 1/2 hour. The reaction mixture was cooled, then poured over a mixture of hydrochloric acid and ice. Separation of the two phases yielded an ether phase which was washed with water and dried over calcium sulfate. Fractional distillation of the ether solution yielded 335 g. or 70 percent of m-allylbromobenzene(B. $P._{35}$ = 117° C).

Synthesis of Dimethylethoxychlorosilane (C2425-58)

Anhydrous ethanol (276 g., 6 moles) was added dropwise to dimethyldichlorosilane (1032 g., 8 moles). When the reaction subsided the mixture was heated at reflux for one hour and was then distilled. Unreacted dichlorosilane (125 g.) was recovered at 58-62° C. Then several other fractions were collected, namely

II	89 g	76-82° C
III	66 g	82-89° C
IV	299 g	89-95° C
V	100 g	95-97° C

The latter two fractions represent 2.90 moles or 36 percent of theoretical.

Synthesis of m-Allylphenyldimethylethoxysilane (C2425-49B)

m-Bromoallylbenzene (250 g., 1.27 moles) was dissolved in anhydrous tetrahydrofuran (400 ml) and the solution was then gradually added to a slurry of magnesium (34 g., 1.42 moles) in anhydrous tetrahydrofuran. The addition took about 1 hour after the reaction had been initiated with iodine and ethylmagnesium iodide. When the addition was completed the mixture was heated at reflux for one hour. This Grignard solution then was added gradually to dimethylchloroethoxysilane (294 g., 2.13 moles) while keeping the reaction cool with an ice bath. When the addition was complete the reaction mixture was heated at reflux for one hour, then diluted with petroleum naphtha. It was then filtered and fractionally distilled to yield (1) 147 g. of pure product (b. p.$_5$ = 90-100° C, n_D^{23} = 1.5028). Another fraction was recovered by redistillation of the forerun. This fraction weighed 27 g., had a boiling point of 85-110° C at 5 torr and a refractive index of n_D^{23} = 1.5040. The combined 174 g. (0.79 mole) of product represents 62 percent of the theoretical yield.

Synthesis of p-Allylphenyldimethylethoxysilane (C1961-82)

p-Allylbromobenzene (332 g., 1.68 moles) in an equal volume of dry tetrahydrofuran was added dropwise, with constant stirring, to dry magnesium (43.1 g, 1.74 moles) in 644 ml dry tetrahydrofuran. The reaction was initiated with a few grams of freshly prepared ethylmagnesium iodide. The mixture had to be heated at the beginning, but then even reflux was maintained, during addition, with an ice bath. After addition, the mixture was stirred at reflux for three quarters of an hour. The resulting Grignard reagent was decanted into a dropping funnel, and added dropwise, with constant stirring, to dimethylethoxychlorosilane (451 g., 3.28 moles) in an equal volume of dry tetrahydrofuran. After initial heating, an ice bath had to be used to keep the reaction at even reflux. After addition, the mixture was stirred at reflux for two hours. The product was taken up in hexane, and solids were separated out by filtration. Absolute ethanol (80.0 g., 1.74 mole) was then added and the mixture was stirred for one hour at ambient temperature. After initial evaporation of solvent, the crude product weighed 298 g. It was then distilled under vacuum, yielding the following fractions:

1F2: 70-75° C at 0.2 torr; 126.0 g. net; $n_D^{24} = 1.4965$

2F1: 60-70° C at 0.5 torr; 30.6 g. net; $n_D^{24} = 1.4930$

2F2: 70-76° C at 0.5 torr; 32.3 g. net; $n_D^{25} = 1.9993$

Redistillation of 1F2 yielded the following:

3F1: 70-73° C at 0.5 torr; 94.3 g. net; $n_D^{25} = 1.5006$

(The redistillation of 1F2 was run because of the presence of impurities, as indicated in the IR absorption spectra.)

Synthesis of p-Allylphenyldimethylchlorosilane (D1151-29)

To a slurry of magnesium (113 g., 4.65 moles) in anhydrous tetrahydrofuran (2 kg.) was added p-bromoallylbenzene (833 g., 4.23 moles)

at such a rate that moderate reflux was maintained. The reaction was initiated with a small amount of ethylmagnesium iodide. Upon completion of the addition, reflux was continued for one hour using an auxiliary heat source.

The cooled Grignard reagent thus prepared was then placed into a dropping funnel and added dropwise to freshly distilled dimethyldichlorosilane (2184 g, 16.9 moles) over a two-hour period. Stirring was then continued for one hour and the reaction mixture was then filtered to remove precipitated salts. These salts were washed with petroleum ether. Tetrahydrofuran and unreacted dimethyldichlorosilane were then removed in large part from the filtrate by distillation. The petroleum ether from the salt wash was then combined with the undistilled crude allylphenyldimethylchlorosilane and the mixture was filtered. Simple distillation of the filtrate gave low boilers and 738 grams of allylphenyldimethylchlorosilane ($B.P._{5} = 70\text{-}100°C$).

Fractional distillation of the impure product was then carried out using a packed column. The purified allylphenyldimethylchlorosilane (382 g, 1.82 moles, $n_D^{23} = 1.5139$) distilled at 102-3°C at five torr. This represents a 43 percent yield.

Synthesis of Bis(p-allylphenyl)tetramethyldisiloxane by Hydrolysis of p-Allylphenyldimethylchlorosilane (D1151-31A):

p-Allylphenyldimethylchlorosilane (382 g, 1.82 moles) was added dropwise to water (1.5 l) while stirring vigorously. When the reaction was completed the mixture was cooled and the two phases were separated. Distillation of the disiloxane was then carried out at 6×10^{-3} torr and the fraction boiling between 130° and 140°C was collected. It weighed 300 g (0.82 mole) and represented a 90 percent yield. Its refractive index (n_D^{23}) was 1.5209.

Synthesis of 1,3-Bis(p-allylphenyl)tetramethyldisiloxane by Hydrolysis of p-Allylphenyldimethylethoxysilane (C2425-52):

A mixture of water (10 ml) and glacial acetic acid (1 ml) was gradually added to p-allylphenyldimethylethoxysilane (74.4 g, 0.34 mole, sample C1961-73F2, $b.p._{0.5} = 60\text{-}85°C$). After shaking

vigorously the two phases were separated and the upper layer was collected and distilled at 0.015 torr. Two fractions of product were recovered, to wit: I. 23.7 g, b.p.$_{0.015}$ = 130-140°C, n_D^{22} = 1.5206, and II. 24.7 g, b.p.$_{0.015}$ = 130-140°C, n_D^{22} = 1.5193. The total yield of product (48.4 g, 0.14 mole) represents a 77 percent yield.

Synthesis of 1,3-Bis(m-allylphenyl)tetramethyldisiloxane by Hydrolysis of m-Allylphenyldimethylethoxysilane (C1961-68):

Water (1.5 ml, 0.086 mole) which had been slightly acidified (one drop of glacial acetic acid per 10 ml water) was added to m-allylphenyldimethylethoxysilane (16.7 g, 0.076 mole) with constant stirring. The mixture was stirred for 48 hours at room temperature. A total of 3.3 g of water-ethanol mixture was then distilled from the crude product at 1 atmosphere. No further purification was attempted on the product, since 1.5 g of a fraction distilled under vacuum (3×10^{-3} torr, 133°C) had a refractive index of n_D^{23} = 1.5210, while that of the undistilled portion was n_D^{23} = 1.5208. Infrared spectrograms were run on both distilled and undistilled products.

Elemental Analysis (Undistilled Product)

Element	Si	C	H
Theoretical percent	15.35	72.20	8.26
Experimental percent	13.48	72.43	8.14

Epoxidation of 1,3-Bis(p-allylphenyl)tetramethyldisiloxane (C1961-97)

Trifluoroperacetic acid was prepared by the dropwise addition of a solution of trifluoroacetic anhydride (106 g, 0.504 mole) in methylene chloride (110 ml) to a stirred mixture of hydrogen peroxide (89 percent, 15.7 g, 0.410 mole) in dry methylene chloride (50 ml) at a temperature of 0-5°C.

The peracid was not used immediately but was allowed to set for 3 hours during which the temperature gradually rose to ambient.

It was then added dropwise to a slurry of 1, 3-bis(p-allylphenyl)-tetramethyldisiloxane (75. 0 g, 0. 205 mole) and anhydrous powdered sodium carbonate (163 g, 1. 52 moles) in dry methylene chloride (75 ml) while maintaining reflux throughout the addition and for 1/2 hour beyond. After cooling, inorganic salts were removed by filtration and the solvent was removed by distillation. The epoxy compound was then heated at about 85°C and 3×10^{-4} torr to remove low boilers. It then weighed 54. 2 g and had an equivalent weight of 440.

A second portion of the diallyl compound was epoxidized (C1961-97B) as described above except that 79. 8 g (0. 218 mole) of diolefin, 113 g (0. 512 mole) of anhydride, 16. 7 g (0. 410 mole) of peroxide and 173 g (1. 65 mole) of sodium carbonate were used. In this case the peracid was used immediately after being prepared. The final product weighed 85 g and had an equivalent weight of 401.

Another epoxidation (C1961-98) was carried out as described above using 11. 2 g (0. 522 mole) of trifluoroacetic anhydride, 1. 65 g (0. 0432 mole) of 89 percent hydrogen peroxide, 5. 3 g (0. 0122 mole) of bis(allylphenyl)tetramethyldisiloxane and 17 g of sodium carbonate. The epoxy compound was heated at about 80°C and 3×10^{-4} torr to remove volatiles. It then weighed 4. 5 g and had an equivalent weight of 333. It should be noted that a 50 percent theoretical excess of peracid was used in this experiment.

Epoxidation of 1, 3-Bis(p-allylphenyl) tetramethyldisiloxane (D1516-4) 50 percent Excess Peracid-Triple Carbonate

Trifluoroacetic anhydride (107 g, 0. 51 mole) in an equivalent volume of methylene chloride was added dropwise to a slurry of hydrogen peroxide (89 percent, 15. 8 g, 0. 414 mole) in methylene chloride (30 ml) while keeping the temperature below 5°C. After addition, stirring was continued for 15 minutes.

The fresh peracid was then added dropwise to a slurry of the diolefin (50 g, 0. 136 mole) and anhydrous powdered sodium carbonate (162 g, 1. 53 moles) in methylene chloride (200 ml) while maintaining reflux throughout the addition and for 30 minutes thereafter. Salts

were then filtered out and fresh carbonate (15 g) was added. After 15 minutes the carbonate was filtered out. Solvent was removed by distillation and the epoxy compound was devolatilized at 80°C and 10^{-4} torr. Its equivalent weight was 367.

Epoxidation of 1, 3-Bis(p-allylphenyl) tetramethyldisiloxane (D1516-5) 100 percent Excess Peracid-Triple Carbonate

Trifluoroacetic anhydride (142 g, 0.676 mole) in methylene chloride (140 ml) was added dropwise to a stirred slurry of hydrogen peroxide (89 percent, 21.0 g, 0.55 mole) in methylene chloride (60 ml) while keeping the reaction temperature at 0-5°C throughout the addition and for 15 minutes thereafter. The cold peracid was then placed in a cooled dropping funnel and added dropwise to a slurry of bis(allylphenyl)-tetramethyldisiloxane (50 g, 0.137 mole) and dry powdered sodium carbonate (215 g, 2.03 moles) in methylene chloride (200 ml). The reaction was run at reflux. Upon completion of the reaction the inorganic salts were removed by filtration and fresh carbonate (15 g) was added and stirred in for 15 minutes. Again inorganics were removed by filtration. Solvent was then removed by simple distillation and the epoxy compound was heated at 70-75°C and 5×10^{-3} torr for about 12 hours to remove volatiles. Its equivalent weight was 295. The yield was 31 g (57 percent).

Epoxidation of 1, 3-Bis(p-allylphenyl) tetramethyldisiloxane (D1516-6) 100 percent Excess Peracid-Double Carbonate

This experiment was carried out in the same manner as D1516-5 except that 143 grams of Na_2CO_3 (1.35 moles) was used rather than 215 grams. This represents 2 moles of sodium carbonate per mole of trifluoroacetic anhydride rather than 3:1 as used previously. The peracid addition was completed in one hour by using an ice bath to help dissipate the heat of reaction. The epoxidation reaction was carried out at total reflux, even though the flask was cooled in ice. The epoxy compound weighed 36 grams and had an equivalent weight of 232. The yield was 67 percent of theoretical.

Epoxidation of 1, 3-Bis(p-allylphenyl) tetramethyldisiloxane (D1516-7) 100 percent Excess Peracid-One and One-Half Carbonate

Trifluoroacetic anhydride (416. 5 g, 1. 983 moles) in methylene chloride (400 ml) was added dropwise to a well stirred slurry of hydrogen peroxide (89 percent, 61. 4 g, 1. 61 moles) in methylene chloride (180 ml) while keeping the reaction temperature at 0-5°C throughout the addition. The cold peracid was then placed in a cooled dropping funnel and added dropwise to a slurry of bis(allylphenyl)-tetramethyldisiloxane (147. 4 g, 0. 402 mole) and dry finely powdered sodium carbonate (315 g, 2. 97 moles) in methylene chloride (600 ml). This took about 1-1/4 hour during which time total reflux was maintained even though the flask was being cooled externally. Upon completion of the reaction the inorganic salts were removed by filtration, washed with methylene chloride, and the combined filtrates were treated with additional carbonate (approximately 50 g) for 15 minutes and refiltered. Solvent was then removed by simple distillation and the epoxy compound was heated overnight at 75 ± 5°C at 10^{-3} torr to remove residual volatiles. The product weighed 137 grams and had an equivalent weight of 217. Yield, 85 percent; $n_D^{23} = 1.5268$.

Cohydrolysis of p-Allylphenyldimethylethoxysilane and Methyltriethoxysilane (C1961-85)

An aqueous acetic acid solution was prepared by adding ten drops of glacial acetic acid to 5. 83 g(0. 648 eq) of distilled water. Part of this solution (3. 2 g, 0. 324 eq H_2O) was added dropwise with constant stirring to a mixture of p-allylphenyldimethylethoxysilane (95. 0 g, 0. 432 eq) and methyltriethoxysilane (6. 4 g, 0. 108 eq). The reaction temperature was kept at 45-50°C during the addition. Another portion of the methyltriethoxysilane (6. 4 g, 0. 108 eq) was then added to the reaction mixture, after which the remainder of the aqueous acetic acid solution was added dropwise, with constant stirring, at 45-50°C.

After the reaction mixture had become homogeneous, an additional quantity of distilled water (3 g) was added, and the whole mixture was stirred for one hour at 45-50°C.

Ethanol and excess water were distilled from the reaction mixture at 20 torr, the temperature being allowed to reach 80°C. Distillate (35 ml) was collected in a cold trap. A high vacuum distillation was then carried out on a molecular still, yielding four fractions as follows:

F1: 84°C at 10^{-4} torr; 11.8 g, $n_D^{24} = 1.5053$

F2: 85-96°C at 10^{-4} torr; 16.2 g, $n_D^{24} = 1.4986$

F3: 165°C at 10^{-4} torr; 22.2 g, $n_D^{24} = 1.4943$

F4: ≥ 165°C at 10^{-4} torr; 5.9 g, $n_D^{24} = 1.4895$

Cohydrolysis of p-Allylphenyldimethylethoxysilane with Dimethyldiethoxysilane (C1961-93)

Distilled water (7.3 g, 0.40 mole) which contained one drop of glacial acetic acid was added dropwise with constant stirring to a mixture of p-allylphenyldimethylethoxysilane (89.2 g, 0.40 mole) and dimethyldiethoxysilane (30.0 g, 0.20 mole). The mixture was vigorously stirred at ambient temperature for about 18 hours. Absolute ethanol (40 ml) was then added and the mixture was heated at reflux for one hour. After removal of the ethanol by simple distillation, all other low boilers were removed at 85°C and 10^{-3} torr. The undistilled product weighed 48 grams which represented a 55 percent yield. Low boiling products weighed 12.2 g.

Epoxidation of Bis(p-allylphenyl) polymethylsiloxane (C1961-94):

The cohydrolysis product of experiment C1961-93 was used in this epoxidation. Trifluoroacetic anhydride (27.9 g, 0.133 mole) in methylene chloride (25 - 30 ml) was added dropwise to a stirred slurry of hydrogen peroxide (88 percent, 4.0 g, 0.102 mole) in methylene chloride at 0-5°C. When the reaction was completed, the peracid solution was added dropwise with constant stirring to a mixture of the diallyl compound (45.0 g, 0.102 mole) and anhydrous powdered

sodium carbonate (42.2 g, 0.399 mole) in methylene chloride (75 ml). The reaction mixture was maintained at reflux during the addition and for 30 minutes thereafter. It was then filtered to remove inorganic salts. These salts were washed with methylene chloride and the organic phases were combined and retreated with fresh carbonate. After setting overnight and refiltering, most of the solvents were removed by simple distillation and the low boilers were removed at 90°C and 10^{-3} torr. The nonvolatile product weighed 36.6 g, which was 76 percent of theory.

Cohydrolysis of p-Allylphenyldimethylethoxysilane with p-Bis(dimethylethoxysilyl)benzene (C1961-95):

Bis(dimethylethoxysilyl)benzene (46.0 g, 0.080 mole, b.p.$_2$ 110-115°C) and (p-allylphenyl)dimethylethoxysilane (35.2 g, 0.160 mole) were mixed together, and acidified water (2.9 g, 0.16 mole, 0.3 drops acetic acid) was added. The mixture was stirred vigorously for about 16 hours at ambient temperature. When excess water, ethanol, and low boiling products were removed at 70°C and 10^{-3} torr, the undistilled product weighed 40.5 g (60 percent of theory) and had an equivalent weight of 491.

Epoxidation of 1,4-Bis[(p-allylphenyldimethylsiloxy)dimethylsilyl]-benzene (C1961-96)

Trifluoroperacetic acid was prepared by the dropwise addition of a solution of trifluoroacetic anhydride (31.6 g, 0.150 mole) in methylene chloride (35 ml) to a stirred mixture of methylene chloride (35 ml) and hydrogen peroxide (4.66 g, 89 percent, 0.122 mole) at 0-5°C. The freshly prepared peracid was then added dropwise to a slurry of 1,4-bis[(p-allylphenyldimethylsiloxy)dimethylsilyl]benzene (35.0 g) and anhydrous powdered sodium carbonate (47.8 g, 0.45 mole) in methylene chloride (75 ml). Reflux was maintained throughout the addition and was continued for 1/2 hour when the addition was complete. After cooling, the inorganic salts were removed by filtration. Solvent was then removed by distillation and the epoxy compound was heated at about 95°C and 5×10^{-4} torr to remove all volatile constituents. A yield of 18.4 g of epoxy compound was obtained which had an equivalent weight of 491.

2. EPOXYSILAZANES

HISTORICAL

Silazanes constitute a class of compounds which were first synthesized by N. D. Cheronis around the mid 1940's and on which the first patents were issued in 1951.[1] The compounds are generally synthesized by the reaction of halosilanes with a large excess, generally at least fourfold,[2] of ammonia or various other amines.

Polymers of various types have been made from silazanes through hydrolysis,[3] through additions to polyisocyanates, and through condensations with diols.[4] Those silazanes derived from ammonia have also been homopolymerized at 60°C with the liberation of ammonia.[5]

In one report the diglycidyl ether of isopropylidene diphenol was polymerized with hexamethylcyclotrisilazane and octaphenylcyclotetrasilazane. These polymerizations were found to proceed at 100°C or higher. In these cases, gellation occurred within 1 hour at 175°C and the polymerizations were complete within 6 hours at this temperature. Other than this work of Weigel,[6] the only other research in this field appears to be that of R. E. Burke, Jr.,[7] whose investigations dealt with the use of difunctional silazanes such as bis(methylamino)diphenylsilane as epoxy curing agents rather than the trifunctional silazanes such as those reported herein.

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[1] N. D. Cheronis, U.S. 2,564,674, August 21, 1951.

[2] Midland Silicones Ltd., Brit. 737,229, September 21, 1955.

[3] K. A. Andrianov and S. E. Yakushkina, Vysokomolekul. Soedin, 4, 1193-6 (1962).

[4] L. W. Breed and R. L. Elliott, NASA Doc. N-63-19117, 1963.

[5] Cheronis, op. cit.

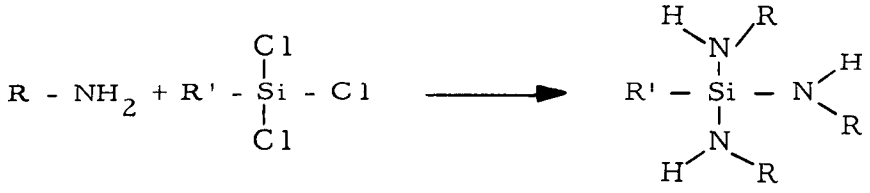
[6] Fritz Weigel, Ger. 1,035,897, August 7, 1958.

[7] Unpublished work reported in the National Aeronautics and Space Administration Summary report on Contract NAS 8-1510, 1965.

DISCUSSION

In work carried out in the Hughes laboratories, silazanes which were studied as epoxy curing agents were noncyclic compounds derived from primary aliphatic amines. In this respect they contrast with the ammonia-based cyclosilazanes studied by Weigel.[8]

Specific compounds investigated in the Hughes research are phenyltris(methylamino)silane, phenyltris(ethylamino)silane and vinyltris(hexylamino)silane. These compounds were synthesized by the reaction of the corresponding trihalosilane with a large excess (ten-fold) of the appropriate anhydrous amine. The general reaction may be illustrated as follows:



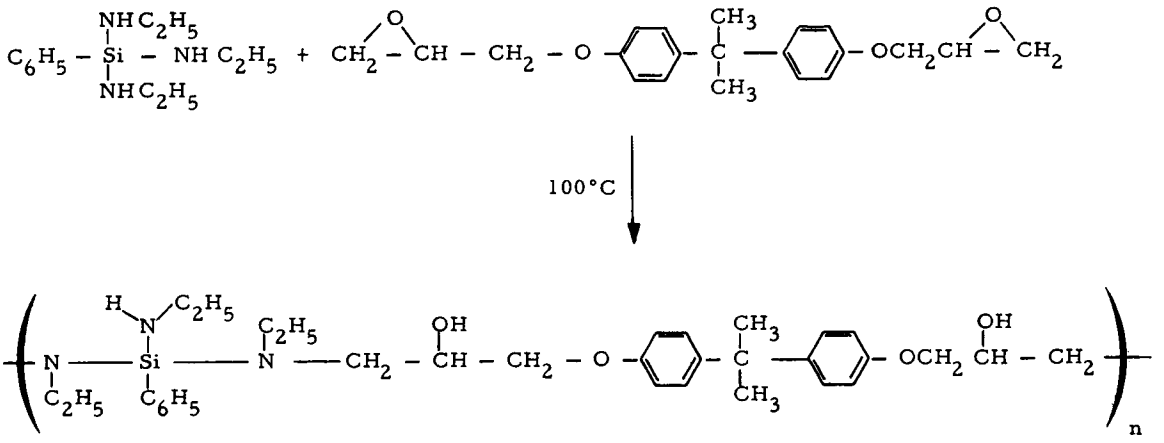
Compound	R	R'
I	$-CH_3$	$-C_6H_5$
II	$-C_2H_5$	$-C_6H_5$
III	$-C_6H_{13}$	$-CH=CH_2$

Structures of these compounds were borne out by elemental analyses which are shown below:

Compound	Empirical Formula	Percent Silicon		Percent Nitrogen	
		Observed	Theoretical	Observed	Theoretical
I	$C_9H_{17}N_3Si$	14.76	14.41	20.30	21.54
II	$C_{12}H_{23}N_3Si$	12.2	11.85	16.36	17.72
III	$C_{20}H_{45}N_3Si$	6.84	7.91	11.40	11.83

[8] op. cit.

Deviations from ideality are attributed to the extremely high moisture sensitivity of these compounds. Fuming invariably occurs in air with the subsequent evolution of the base amine. The most suitable techniques for handling these compounds include storing them in baked syringe bottles and transferring them either in a dry box or via a dry hypodermic syringe. Inadequately dried glassware always promotes the formation of flocculent white precipitates in trace amounts, but this problem can be virtually eliminated when meticulously dried glassware is used. Silazanes of this type function essentially as amines in their reactions with epoxy compounds as illustrated below:



Cured resins derived from 2,2-bis(p-epoxypropoxyphenyl)propane [Epon X-24, Shell Chemical Company] and the above mentioned silazanes were completely colorless transparent products having excellent dielectric and physical properties. For example, the phenyltris-(ethylamino)silane (II) cured resin had the following characteristics:

A.	Compressive strength	21,600 psi
B.	Modulus of elasticity in compression	3.4×10^6 psi
C.	Modulus of elasticity in tension	3.5×10^5 psi
D.	Tensile strength	3,020 psi
E.	Elongation	0.9 percent
F.	Density	1.23 g/cc at 23°C

Coefficients of linear thermal expansion were not determined on pure resin but were determined on specimens filled with silica microballoons (Emerson and Cummings, Eccospheres DI, approximately 20 percent by weight). The following results were obtained:

A. Between -56°C and -4°C : 6.20×10^{-5} in./in./°C

B. Between -4°C and 100°C 7.35×10^{-5} in./in./°C

This resin appeared to have a transition point at about -4°C to -6°C as seen in Figure 2-1.

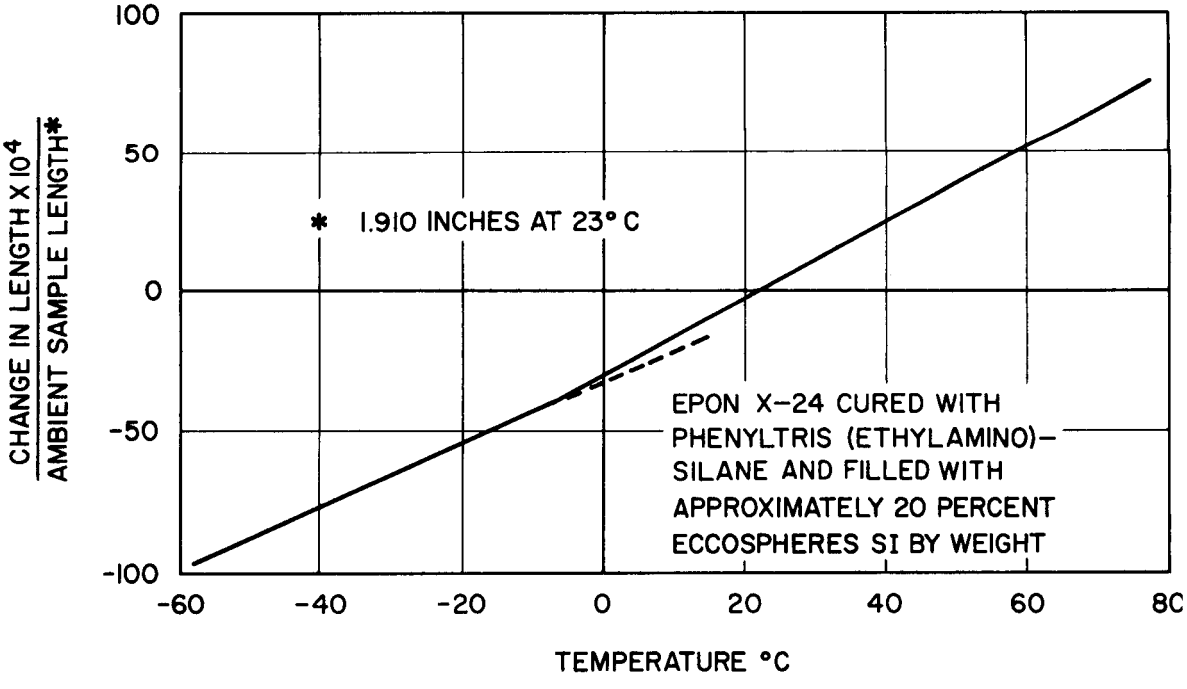


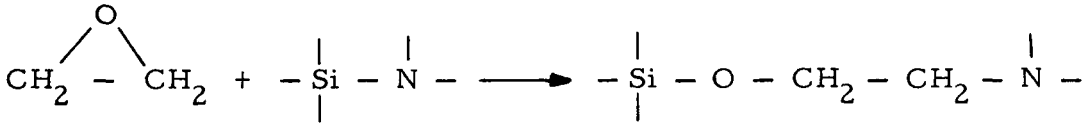
Figure 2-1. Thermal expansion of filled epoxy silazane.

Tests were also carried out on Eccosphere SI filled samples to determine the extent to which they outgassed in high vacuum both at ambient and at elevated temperature. Duplicate samples were evaluated and the following results were obtained:

Time-Temperature	Pressure Range, torr	Total Weight Loss (percent)
72 hours at 23°C	3×10^{-6}	0.080 ± 0.002
72 hours at 23°C plus 24 hours at 100°C	3×10^{-6}	1.06 ± 0.04

Results of these tests were highly promising, not only because of the very small weight losses noted, but more significantly because the volatiles were noncondensable at ambient temperature, even when the specimens were heated at 100°C. Consequently the resins tested appear suitable for aerospace applications.

Ethylene oxide-Freon sterilization tests were also carried out and were in accordance with Voyager specifications. Samples of both filled and unfilled resin were tested. The resin in both was the phenyltris(ethylamino)silane cured Epon X-24 with the filled specimen containing silica microballoons (Eccospheres SI, approximately 20 percent by weight). Surfaces of both specimens were softened by the sterilization conditions but they rehardened when removed from the sterilizing environment. Whether this was due to physical absorption or due to chemical attack was not established. Both processes are feasible. For example, an attack by ethylene oxide on the Si-N bond might proceed as shown below:



However, the subsequent loss in weight observed when the exposed pure resin was heated in the second part of the test essentially negates the possibility that a chemical reaction has occurred. In all probability,

therefore, the changes were due to physical absorption only. Results of these tests are shown in Table 2-1 below:

Sample Number	Test Conditions	Weight, grams	Weight Change, percent	Volume, cc	Volume Change, percent
C2425-79-3	–	0.8464	–	0.69	–
(unfilled)	A	0.8720	+3.0	0.71	+2.9
	B	0.8351	-1.3	0.75	+8.7
C2425-79-3F	–	0.7245	–	0.86	–
(filled)	A	0.8178	+12.9	–	–
	B	0.7180	-0.9	–	–

Table 2-1. Results of sterilization tests on cured epoxysilazanes.

Under test conditions A, samples were carried through six 24 hour cycles at 23°C using an atmosphere of 12 percent ethylene oxide and 88 percent Freon 12 humidified to 50 percent relative humidity. Under test conditions B, specimens were heated at 135°C for 200 hours under dry nitrogen upon completion of the ethylene oxide-Freon exposure.

It is quite apparent that the microballoon filled specimen was somewhat more susceptible to ethylene oxide-Freon absorption than was the unfilled sample. This effect can be attributed to the higher degree of porosity of the filled specimen and can probably be remedied by the use of less than the maximum amount of filler.

Dielectric properties of the various silazane cured epoxies were determined using cylindrical 4-rod embedded electrode specimens 4-1/2 inches long by 5/8 inch wide with 0.16 inch diameter brass electrodes placed 0.33 inch apart on center. The composition of these specimens is given in Table 2-2.

The first three specimens, namely 66-1, 68-8, and 70-3 were unfilled resins derived from Epon X-24 and phenyltris(methylamino)-silane, phenyltris(ethylamino)silane and vinyltris(hexylamino)silane, respectively. In formulating these resin compositions, it was noted that the phenyltris(methylamino)silane yielded homogeneous prepolymer

Code	Composition			Cure Conditions ‡	
	Components	Weight, grams	Eq.	Time, hours	Temperature, °C
C2425-66-1	A	9.75	0.15	16	85
	D	25.5	0.15	6	100
-68-8	B	11.1	0.14	2	23
				5.5	75
	D	23.8	0.14	15	85
				4	100
-70-3	C	14.3	0.12	18	100
	D	20.4	0.12		
-70-4	B	5.5	0.07	64	75
	D	11.9	0.07	5	100
	I	*			
-70-5	C	10.7	0.09	21	100
	D	15.3	0.09		
	I	*			
79-1; Same as 70-4 except for milder postcure	B	7.9	0.10	15	75
	D	17.0	0.10	4	100
	I	*			
-68-9	B	5.5	0.07	1	23
	D	11.9	0.07	5	75
				15	85
	G	43		4	100

Table 2-2. Composition of epoxysilazane dielectric test specimens.

Code	Composition			Cure Conditions‡	
	Components	Weight, grams	Eq.	Time, hours	Temperature, °C
C2425-68-10	B	6.3	0.08	2.5	75
	E	2.2	0.08	15	85
	D	27.3	0.16	4	100
-68-11	B	5.5	0.07	1.5	75
	F	7.9	0.07	15	85
	D	23.8	0.14	4	100
-68-12	B	5.5	0.07	15	85
	H	7.4	0.07	4	100
	D	23.8	0.14		

‡All cures carried out under nitrogen.

*Maximum obtainable – about 20 percent by weight.

Code: A = phenyltris(methylamino)silane
B = phenyltris(ethylamino)silane
C = vinyltris(hexylamino)silane
D = 2, 2-bis(2, 3-epoxypropoxyphenyl)propane [Epon X-24]
E = m-phenylenediamine
F = N-methylaniline formaldehyde (C2425-59B)
G = "OO" smoked silica
H = N, N'-diphenylethylenediamine
I = Eccospheres SI (dried at 250°C)

Table 2-2. (continued)

mixtures which tended to cure very rapidly and care was required to obtain specimens free of cracks. Phenyltris(ethylamino)silane, in contrast, also formed homogeneous prepolymer mixtures,

but no exotherm problems were encountered. Cures proceeded smoothly at 85 to 100°C with the higher temperature being preferred. Vinyltris(hexylamino)silane, on the other hand, was difficult to work with in that it was incompatible with Epon X-24. To obtain homogeneous cured resins, therefore, it was necessary to react this epoxy compound and the silazane under nitrogen at 90 to 100°C with constant stirring until sufficient interaction occurred to produce a homogeneous mixture. This mixture could then be cast and cured at 100°C to produce colorless, transparent, homogeneous castings.

The second set of specimens, namely 70-4, 70-5, 79-1, and 68-9 were filled resins derived from Epon X-24 and either phenyltris-(ethylamino)silane or vinyltris(hexylamino)silane. Phenyltris(methyl-amino)silane was not used in making filled samples. The first three contained silica microballoons (Eccospheres SI) and the fourth contained "O O" smoked silica. Because of its high packing density, the smoked silica did not yield void-free specimens when vacuum impregnation techniques were used; however, it was not evaluated extensively. Microballoon filled specimens were prepared from vacuum degassed resin-filler-premixes.

Specimens 70-4 and 79-1 were phenyltris(ethylamino)silane-based resins and differed in their cure procedure. The former, which had the more extensive cure, had significantly better dielectric properties, as will be noted later.

Dielectric specimens in the last group, specifically 68-10, 68-11, and 68-12 were terpolymers derived from phenyltris(ethyl-amino)silane, Epon X-24 and an aromatic amine. In each case, stoichiometrically equivalent amounts of the silazane and the aromatic amine were used. These amines included m-phenylenediamine, N-methylaniline formaldehyde, and N,N'-diphenylethylenediamine. As far as dielectric properties were concerned, the copolymerization of the aromatic amines with the silazane did not appear to have any special merit and, in fact, detracted from the dielectric properties. Dielectric measurements made on the various epoxy-silazanes described above are presented in Table 2-3.

Code	Dielectric Constant, 1 kc					Dissipation Factor, percent					Insulation Resistance, megohms at 500 VDC					Filler	Curing Agent
	25°C	100°C	125°C	150°C	25°C‡	25°C	100°C	125°C	150°C	25°C‡	25°C	100°C	125°C	150°C	25°C‡		
C2425-68-8	3.68	3.74	3.97	4.27	3.68	0.81	1.12	2.14	7.30	0.81	0.5×10^7	1×10^3	1×10^3	85	1×10^7		A
C2425-70-3	3.47	4.17	4.35	4.87	3.42	0.04	0.76	0.94	0.55	0.07	$>5 \times 10^7$	2×10^4	7×10^2	90	$>5 \times 10^7$		B
C2425-70-4	2.40	2.54	2.56	2.86	2.34	0.12	0.44	0.55	2.26	0.14	3×10^6	9×10^2	2×10^2	40	5×10^6	G	A
C2425-70-4*	2.31	2.29			2.30	1.71	4.69			1.71	3×10^6	5.8			3×10^6	G	A
C2425-70-5	2.41		2.91	2.94	2.41	0.02	0.13	0.28	1.21	0.06	4×10^6	1×10^3	2×10^2	50	$>5 \times 10^7$	G	B
C2425-79-1, 2**	2.38	2.80			2.41	1.96	7.29			2.32	3×10^6	4.0			3×10^6	G	A
C2425-68-9	6.62	7.10	6.92	7.19	6.59	0.42	1.22	1.78	3.10	2.54	1×10^7	3.4×10^3	1.4×10^3	260	5×10^7	F	A
C2425-68-10	4.00	4.57	5.23	6.17	4.27	1.20	1.78	5.96	10.18	1.22	5×10^7	1.1×10^4	4×10^2	28	5×10^7		E
C2425-68-11	3.79	4.04	4.38	5.10	3.82	0.91	0.96	3.46	7.02	0.86	5×10^7	4×10^5	7.5×10^3	120	5×10^7		C
C2425-68-12	3.70	5.86	6.31	6.44	3.69	0.80	9.6	22.36	34.82	0.64	$>10^7$	2.5×10^2	15	2.2	5×10^7		D

A – phenyltris(ethylamino)silane.

B – vinyltris(hexylamino)silane..

C – phenyltris(ethylamino)silane plus N-methylaniline formaldehyde (1 eq:1 eq).

D – phenyltris(ethylamino)silane plus N, N'-diphenylethylenediamine (1 eq:1 eq).

E – phenyltris(ethylamino)silane plus m-phenylenediamine (1 eq: 1 eq).

F – "oo" smoked silica.

G – silica microballoons, Eccospheres SI.

‡Reevaluated after the elevated temperature tests were complete.

*Reevaluated after being submerged in boiling water for 40 minutes and redrying for 3 days at 24°C and 5 torr.

**Same as 70-4 except for a much shorter cure period.

Table 2-3. Dielectric properties of various silazane cured Epon X-24 specimens.

A study has also been made on the effect of water on the silazane cured Epon X-24 resins. Specimens used in these tests were approximately 1/8 x 1/4 x 1/2 inch. Moisture resistance was far better than anticipated both from the standpoint of dimensional stability and weight. With total immersion at ambient temperature the phenyltris(ethylamino)-silane cured samples swelled about 0.1 - 0.2 percent, both filled and unfilled, and then showed no significant further change for about 50 hours. Weight gains in this period were below 1 percent for the tris(ethylamino)silane cured sample and below 1.6 percent for the vinyltris(hexylamino)silane cured sample.

With total submersion at 100°C, the vinyltris(hexylamino)silane cured resin was highly superior to the phenyltris(ethylamino)silane cured resin in that the former increased in weight by only 3.4 percent in seven hours, whereas the latter gained 20 percent in weight in two hours. It was also noted that the silica microballoon filled specimens were inferior in all cases to the corresponding unfilled resins. This can probably be attributed to a high degree of porosity. Moisture resistance on the filled samples thus probably can be improved markedly if less than the maximum amount of filler is incorporated.

Data showing the effect of water on these resins are presented in graphical form in Figures 2-2 through 2-5.

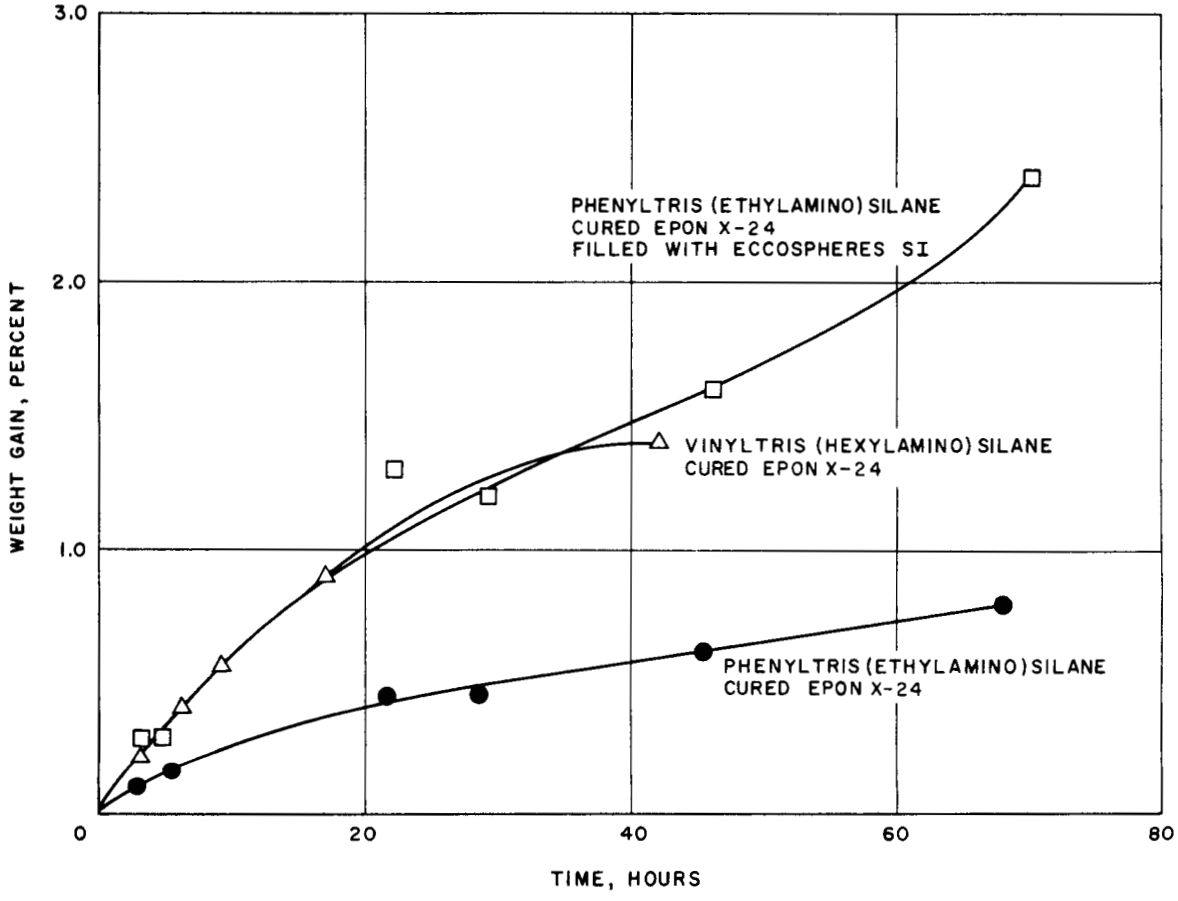


Figure 2-2. Effect of water on silazane cured epoxy resins (total immersion at 24°C).

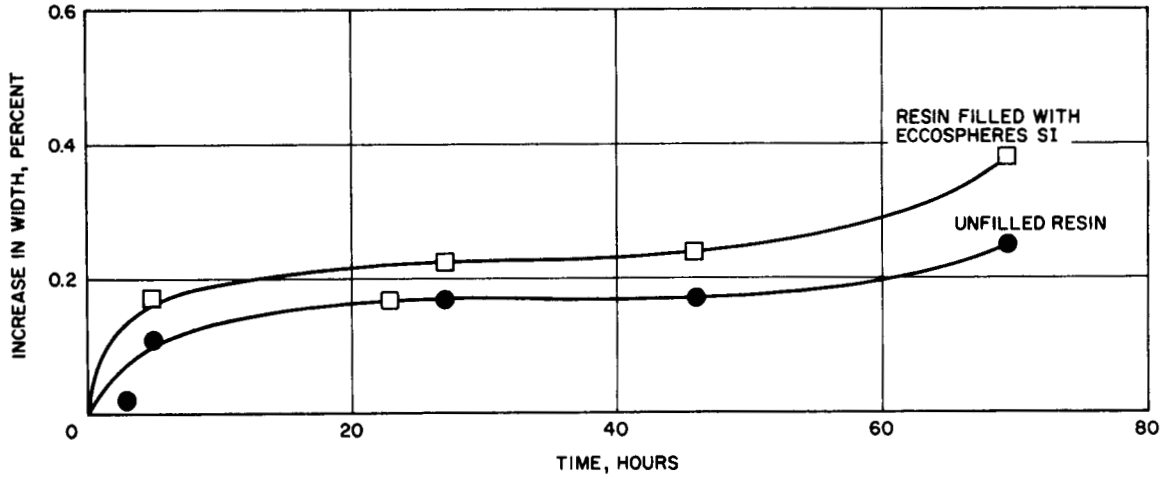


Figure 2-3. Effect of water on phenyltris(ethylamino)silane cured Epon X-24 (total immersion at 24°C).

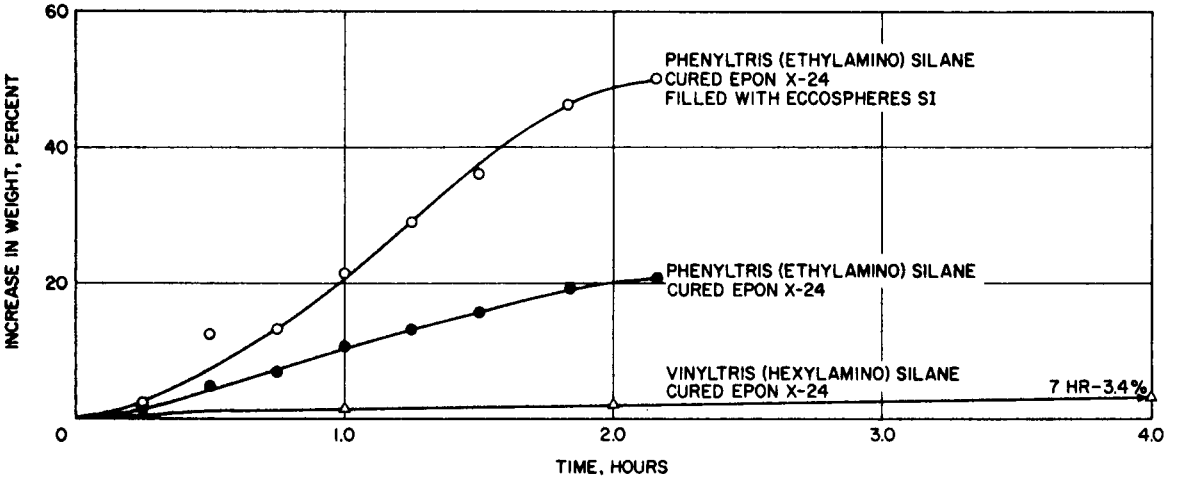


Figure 2-4. Water absorption of silazane cured Epon X-24 resins (total immersion at 100°C).

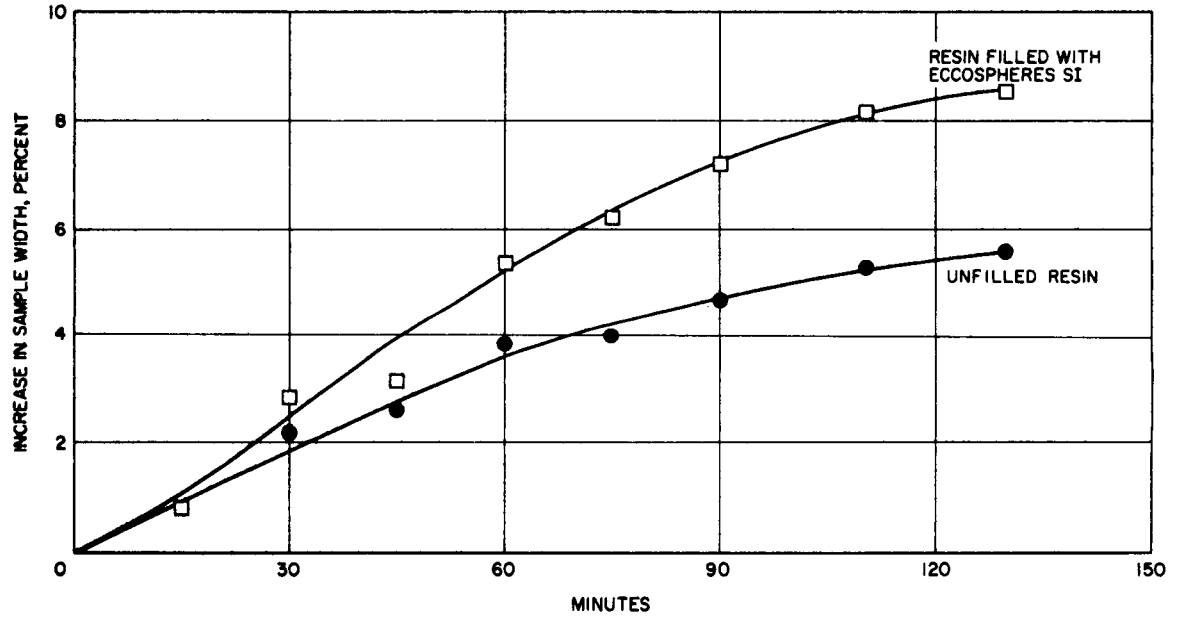


Figure 2-5. Effect of water on dimensional stability of phenyltris(ethylamino)silane cured Epon X-24 (total immersion at 100°C).

EXPERIMENTAL

Phenyltris(ethylamino)silane (D1151-21)

To a mixture of anhydrous ethylamine (450 g, 10 moles) in anhydrous ether (1 l) was added dropwise a solution of freshly distilled phenyltrichlorosilane (211 g, 1 mole) in anhydrous ether (200 ml). Upon completion of the addition, the mixture was heated at reflux for one hour. After cooling and settling, the fluid phase was decanted and filtered. Ether and excess amine were then removed by simple distillation and the phenyltris(ethylamino)silane was distilled under reduced pressure (B.P. 123°C at 5 torr). A yield of 196 g, (0.83 mole, 83 percent) was obtained.

Phenyltris(methylamino)silane (D1151-4A)

A solution of phenyltrichlorosilane (23.3 g, 0.11 mole) in anhydrous ether (50 ml) was gradually added to a solution of dry methylamine (34.2 g, 1.1 moles) in anhydrous ether (200 ml). After completing the addition the reaction mixture was heated at reflux for 45 minutes and excess methylamine was distilled off. It was then filtered to remove methylammonium chloride and the filtrate was then distilled at ambient pressure to remove ether. Distillation of the high boilers at 3 torr yielded 11 g of phenyltris(methylamino)silane boiling between 104 and 115°C. Virtually all of the product boiled at 105°C. The yield represents 51 percent of theoretical.

Preparation of Vinyltris(hexylamino)silane (D1151-8A)

Freshly distilled vinyltrichlorosilane (B.P. 90°C) and n-hexylamine (B.P. 132 ± 1°C) were used in this preparation. The amine was dried over KOH before distilling.

To a cold solution (-10°C) of n-hexylamine (208 g, 2.05 moles) in anhydrous ether (100 ml) was added dropwise (one hour) a solution of vinyltrichlorosilane (32.3 g, 0.20 mole) in anhydrous ether (75 ml). Upon completion of the reaction the mixture was allowed to warm to room temperature and was then filtered to remove the hexylamine

hydrochloride. Ether and excess amine were removed by distillation at ambient pressure and the residue was then extracted with naphtha. This naphtha solution was distilled first at ambient and then at reduced pressure (approximately five torr). Because of the high boiling point of the product (132-155°C) it was redistilled at 1.5×10^{-3} torr and 115-140°C. Some degradation occurred at these temperatures, probably due to the high pot temperature (160-175°C). A final distillation on a molecular still was carried out at 10^{-3} torr and two fractions were collected, namely

I 95-105°C (27.5 g), pot temperature 98-107°C

II 105-150°C (5 g), pot temperature 107-160°C

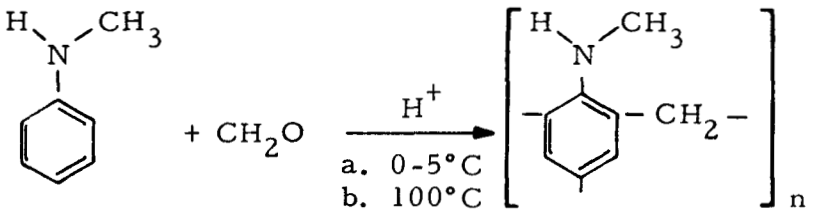
The total product ($\simeq$30 g) represents a 42 percent yield.

In a previous preparation a yield of only 20 percent was obtained.

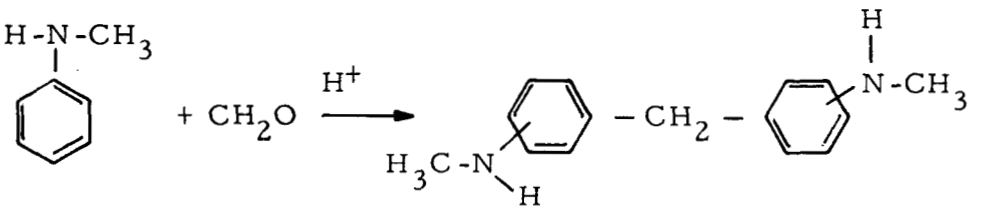
3. N-METHYLANILINE FORMALDEHYDE – EPOXIES

DISCUSSION

N-Methylaniline formaldehyde is a condensation product obtained from the acid catalyzed reaction of N-methylaniline with formaldehyde. The material has been found to be an excellent curing agent for epoxy resins. Its preparation may be illustrated in the following general form.



The first of these syntheses utilized 2 moles of the aromatic amine and one mole of formaldehyde and may be illustrated as follows:



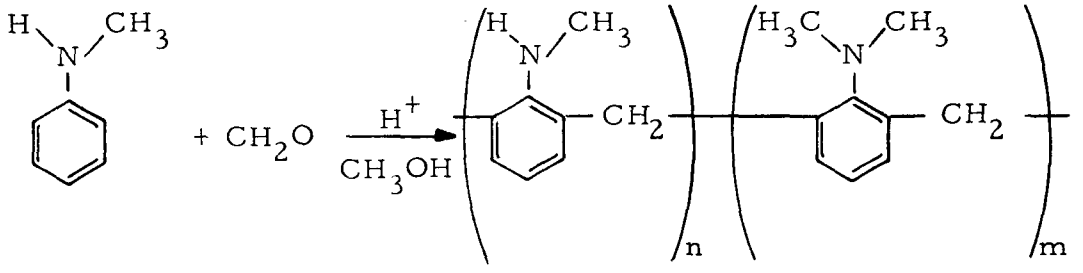
Rather than producing a single compound, the reaction yields a mixture of isomers which include 4, 4'-bis(methylamino)diphenylmethane, 2, 2'-bis(methylamino)diphenylmethane, and 2, 4'-bis(methylamino)-diphenylmethane, as well as a small amount of higher telomers. To some extent the various isomers can be separated by molecular distillation at 10^{-3} torr and temperatures of 80-150°C. That portion which distills at the lower temperature tends to crystallize more readily than the higher boiling portion and thus is probably the more symmetrical 4, 4'-isomer.

When the volatile diamine mixture was used to cure 2, 2-bis-(epoxypropoxyphenyl)propane (Epon X-24) the cured resins were quite brittle; however, the undistilled reaction product (which contained higher telomers), or the nonvolatile higher telomers alone, produced tough resins.

Further synthesis efforts were thus directed to the preparation of higher telomers only. This was accomplished by using various amine:formaldehyde molar ratios between one and two. One to one molar ratios were of no interest because they produce high polymers.

After synthesizing and evaluating these condensation products, it was demonstrated that the lower the molar ratio of N-methylaniline to formaldehyde the better the condensation product functioned as a curing agent relative to its high temperature dielectric properties. This was attributed to the gradual increase in the degree of polymerization (D. P.) of the condensation product as the ratio approached the value 1; furthermore, the higher the degree of polymerization, the higher the second order glass transition temperature of the prepolymer that could be expected, and the higher the second order glass transition temperature which might be expected of the cured epoxy resin made therefrom. The gradual improvement of dielectric properties as the D. P. of the curing agent increased thus may be due to this factor. It would, of course, be necessary to measure the various second order glass transition temperatures on cured resins in order to support this explanation.

There is, of course, another highly plausible explanation for this effect. Since inhibited formaldehyde, which contains methanol, was used in these experiments, it is quite possible that as the relative formaldehyde concentration was increased condensation products had successively higher degrees of N-methylation. This is illustrated as follows:



Tertiary amino groups in these prepolymers would, of course, not be capable of adding to epoxy groups although they would still be catalytic. However, the polyfunctional nature of the products would permit them to continue to function in a curing capacity via additions of the unchanged secondary amino groups.

This explanation could be tested by studying condensation products derived from uninhibited formaldehyde. A comprehensive study of this type was not made although two such experiments were carried out in which the N-methylaniline to formaldehyde ratio was 1.59 and 1.38.

Dielectric properties of epoxy resins made from these amines again indicated that the lower ratio was superior. Thus it appears that the degree of polymerization is a more important factor in bringing about improved high temperature dielectric properties than is the extent of methylation. It should also be pointed out that methylation by methanol can also occur on the ring under acid catalysis as well as on the amino groups. If this occurs the secondary amino groups remain unalkylated and can continue to cure via addition across epoxy groups. It should also be noted that condensations carried out under nitrogen yield very light colored products which are capable of producing almost colorless cured epoxies. Distillation of the N-methylaniline under nitrogen prior to use also helps considerably in providing chromophore-free polyamines.

After having prepared a series of these polyamines, several experiments were carried out to determine the optimum ratio of the N-methylaniline formaldehyde to the epoxy compound. For these tests the curing agent that was used had an amine:formaldehyde molar ratio of 1.5. When the epoxy:amine equivalent weight ratio exceeded 2, the reaction products were brittle and melted below 100°C; however, when this ratio was between 1 and 1.5, tough resins were formed.

Optimum dielectric properties were observed when the epoxy: amine equivalent weight ratio was 1. This data is presented in Table 3-1. Data was also obtained on two specimens which were filled with glass microballoons (Eccospheres R', from Emerson and Cummings) and is presented in Table 3-2.

Specimen No.	* Epoxy:Amine Eq. Wt. Ratio	Dielectric Constant, 1 kc		Dissipation Factor, percent		Insulation Resistance, megohms @ 500 VDC	
		25°C	100°C	25°C	100°C	25°C	100°C
73-1, 2	1.00	3.9	3.9	0.5	0.2	$>1\times10^{7}$	3×10^{6}
77-2	1.13	4.5	4.8	0.5	0.3	$>1\times10^{7}$	2×10^{6}
77-1	1.50	4.5		0.3	4.9	5×10^{6}	3×10^{3}
78-3	2.27	Brittle cracked specimen					
78-4	5.00	No cure					

*Epon X-24 (Shell Chemical Co.)

Table 3-1. Dielectric properties of several early N-methylaniline formaldehyde cured epoxies.

Specimen No.	* Epoxy:Amine Eq.Wt. Ratio	Dielectric Constant, 1 kc		Dissipation Factor, percent		Insulation Resistance, megohms @ 500 VDC	
		25°C	100°C	25°C	100°C	25°C	100°C
80-X3	1.00	4.0	3.8	0.4	0.1	1×10^{7}	5×10^{6}
80-X2 (distilled diamine)	1.00	3.5	4.9	4.1	34	6×10^{5}	2×10^{3}
77-1A	1.50	3.8	4.8	2.5	28	7×10^{5}	7×10^{2}

*Filled with Eccospheres R

Table 3-2. Dielectric properties of several early N-methylaniline formaldehyde cured epoxies (filled).

From this data several conclusions may be drawn. The first is that the distilled diamine [bis(methylamino)diphenylmethane] is highly inferior to the polyamine. This is quite apparent in a comparison of results from specimens 80-X2 and 80-X3. Diamine cured epoxies were too brittle (unfilled) to yield useful test specimens. A comparison of results from 77-1A and 80-X3 further demonstrated the superiority of the 1:1 epoxy:amine equivalent weight ratio of reactants over the 1.5:1 ratio.

A more comprehensive study of these curing agents was subsequently undertaken utilizing in all cases an Epon X-24 to methylaniline formaldehyde equivalent weight ratio of one to one. Theoretical equivalent weights were used for the methylaniline formaldehyde condensation products. Dielectric constants, dissipation factors, and insulation resistances of the cured epoxies are graphically illustrated in Figures 3-1, 3-2, and 3-3, respectively. Each of these sets of data verifies the superiority of the lower methylaniline formaldehyde ratios over the higher ratios with the major improvement being observed at temperatures above 100°C. Below this temperature little advantage of ratio changes were noted. Efforts were also made to study condensation products in which the methylaniline to formaldehyde mole ratio was below 1.3. However, these materials were solids with melting points and viscosities in the molten state too high to permit them to be used conveniently. Graphical comparisons of observed dielectric properties are shown in the above mentioned figures.

The compositions of the various dielectric test specimens are presented in Table 3-3 and a tabulation of additional dielectric test data is presented in Table 3-4.

One series of dielectric tests was carried out under high vacuum (10^{-6} torr). This data is presented in Table 3-5. Samples used in these tests (C1980-73) had been tested previously in air. The aniline formaldehyde curing agent in this case was one having an amine formaldehyde ratio of 1.6. Differences between the results of these tests and the results obtained in air were of a minor nature.

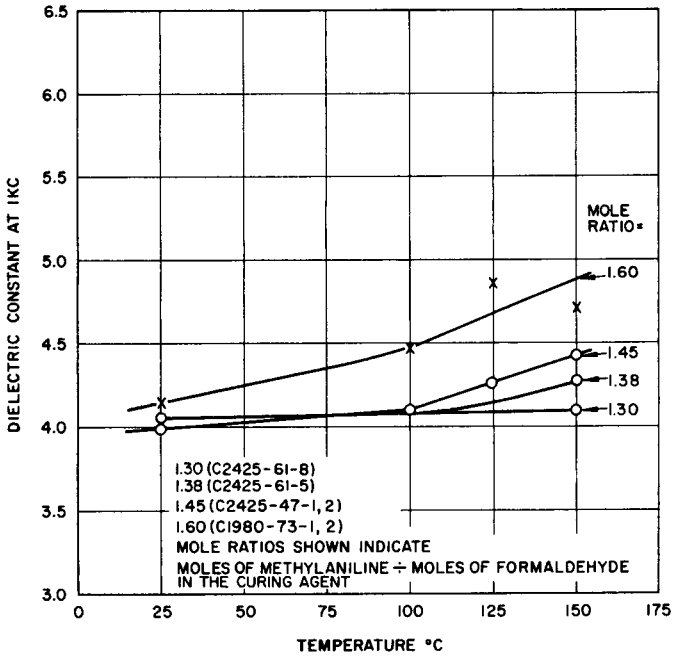


Figure 3-1. Dielectric constants of N-methylaniline cured Epon X-24 as a function of temperature.

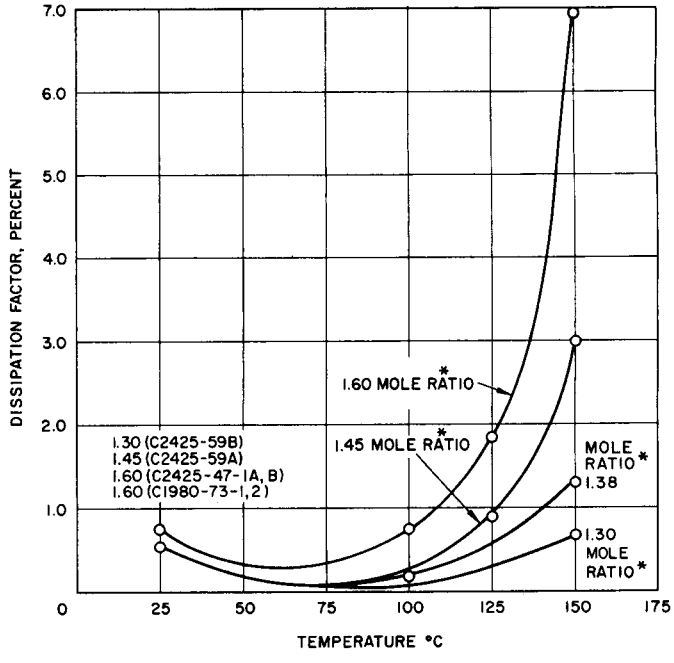


Figure 3-2. Dissipation factors as a function of temperature — N-methylaniline formaldehyde cured Epon X-24.

*Mole ratios refer to the methylaniline:formaldehyde mole ratio. The amines were formulated with the epoxy compound on a 1:1 equivalent weight basis.

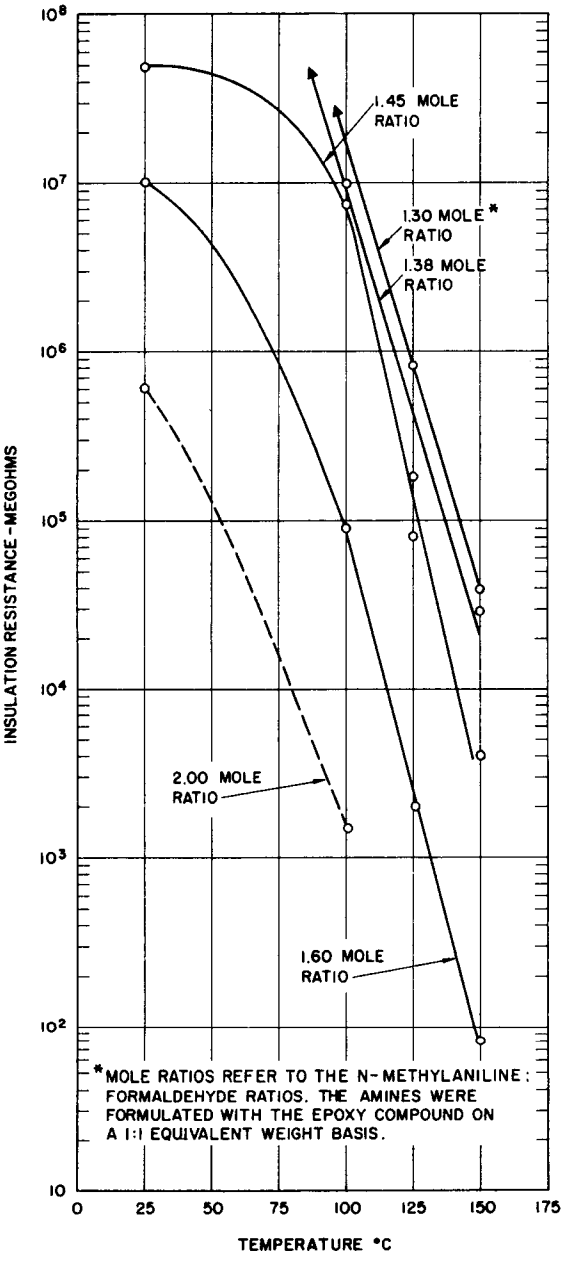


Figure 3-3. Insulation resistance as a function of temperature for N-methylaniline formaldehyde cured Epon X-24.

Code	Epoxy Amine Eq. Wt. Ratio	Amine CH_2O Mole Ratio	Resin Designation	Weight, grams	Eq.	Filler	Cure Schedule	Comments
C1980-77-1A	1.5	1.60	X-24 A	15.4 6.9	0.09 0.06	Eccospheres R	74°C – 3 days	Vacuum fill white – tough
-77-1	1.5	1.60	X-24 A	23.1 10.3	0.136 0.09	–	74°C – 16 hours + 8 hours at 100°C	Light yellow tint, somewhat flexible at 100°C – tough
-77-2	1.1	1.60	X-24 A	23.1 13.8	0.136 0.12	–	74°C – 16 hours + 8 hours at 100°C	Light yellow tint, tough, more rigid than 77-1 but still flexible at 100°C
-78-3	2.3	1.60	X-24 A	23.1 6.9	0.136 0.06	–	74°C – 16 hours + 8 hours at 100°C	Fluid at 100°C. Very brittle at 25°C. Light yellow tint
-78-4	5.0	1.60	X-24 A	30.8 4.6	0.20 0.04	–	75°C – 16 hours + 8 hours at 100°C	No cure fluid at 25°C
-80-X1	1.0	2.00	X-24 B	17.0 11.3	0.10 0.10	–	74°C – 48 hours	Very brittle, cracked, light yellow tint
-80-X3	1.0	–	X-24 C	17.0 11.3	0.10 0.10	Eccospheres R	74°C – 48 hours	Tough – amber color
-81-X1	1.0	2.00	X-24 B	17.0 11.3	0.10 0.10	–	74°C – 16 hours	Very brittle cracked
-80-X2	1.0	2.00	X-24 B	17.0 11.3	0.10 0.10	Eccospheres R	74°C – 16 hours	Vacuum fill cracked
-73-1.2	1.0	1.60	X-24 D	34.0 23.4	0.20 0.20	–	74°C – 16 hours in N_2 – 140°C 3 hours vacuum	Tough, vacuum fill, amber color
C2425-47-	1.0	1.45	X-24 F	18.7 13.2	0.11 0.11		75°C – 21 hours 100°C – 3 hours	Very tough, very light color
-60-1	1.1	1.38	X-24 G	18.7 11.3	0.11 0.10		85°C – 18 hours 100°C – 6.5 hours	Clear no voids, good specimen
-60-2	1.0	1.30	X-24 H	18.7 12.6	0.11 0.11		85°C – 16 hours 100°C – 6.5 hours	No voids, some evidence of unmixed amine
-60-3	1.0	1.38	X-24 G	18.7 12.6	0.11 0.11	Al_2O_3	85°C – 21.5 hours 100°C – 6 hours	Filler was vibrated full and impregnated. No voids, good specimen
-60-4	1.0	1.30	X-24 H	18.7 12.6	0.11 0.11	Al_2O_3	85°C – 16 hours 100°C – 6 hours	Filler vibrated in but only about 95 percent filled, no voids

Table 3-3. Composition of N-methylaniline formaldehyde cured epoxy resins.

Code	Epoxy Amine Eq. Wt. Ratio	Amine CH_2O Mole Ratio	Resin Designation	Weight, grams	Eq.	Filler	Cure Schedule	Comments
C2425-61-5	1.0	1.38	X-24 G	18.7 12.6	0.11 0.11		85°C – 18 hours 100°C – 6 hours	No voids, good specimen
-61-6	1.0	1.38	X-24 G	18.7 12.6	0.11 0.11	"OO" smoked silica, 31.3 g	85°C – 16 hours 100°C – 6 hours	No voids, some packing of filler at bottom
-61-7	1.0	1.38	X-24 G	18.7 12.6	0.11 0.11	"OO" smoked silica, 62.6 g	85°C – 20 hours 100°C – 6 hours	No voids, some packing of filler at bottom
-61-8	1.0	1.30	X-24 H	18.7 12.6	0.11 0.11		85°C – 17.5 hours 100°C – 6 hours	No voids, good specimen
-61-9	1.0	1.30	X-24 H	18.7 12.6	0.11 0.11	Al_2O_3	85°C – 16 hours 100°C – 6 hours	Filler vibrated in no voids, good specimen
-61-10	1.0	1.38	X-24 G	18.7 12.6	0.11 0.11	Eccospheres R	85°C – 20 hours 100°C – 6 hours	Filler vibrated in, couldn't impregnate sample. Not usable
-62-11	1.0	1.30	X-24 H	18.7 12.6	0.11 0.11	Eccospheres R	85°C – 18 hours 100°C – 6 hours	Filler vibrated in, couldn't impregnate sample. Not usable
-62-12	1.0	1.30	X-24 H	18.7 12.6	0.11 0.11	"OO" smoked silica, 62.6 g	85°C – 15.5 hours 100°C – 6 hours	No voids, good specimen
-62-13	1.0	1.38	X-24 G	18.7 12.6	0.11 0.11	Eccospheres R, 8 g	85°C – 17 hours 100°C – 6 hours	One small cavity, but was filled
-62-14	1.0	1.30	X-24 H	18.7 12.6	0.11 0.11	Eccospheres R, 8 g	85°C – 20 hours 100°C – 6 hours	Several cavities, but were filled
-67-2	1.0	1.59*	X-24 I	18.7 12.6	0.11 0.11		85°C – 17 hours 100°C – 6 hours	No voids, good specimen
-67-3	1.0	1.38*	X-24 J	18.7 12.6	0.11 0.11		85°C – 16 hours 100°C – 6 hours	No voids, good specimen
-67-4	1.0		X-24 K	18.7 12.6	0.11 0.11		85°C – 16 hours 100°C – 6 hours	No voids, good specimen
-67-5	1.0	1.59*	X-24 I	18.7 12.6	0.11 0.11	"OO" smoked silica, 62.6 g	85°C – 65 hours 100°C – 3 hours	No voids, some settling of filler
-67-6	1.0	1.38*	X-24 J	18.7 12.6	0.11 0.11	"OO" smoked silica, 62.6 g	85°C – 64 hours 100°C – 3 hours	No voids, some settling of filler
-67-7	1.0	1.38*	X-24 K	18.7 12.6	0.11 0.11	"OO" smoked silica, 62.6 g	85°C – 63 hours 100°C – 3 hours	No voids, some settling of filler

Code:
X-24 = Epon X-24 (Shell Chemical Co.)
A = C2425-15B; B = C2942-31A; C = C2942-31B; D = C1961-55Φ; F = C2425-46; G = C2425-59A; H = C2425-59B;
I = C2425-65A; J = C2425-65B; K = C2425-66C; I, J, K are derived from uninhibited formaldehyde;
L = 4, 4'-diaminodiphenylmethane.

Table 3-3 (continued).

Code	Dielectric Constant at 1 kc				Dissipation Factor, percent				Insulation Resistance, megohms at 500 VDC				Filler, percent	Ratio ‡
	25°C	100°C	125°C	150°C	25°C	100°C	125°C	150°C	25°C	100°C	125°C	150°C		
C2425-47	4.0	4.1	4.3	4.4	0.5	0.2	0.9	3.0	5×10^7	1×10^7	1×10^5	4×10^3	–	1.45
C1980-73-1	3.9	3.9			0.5	0.2			$>10^7$	3×10^6				1.60
C2425-61-5	4.1	4.1	4.1	4.3	0.5	0.1	0.20	1.3	$>10^7$	1×10^7	2×10^5	3×10^4	–	1.38
-61-8	4.1	4.1	4.1	4.2	0.5	0.2	0.22	0.6	$>10^7$	1×10^7	1×10^6	4×10^4	–	1.30
-67-2	4.1	4.2	4.2	4.7	0.8	0.1	0.5	3.5	5×10^7	7×10^6	2×10^5	4×10^3	–	1.59*
-67-3	4.2	4.2	4.2	4.5	0.7	0.1	0.3	2.4	5×10^7	5×10^6	18×10^5	1×10^4	–	1.38*
-60-3	6.7	6.8	6.8	6.9	0.2	0.1	0.1	0.9	5×10^7	1×10^7	1×10^4	4×10^4	76 A'	1.38
-60-4	6.9	7.0	7.0	7.1	0.2	0.1	0.2	0.7	$>10^7$	5×10^6	0.7×10^6	4×10^4	76 A'	1.30
-61-6	5.4	5.4	5.5	5.5	0.4	0.1	0.4	0.50	$>10^7$	3×10^7	4×10^5	4×10^4	50 B'	1.38
-61-7	6.3	6.4	6.5	6.6	0.3	0.1	0.6	1.5	5×10^7	1×10^7	4×10^5	2×10^4	67 B'	1.38
-62-12	6.1	6.0	6.2	6.4	0.3	0.1	0.2	1.7	$>10^7$	1×10^7	1×10^6	6×10^4	67 B'	1.30
-67-5	6.2	6.3	6.5	6.9	0.3	0.1	1.0	1.0	5×10^7	5×10^6	9×10^4	4×10^3	67 B'	1.51*
-67-6	6.2	6.2	6.3	6.4	0.4	0.1	0.1	0.6	5×10^7	1×10^7	1×10^6	2×10^4	67 B'	1.38*
-62-13	4.1	4.3	4.4	4.9	1.1	4.9	7.1	15.9	3×10^6	1×10^6	1×10^5	6×10^3	20 C'	1.38
-62-14	4.1	4.3	4.2	4.9	1.0	4.2	9.0	15.2	4×10^6	1×10^6	1×10^5	3×10^3	20 C'	1.30

A' – alumina

B' – "OO" smoked silica

C' – Eccospheres "R"

* – Uninhibited formaldehyde was used in preparing this curing agent

‡ – Ratio refers to the N-methylaniline to formaldehyde ratio – all epoxies were formulated stoichiometrically

Table 3-4. Dielectric properties of various N-methylaniline formaldehyde cured epoxy resins.

Time, hour	20	21	57	83	105	178
Temperature, °C	25°	25°	100°	125°	150°	150°
Pressure (torr)	760	6×10^{-7}	9×10^{-6}	4×10^{-6}	1×10^{-6}	3×10^{-6}
Dielectric constant (at 1 kc)	4.1	4.1	4.4	4.9	4.7	4.7
Insulation resistance, megohms	2×10^4	$>1\times10^7$	1×10^5	1×10^3	0.8×10^2	1×10^2
Dissipation factor, percent	0.74	0.74	0.76	1.8	8.0	7.4

Table 3-5. Dielectric properties of N-methylaniline formaldehyde cured Epon X-24 under high vacuum.

Several physical property measurements have also been made on the 1.30 mole ratio N-methylaniline formaldehyde cured Epon X-24. The amine was derived from inhibited formaldehyde. The results are compared to those obtained with a 1.60 mole ratio condensation product and are tabulated below.

Amine Epon Eq. Wt. Ratio	Methylaniline Formaldehyde Ratio	Compressive Strength, psi	Tensile Strength, psi	Elastic Modulus, psi
1:1	1.30‡	15,400	14,100	1.1×10^6
1:1	1.60*	14,500	12,200	3.7×10^6

‡Resin No. C2425-59B
*Resin No. C2425-15B

Other physical test data on the 1.60 mole ratio product include the following:

1. Elongation: 10 percent
2. Compressive yield strength: 5640 psi
3. Modulus of elasticity: 1.2×10^6 psi
4. Thermal conductivity: 3.46×10^{-4} cal/sec/cm^2/°C/cm
5. Coefficient of expansion:
   a. Between 25° and 100°C: 0.639×10^{-4} in/in/°C
   b. Between -75° and 25°C: 0.502×10^{-4} in/in/°C
6. Weight loss at 2×10^{-6} torr (> 178 hours total, > 73 hours at 150°C): 0.11 percent

Also studied was the resistance of two N-methylaniline formaldehyde cured Epon X-24 specimens to ethylene oxide-Freon mixtures. Tests were conducted according to the new Voyager specifications. Results of these tests are shown in the following tabulation.

Amine Epon Eq. Wt. Ratio	Methylaniline Formaldehyde Ratio	Change After Six 24-Hour Cycles at 40°C		Change After 168 Hours at 135°C	
		Percent Weight	Percent Volume	Percent Weight	Percent Volume
1:1	1.38	+0.163	-0.03	-0.108	-0.71
1:1	1.30	+0.144	+0.45	-0.104	+0.45

Microwave frequency dielectric tests were also carried out using a specimen of N-methylaniline formaldehyde (1.30 mole ratio) cured Epon X-24 which had been machined to a flat disc 2.135 inches diameter by 0.333 inch thick to allow permittivity measurements in an X-band resonant cavity dielectrometer. The thickness was chosen on the basis of an estimated dielectric constant of 4.0 to provide a half-wave ($\lambda/2$) specimen. The diameter was chosen to conform to the cavity diameter (2.1609 inches).

Volume resistivity was measured with a 3-electrode system as per Specification ASTM D 257-61, using polished copper electrodes firmly pressed against the specimen. Contact area of the guarded electrode was 10 cm^2 and the test voltage was 100 volts dc. Current readings were essentially constant 4 minutes after application of voltage.

Permittivity measurements were made at 9.28 GHz (9.28×10^9 cycle/sec) in an invar variable-length cavity resonator operating between TE_{014} and TE_{015} modes. The cavity is tuned to resonance with and without the specimen. The shift in resonance length is a function of the specimen dielectric constant. The half-power bandwidth at resonance with the specimen in the cavity is a measure of the dielectric losses in the specimen. Measurements were made at a specimen temperature of 23°C, 67°C, then at 23°C again. Results of these tests are presented in the following table.

Temp. °C	Dielectric Constant	Loss Tangent	DC Volume Resistivity — ohm cm
23	3.26	0.053	1.4×10^{15}
67	3.66	0.145	
23*	3.27	0.053	

*after the heat test

The complex permittivity of the dielectric specimen is defined by:

$$\epsilon = \epsilon' - j\epsilon'' \tag{3-1}$$

where ϵ' and ϵ'' are the real and imaginary components respectively. Values relative to vacuum (permittivity $= \epsilon_o$) are defined by:

$$\frac{\epsilon}{\epsilon_o} = \bar{\epsilon} = \bar{\epsilon}' - j\bar{\epsilon}'' = \bar{\epsilon}'(1 - j \tan \delta) \tag{3-2}$$

where $\bar{\epsilon}'$, $\bar{\epsilon}''$, and tan δ denote the relative dielectric constant, relative loss factor, and loss tangent, respectively.

Since the permittivity of air (ϵ_{air}) is almost but not quite the same as that of vacuum, dielectric constant values of a specimen relative to air are approximately the same as those relative to vacuum. The permittivity of air varies with several factors including humidity content and temperature. The values of specimen dielectric constant reported herein are relative to air, that is,

$$\bar{\epsilon}'_{s,air} = \epsilon'_{specimen} / \epsilon'_{air}.$$

The loss tangent, defined by

$$\tan \delta = \frac{\epsilon''}{\epsilon'} = \frac{\bar{\epsilon}''}{\bar{\epsilon}'} \tag{3-3}$$

is equivalent to the dissipation factor. The latter, for convenience, is often expressed as a percentage.

Calculation of the specimen relative dielectric constant was made by means of the following expression:

$$\bar{\epsilon}'_{s,air} = \frac{\epsilon'_s}{\epsilon'_{air}} = \frac{\beta_s^2 + k^2}{\beta_g^2 + k^2}\left(1 - \frac{\beta_s^2 + k^2}{\beta_s^2} \cdot \frac{\tan^2\delta}{4}\right) \tag{3-4}$$

where

β_s = phase constant in specimen,

β_g = phase constant in cavity (guide), and

k = transverse wave number

The value of β_g was calculated from the measured guide wavelength, λ_g, by:

$$\beta_g = \frac{2\pi}{\lambda_g} = \frac{\pi}{TE_{015} - TE_{014}} \tag{3-5}$$

The value of k is determined by:

$$k = \frac{x_1}{a} \tag{3-6}$$

where a is the cavity radius, and x_1 is equal to 3.8317, the least root of the Bessel function $J_1(x)$.

The value of β_s was calculated from the following transcendental equation.

$$\frac{\tan \beta_s b}{\beta_s b} = -\frac{\tan \beta_g (X - b)}{\beta_g b} \tag{3-7}$$

where $X = \ell - L$, ℓ is the TE_{015} resonance length with specimen in the cavity, and L is the length of the empty cavity in the TE_{014} mode

For low - loss specimens ($\tan \delta \ll 1$), Equation (3-4) simplifies to:

$$\bar{\epsilon}'_{s,air} \cong \frac{\beta_s^2 + k^2}{\beta_g^2 + k^2} \tag{3-8}$$

Dielectric constant values obtained with Equation (3-8) were used in Equation (3-9) to calculate the loss tangent. In turn these loss tangent values were then used in Equation (3-4) to obtain corrected values of relative dielectric constant.

Loss tangent was calculated by:

$$\tan \delta = \frac{\beta_g^2}{\beta_o^2} \cdot \frac{1}{\bar{\epsilon}' B^2 b'} (\Delta \ell - C) \tag{3-9}$$

where β_o is the free-space phase constant, b' is a modified specimen thickness, related to the actual thickness, b, by

$$b' = b\left(1 - \frac{\sin 2\beta_s b}{2\beta_s b}\right) \tag{3-10}$$

B is given by:

$$B = \left[1 + \left(\frac{\beta_s^2}{\beta_g^2} - 1\right) \cos^2 \beta_s b\right] \tag{3-11}$$

and C is a (measurable) correction term, generally small with respect to $\Delta \ell$, the half-power bandwidth of the resonance peak.

EXPERIMENTAL

Synthesis of Bis(methylamino)diphenylmethane (C2942-31)

N-Methylaniline (172 g, 1.61 moles) was dissolved in concentrated hydrochloric acid (72 ml, 0.84 mole) and the mixture was cooled to 3 ± 2°C. Aqueous formaldehyde (64 g, 37 percent) was then added slowly while maintaining the temperature between 0 - 5°C. After the addition was completed the temperature was maintained below 5°C for one hour. The reaction mixture was then heated to boiling and refluxed for 10 hours under a nitrogen atmosphere. It was then diluted to 1500 ml with water and its pH was adjusted to 7 by the gradual addition of aqueous NaOH solution (20 percent). The precipitated amine was then extracted with benzene, and the benzene solution was washed with dilute alkali (10 percent NaOH), followed by distilled water. After drying with potassium carbonate the benzene was removed by simple distillation and the amine was recovered on a molecular still. An attempted simple distillation of the amine at 1-2 torr and 170°C proved unsatisfactory (only 6.2 g of unreacted N-methylaniline was recovered). Distillation at 10^{-3} torr and 100-130°C followed by a subsequent distillation at 150-160°C at 10^{-3} torr yielded 153 g (85 percent) of a light yellow mixture of bis(methylamino)diphenylmethane isomers. This portion was designated 31A. The nonvolatile fraction (25 g) was designated 31B.

N-Methylaniline Formaldehyde Prepolymer (C2425-15A)

N-Methylaniline (172 g, 1.61 moles) was dissolved in concentrated hydrochloric acid (72 ml, 0.84 mole) and was cooled to 0-5°C. Aqueous formaldehyde solution (37 percent, 80 g, 1.00 mole, stabilized with 10-15 percent methanol) was then added dropwise to the amine solution over a half hour period while maintaining the temperature at 0-5°C. After completion of the addition the same temperature was maintained for one hour. The reaction mixture was then heated by reflux for 8-1/2 hours and after cooling it was diluted threefold. Sufficient hydrochloric acid was added to yield a clear solution. Then dilute alkali (≃ 15 percent NaOH) was added dropwise, while stirring vigorously, until the final

pH was 8. The precipitated solid was diluted with ethanol (100 ml) and benzene (500 ml) and the organic phase which separated was washed with alkali (20 percent NaOH). After three water washes the solution was dried over Na_2CO_3 and filtered. Solvents were then removed by vacuum distillation (up to 135°C at 2 torr) yielding a dark amber polyamine weighing 167 g (91 percent).

A second batch was prepared under nitrogen by a modified procedure using purer reagents (C2425-15B). Details of this rerun are presented below.

N-Methylaniline (186 g, 1.74 moles), which was freshly distilled under nitrogen, was dissolved in concentrated hydrochloric acid (80 ml, 0.93,mole) while maintaining a nitrogen atmosphere. The solution was cooled to 0°C and uninhibited formalin (37 percent CH_2O, 88 g, 1.09 moles) was slowly added while maintaining the temperature at 0-5°C. Upon completion of the addition the temperature was maintained for 1 hour; then the mixture was heated to reflux for 10-11 hours. The solution was then diluted threefold with water and benzene (≃350 ml) was added. It was then neutralized to a phenolphthalein end point using 10 percent NaOH solution. The benzene layer was collected, thoroughly washed with water, and dried with Na_2CO_3. Benzene was then removed under nitrogen at ambient pressure followed by vacuum (4 torr) at 135°C. The very light tan colored product weighed 192 g (95 percent of theoretical).

N-Methylaniline Formaldehyde (C2425-43)

Freshly distilled N-methlylaniline (266 g, 2.49 moles) was dissolved in concentrated hydrochloric acid and the mixture was cooled to -5°C. Formalin (152 g, 1.87 mole, 37 percent, uninhibited) was then added while maintaining the temperature at 5 ± 5°C. After the addition was completed the reaction mixture was maintained at 5 ± 5°C for 1 extra hour. It was then heated to boiling and maintained at reflux for 8 hours. Water (100 ml) was added to the mixture during the course of the reaction in the hope of redissolving a large mass of congealed material; however, this was not too successful. When the

mixture was cooled and the fluid phase decanted the large mass of polymer was successfully dissolved in concentrated hydrochloric acid (approximately 150 ml). Both dissolved polymer phases were then recombined and, after diluting twofold with water, were treated with 20-25 percent sodium hydroxide solution. Precipitated polymer was then dissolved in a mixture of ethanol and benzene and the solution was washed with a 10 percent sodium hydroxide solution and then twice with water. After drying azeotropically, the solvents were removed under vacuum while allowing the pot temperature to approach 175° C gradually. Because of its hazy appearance, however, the polymer was redissolved in methylene chloride, filtered; reconcentrated under vacuum (to 175°C) and finally cooled to a resinous mass.

N-Methylaniline Formaldehyde (C2425-46)

Concentrated hydrochloric acid was gradually added to ice cold freshly distilled N-methylaniline (334 g, 3.12 moles). The solution was then cooled to 0°C and the temperature maintained between 0-5°C while uninhibited formaldehyde (174 g, 2.14 moles, 37 percent) was gradually added. After the addition was completed the solution temperature was maintained at 0-5°C for 1 hour. It was then heated at reflux for 8 hours and then cooled. After 2 days benzene (500 ml) was added and the solution was treated with excess aqueous sodium hydroxide. The benzene phase was separated, washed twice with water, dried azeotropically, cooled, and filtered. Solvent was then removed under vacuum (≃5 torr) while gradually heating to 180°C. The viscous cooled product weighed 320 g (90 percent yield).

Preparation of N-Methylaniline Formaldehyde Prepolymers (C2425-59 A&B)

C2425-59A is for the 1.38 mole ratio prepolymer. Formalin (230 g, 37 percent, 2.84 moles inhibited) was added to a solution of redistilled N-methylaniline (419 g, 3.92 moles) in aqueous hydrochloric acid (163 ml, 12 molar, 0.96 mole) while maintaining the temperature at 0-5°C. After 1 to 1-1/2 hours at this temperature, the mixture was

heated at reflux for 8 hours. Toluene (700 ml) was then added and the pH adjusted to 8-10 with sodium hydroxide solution (47 g/200 ml H_2O). After cooling, the toluene phase was separated, washed twice with water, dried azeotropically, filtered, and concentrated under vacuum (8 torr) while the temperature gradually rose to 180°C. The product weighed 390 g and melted at 40-45°C. It represented an 85 percent yield.

C2425-59B represents a 1.30 mole ratio product. The same procedure was used in this preparation except that 217.5 g of N-methylaniline (2.03 mole), 126.8 g of formalin (1.564 mole) and 85 ml of concentrated aqueous hydrochloric acid (1.02 mole) were used. The product weighed 212 g, melted at 53-69°C and was 88 percent of theoretical.

C2425-65A represents a 1.59 mole ratio product derived from uninhibited formaldehyde. The formaldehyde used in this preparation was obtained from the hydrolysis of 200 g of paraformaldehyde in 500 ml of water and 10 ml of concentrated hydrochloric acid. Aliquots of the hydrolyzed paraformaldehyde were used in the next two preparations. This reaction was carried out the same as the first two except for the reactant quantities, namely

N-Methylaniline, 172 g, 1.61 moles

Formalin (28.2 percent), 108 g, 1.015 moles

Twelve molar HCl, 61 ml, 0.73 mole

A yield of 166 g (89 percent) of light amber product was obtained.

C2425-65B represents a 1.38 mole ratio product derived from uninhibited formaldehyde. The reactants used were

N-Methylaniline, 204 g, 1.91 moles

Formalin (28.2 percent), 147 g, 1.38 moles

Twelve molar HCl, 79 ml, 0.95 mole

A yield of 206 g (84 percent) was obtained.

C2425-66C is the same as 65B above.

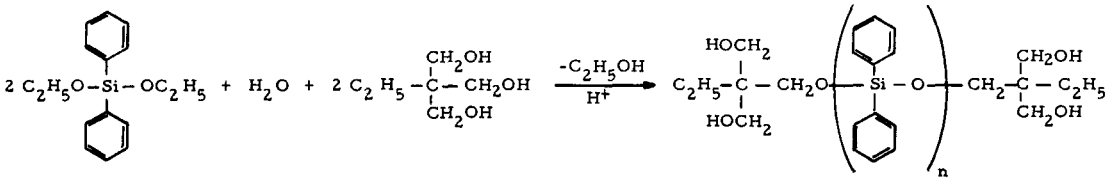
4. SILOXYURETHANES

DISCUSSION

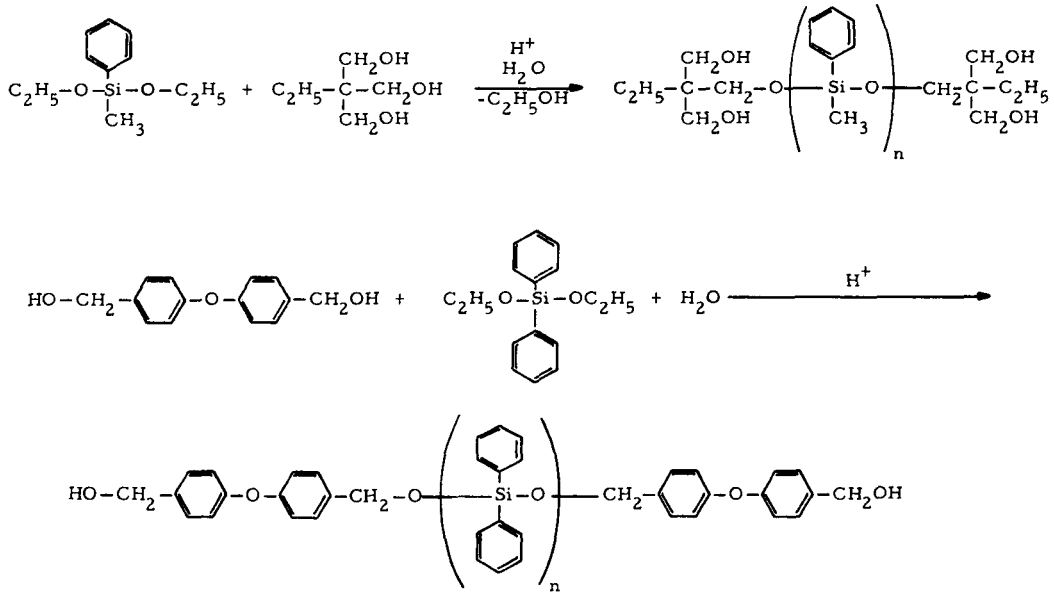
An investigation has been carried out on the synthesis of siloxypolyols suitable for formulating siloxyurethanes with good dielectric properties, low temperature flexibility, low outgassing characteristics in high vacuum, sterilizability, etc. This combination of properties is required for conformal coatings suitable for aerospace applications.

Earlier work on siloxyurethanes which was carried out under this program was directed toward the synthesis of siloxypolyols from trimethylolpropane and dimethyldiethoxysilane.[1] It was observed in the course of this work, however, that stable homogeneous polyols were obtained only when the siloxypolyols contained less than three repeating dimethylsiloxane units. Unfortunately, however, much longer siloxane moieties were required to produce siloxyurethanes having a sufficiently large percentage of silicone content to exhibit suitable dielectric properties.

Work was, therefore, subsequently directed toward the investigation of other siloxypolyols derived from either trimethylolpropane or bis(hydroxymethyl)diphenyloxide and diphenyldiethoxysilane, phenyltriethoxysilane and/or methylphenyldiethoxysilane. Three of these syntheses are illustrated below:



[1] Norman Bilow, Development of Improved Sterilizable Potting and Encapsulating Compounds for Space Applications, 2nd Annual Summary Report NAS 8-5499, 1965.



In the reactions of trimethylolpropane with diphenyldiethoxysilane, stable, completely homogeneous polyols generally could not be obtained regardless of the ratio of reactants and the degree of polymerization. The products were translucent heterogeneous waxes. Phenyltriethoxysilane and methylphenyldiethoxysilane on the other hand were capable of forming homogeneous polyols from this triol. Siloxyurethanes which were subsequently derived from these latter polyols by reaction with conventional isocyanate prepolymers such as Adiprene L-100, Adiprene L-315, or diphenylmethane-4, 4'-diisocyanate, were often clear light colored tough resins or elastomers. Their dielectric properties were, however, never sufficiently good to meet the objectives of this program. They might of course have other uses.

The most promising of these materials were those derived from 1, 4 bis(hydroxymethyl)diphenyloxide. This diol was considered worthy of study because its stereochemistry was such as to lower its tendency to form cyclic condensation products like the cyclosiloxanes when reacted with alkoxysilanes. Cyclics are of course undesirable because of their lack of functionality and their inability to polymerize when reacted with the isocyanates. As unpolymerized compounds, therefore, these cyclics would tend to outgas in the high vacuum of outer space if they remained in the polymer matrices.

Of the various 1, 4-bis(hydroxymethyl)diphenyloxide condensation products investigated, only those derived from 2 moles of the diol and one mole of methylphenyldiethoxysilane cured completely upon reaction with the various polyisocyanates. Dielectric tests carried out on these siloxyurethanes were, however, not sufficiently good as to meet the objectives of this program.

The reactants used in preparing the various siloxypolyols are presented in Tables 4-1 and 4-2. Composition of the siloxyurethanes are presented in Table 4-3 and dielectric properties are presented in Table 4-4. Acid catalyzed condensations of the alkoxysilanes with the trimethylolpropane and bis(hydroxymethyl)diphenyloxide were carried out in vacuum while removing evolved ethanol as it was formed. The condensation products were then equilibrated at higher temperatures before use.

Several isocyanate prepolymers were also prepared by the addition of a twofold excess of diphenylmethanediisocyanate to several of the bis(hydroxymethyl)diphenyloxide based siloxypolyols.

Reaction Number	Trimethylol-propane		Diphenyl-diethoxysilane		Water		Theoretical Equivalent Weight	Comments
	g	mole	g	mole	g	mole		
C2942-18B	17.9	0.13	54.4	0.20	1.8	0.10	278	White opalescent soft glass
C2942-19C	9.0	0.07	54.4	0.20	2.7	0.15	476	Clear greenish hard glass
C2942-30D	17.9	0.13	81.7	0.30	3.6	0.20	378	Opalescent brown hard glass
C-1980-74A	13.4	0.10	27.2	0.10	0.9	0.05		White heterogeneous soft wax
C-1980-74B	13.4	0.10	40.8	0.15	1.8	0.10		Brownish heterogeneous hard glass

Table 4-1. Reactants used in the synthesis of siloxypolyols from diphenyldiethoxysilane and trimethylolpropane.

Reaction Number	bis(hydroxymethyl)-diphenyl oxide		Diphenyl-diethoxysilane		Phenyl-triethoxysilane		Water		Equivalent Weight		Comments
	weight, g	mole	weight	mole	weight	mole	weight	mole	Observed	Theory	
C-2425-13B	46.0	0.19	27.2	0.10					404	355	Very viscous fluid - almost clear
C-2425-13C	48.4	0.20			16.0	0.07				292	Hard white wax
C-2425-14A	60.0	0.25	55.0	0.20	8.0	0.033			308	320	Almost clear, amber color very viscous
C-2425-14B	60.0	0.25	55.8	0.21	4.4	0.018	1.8	0.10		430	Pale yellow heterogeneous very viscous
C-2942-9D	24.2	0.10	82.0	0.30			3.6	0.20	914 ave. of 4		Flows readily clear, colorless
C-2942-10D	24.2	0.10	82.0	0.30			3.6	0.20	1830 ave. of 3	∞	Quite fluid clear, colorless
C-1090-73	48.0	0.20	55.8	0.21			1.8	0.10	459 ave. of 4	432	White, opalescent very tacky

Table 4-2. Reactants used in the synthesis of various siloxypolyols from bis(hydroxymethyl)diphenyloxide.

Code	Composition			Product Weight			Ethanol Removed		Comments***
	Reactants	Weight g.	Eq.	Theory g.	Actual g.	%	Theory g.	Actual g.	
C2425-18-1	HMDPO* MPDES** Acetic Acid	23 10.5 5 dps	0.2 0.1	28.9	28.2	97.6	4.6	5.4	Off white milky color, tacky and opaque solid.
C2425-19-2	HMDPO MPDES Acetic Acid	23 14 6 dps	0.2 0.134	30.84	29.3	94.9	6.16	7.4	Light pea green color, translucent, tacky, and very viscous liquid.
C2425-19-3a	HMDPO MPDES † Acetic Acid	23 17.3 7 dps	0.2 0.2 ?	35.7	34.5	96.7	4.6	7.9	Amber color, translucent, tacky and very viscous liquid.
C2425-19-3b	HMDPO MPDES H_2O Acetic Acid	23 21 0.9 7 dps	0.2 0.2 0.10	35.7	33.4	93.6	9.2	10.7	Amber color, translucent, tacky and very viscous liquid.
C2425-20-2b	HMDPO MPDES Acetic Acid	23 10.5 5 dps	0.2 0.1	28.9	27.0	93.4	4.6	5.3	Pea green color, tacky, translucent and solid.
C2425-20-4	HMDPO MPDES H_2O Acetic Acid	23 31.5 1.8 8 dps	0.2 0.3 0.2	42.5	41.5	97.6	13.8	16.2	Light amber color, clear, tacky and liquid.
C2425-20-5	HMDPO MPDES H_2O Acetic Acid	23 42 2.7 9 dps	0.2 0.4 0.3	49.3	49.8	101	18.4	17.4	Light pea green color, translucent, tacky, and very viscous.
C2425-20-6	HMDPO MPDES Acetic Acid	23 16 7 dps	0.2 0.15	32.6	31.7	97	6.9	7.1	Amber color, tacky, translucent, and solid.
C2425-37-2	HMDPO MPDES H_2O Acetic Acid	69 63 2.7 10 dps	0.6 0.6 0.3	107.1	108.0	101	27.6	31.1	Light amber color, tacky, translucent, and very viscous liquid.
C2425-37-3	HMDPO MPDES Acetic Acid	69 31.5 10 dps	0.6 0.3	86.7	84.9	98	13.8	16.7	Light amber color, tacky, translucent, and solid (no flow).

*Bis(hydroxymethyl)diphenyloxide
**Methylphenyldiethoxysilane
***Reactions run at 100°C with vacuum gradually falling to ≈5 torr
†Contains some dimer

Table 4-2. (continued)

Code	Composition‡	Weight g.	Eq.	Cure Schedule	Comments		
					100°C	24°C	-78°C*
C2425-42-1	C2425-18-1(2b) Adiprene L315	17.5 22.25	0.05 0.05	16 hrs at 75°C 3 hrs at 100°C	Very soft	Soft and rubbery	Tough and rubbery, but did break.
C2425-42-6	C2425-37-2** Adiprene L315	14.3 17.8	0.04 0.04	16 hrs at 75°C 3 hrs at 100°C	Sample clear Very soft	Fair dimensional stability, rubbery	Brittle at -78°C
C2425-42-7	C2425-37-2 Adiprene L315	17.0 17.8	0.04 0.04	16 hrs at 75°C 3 hrs at 100°C	Very soft Sample clear.	Fair dimensional stability.	Brittle
C2425-44-10	C2425-37-2† Adiprene L315	16.0 17.8	0.04 0.04	16 hrs at 75°C 3 hrs at 100°C	Soft Sample clear.	Fair dimensional stability.	Rubbery and tough, but breakable.
C2425-42-8	C2425-37-2** C1980-57 Adiprene L315	11.8 1.0 19.6	0.033 0.011 0.044	16 hrs at 75°C 3 hrs at 100°C	Rubbery Sample cloudy.	Good dimensional stability.	Rubbery and tough, breakable.
C2425-44-9	C2425-37-2 C1980-57 Adiprene L315	12.7 0.9 17.8	0.03 0.01 0.04	16 hrs at 75°C 3 hrs at 100°C	Rubbery Sample cloudy.	Good dimensional stability.	Rubbery and tough, but breakable.
C2425-44-11	Adiprene L100 C1980-57	30.8 2.7	0.03 0.03	16 hrs at 75°C 3 hrs at 100°C	Soft Sample cloudy.	Fair dimensional stability.	Flexible and tough. Couldn't break.
C2425-44-12	C2425-37-3 Adiprene L315	12.2 17.8	0.04 0.04	16 hrs at 75°C 3 hrs at 100°C	Soft Sample clear.	Good dimensional stability.	Flexible, but not too tough, breakable.
C2425-44-13	C2425-37-3 C1980-57 Adiprene L315	10.1 1.2 20.8	0.033 0.013 0.046	16 hrs at 75°C 3 hrs at 100°C	Semi-rigid Sample cloudy.	Good dimensional stability.	Flexible, but brittle, broke easily.
C2425-45-14	C2425-37-3 C1980-57 Adiprene L315	15.3 0.9 26.7	0.05 0.01 0.06	16 hrs at 75°C 3 hrs at 100°C	Semi-rigid Sample cloudy.	Good dimensional stability.	Tough, but breakable.
C2425-45-15	C2425-37-3 C1980-57 Adiprene L100	7.8 0.9 36.7	0.025 0.010 0.035	64 hrs at 75°C 3 hrs at 100°C	Rubbery Sample cloudy.	Fair dimensional stability.	Semi-rigid and tough. Couldn't break.
C2425-45-16	C2425-37-3 C1980-57 Adiprene L100	6.1 1.8 30.5	0.02 0.01 0.03	64 hrs at 75°C 3 hrs at 100°C	Rubbery Sample cloudy.	Good dimensional stability.	Flexible and tough. Couldn't break.

*Samples used were of surplus material removed from the mold used in the 4-rod preparation. They were about 1/4 inch thick 2 inch squares. Therefore specimens listed as tough, but breakable,would probably have satisfactory flexibility in thin films at these low temperatures.
**Theoretical equivalent used
†Mean value of theoretical and observed equivalent weights
‡Observed equivalent weights used except where noted otherwise

Table 4-3. Composition of siloxyurethane test specimens.

Specimen Number	Composition			Cure	Observations	
	Reactants	Weight g.	Eq.		24°C	-78°C
C2425-23-1	DPMDIC*	0.85	0.0068		Immediate Reaction	
	C2425-21-1	1.54	0.0068			
C2425-23-3	DPMDIC*	0.85	0.0068	2 hrs at room temp	Hard, but brittle.	
	C2425-21-2	3.00	0.007			
C2425-24-8	DPMDIC*	1.25	0.01	24 hrs at 75°C	Only semi-cured.	
	C2425-21-5	4.98	0.01			
C2425-24-7	DPMDIC*	1.25	0.01	18 hrs at 75°C	Semi-rigid, brittle.	
	C2425-21-6	6.34	0.01			
C2425-24-11	DPMDIC*	2.50	0.02	1 hr at 65°C 22 hrs at 75°C	Brittle	
	C2425-21-3b	6.68	0.02			
C2425-24-12	DPMDIC*	1.25	0.01	25 hrs at 75°C	Semi-cured.	
	C2425-21-4**	4.15	0.01			
C2425-24-13	DPMDIC*	1.25	0.01	22 hrs at 75°C	Semi-cured.	
	C2425-21-4	4.70	0.011			
C2425-23-5	Adiprene L315	8.9	0.02	16 hrs at 75°C	Slight foam structure, hard.	Tough, couldn't break.
	C2425-21-1	3.6	0.02			
C2425-23-6	Adiprene L315	3.0	0.007	16 hrs at 75°C		Hard and brittle
	C2425-21-2	3.0	0.007			
C2425-25-14	Adiprene L315	4.45	0.01	5 hrs at 75°C	Flexible, tough	Extremely tough, unable to break.
	C2425-21-3	3.34	0.01			
C2425-25-15	Adiprene L315	4.45	0.01	23 hrs at 75°C	Very viscous, uncured.	
	C2425-21-4	4.15	0.01			
C2425-25-17	Adiprene L315	4.45	0.01	22 hrs at 75°C	Very viscous, uncured.	
	C2425-21-5	4.98	0.01			
C2425-25-16	Adiprene L315	4.45	0.01	23 hrs at 75°C	Flexible	Brittle
	C2425-21-6	6.34	0.01			
C2425-26-23	Adiprene L315	2.3	0.005	16 hrs at 75°C 3 hrs at 100°C	Strength poor	
	C2425-21-4	5.2	0.005			
C2425-26-24	Adiprene L315	2.3	0.005	16 hrs at 75°C 3 hrs at 100°C	Strength poor	
	C2425-21-5	5.6	0.005			
C2425-27-25	Adiprene L315	4.45	0.01	16 hrs at 75°C 3 hrs at 100°C	Very tough	Tough, but broke
	C2425-37-1 ***	5.43	0.01			
C2425-25-18	DPMDIC	2.50	0.02	45 hrs at 75°C	Bottom not cured, not very tough.	
	C1980-57	0.92	0.01			
	C2425-21-4	4.15	0.01			
C2425-25-19	DPMDIC	2.50	0.02	45 hrs at 75°C	Sample not cured	
	C1980-57	0.92	0.01			
	C2425-21-5	4.98	0.01			
C2425-26-22	DPMDIC	3.75	0.03	40 hrs at 75°C	Not cured	
	C1980-57	1.84	0.02			
	C2425-21-4	4.15	0.01			
C2425-26-20	Adiprene L315	8.90	0.02	45 hrs at 75°C	Flexible	Very tough, but did break.
	C1980-57	0.92	0.01			
	C2425-21-5	4.98	0.01			
C2425-26-21	Adiprene L315	8.90	0.02	40 hrs at 75°C	Flexible, not cured on bottom.	Very tough, but did break.
	C1980-57	0.92	0.01			
	C2425-21-4	4.15	0.01			
C2425-27-26	Adiprene L315	6.67	0.015	16 hrs at 75°C 3 hrs at 100°C		Very tough, unable to break.
	C1980-57	0.45	0.005			
	C2425-37-1 ***	5.43	0.01			

*DPMDIC is diphenylmethane-4, 4'-diisocyanate
**theoretical equivalent weight of siloxypolyol was used rather than analyzed equivalent weight
***equivalent weight in doubt

Table 4-3. (continued)

Code	Composition	Weight g.	Eq.	Cure Schedule	Comments
C1980-76-1	Siloxypolyol C2942-10D	26	0.05	74°C - 16 hrs	No cure
	2,4-Tolylenediisocyanate	4.3	0.05	121°C - 9 hrs	
-76-2	C2942-10D	19.5	0.037	74°C - 16 hrs	No cure
	Adiprene L-315	16.5	0.037	121°C - 9 hrs	
-76-3	C2942-10D	26.0	0.05	74°C - 16 hrs	No cure
	Siloxypolyol C1980-57	0.9	0.01	121°C - 9 hrs	
	2,4-Tolylenediisocyanate	5.2	0.06		
-76-4	Siloxypolyol C2942-9D	29.0	0.025	74°C - 16 hrs	No cure
	2,4-Tolylenediisocyanate	2.6	0.030	121°C - 9 hrs	
-79-6	Adiprene L-315	22.2	0.05	74°C - 48 hrs	Satisfactory
	Siloxypolyol C2942-30D	11.3	0.03		
	Siloxypolyol C1980-57	1.8	0.02		
-79-7	Adiprene L-315	22.2	0.05	74°C - 48 hrs	Satisfactory
	Siloxypolyol C2942-18B	8.3	0.03		
	Siloxypolyol C1980-57	1.8	0.02		
-79-8	Adiprene L-315	22.2	0.05	74°C - 48 hrs	Very soft at 74°C
	Siloxypolyol C2942-19C	14.3	0.03		
	Siloxypolyol C1980-57	1.8	0.02		

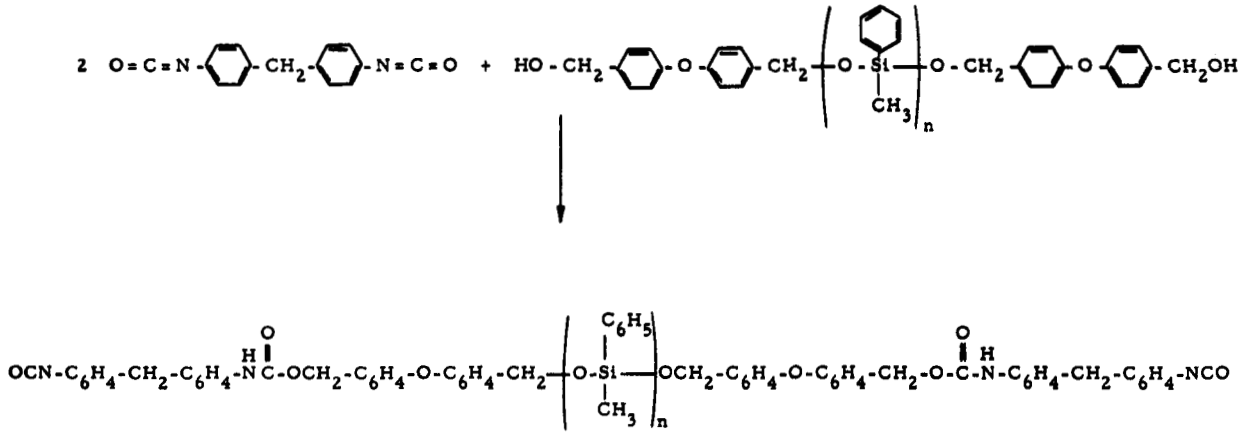
Notes: Siloxypolyols C2942-9D and 10D are derived from bis(hydroxymethyl)diphenyl oxide (see Table 4-2).

Siloxypolyols C2942-18B, 19C and 30D are derived from trimethylolpropane (see Table 4-1).

Siloxypolyol C1980-57 is derived from trimethylolpropane (2 moles) and diethoxytetramethyldisiloxane (1 mole), a previously reported synthesis.

Table 4-3. (continued)

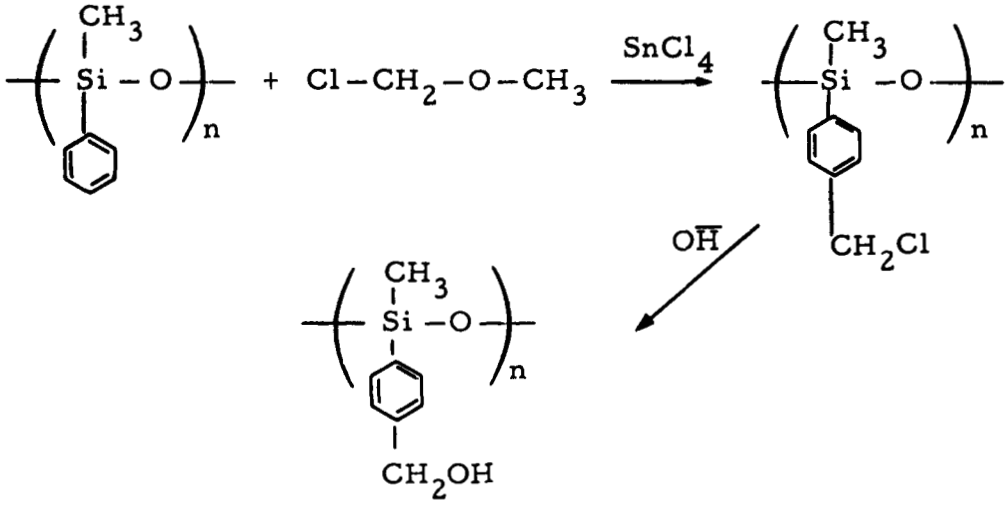
A typical reaction is illustrated below



Data on the composition of these siloxyisocyanate prepolymers is presented in Table 4-5. Little effort was made to utilize them in polyurethane formulations because of the unsatisfactory dielectric properties which the other siloxyurethane polymers of this type exhibited.

An entirely different approach to the siloxyurethane development problem was made by attempting to chloromethylate, and subsequently hydrolyze, a long chain phenylated silicone, with the intention of ultimately using the hydroxymethylated hydrolysis product as the siloxypolyol in polyurethane formulations.

The reactions are



Specimen Number	Dielectric Constant at 1 KC		Dissipation Factor Percent		Insulation Resistance Megohms at 500 VDC	
	25°C	100°C	25°C	100°	25°	100°
C1980-79-6	4.3	6.5	3.4	33	6×10^4	140
-79-7	4.5	-	3.7	11	5×10^6	45
-79-8	5.3	-	7.5	-	7×10^3	-
C2425-42-7	5.4	6.9	7.8	58	2×10^4	4.5
-42-8	5.4	8.2	6.9	27	2×10^4	4.5
-44-9	5.3	9.1	6.4	54	3×10^4	4.0
-44-10	5.5	5.7	7.7	36	2×10^4	4.5
-44-11	9.6	12.2	6.0	67	6×10^2	15
-44-12	5.3	12.7	8.0	95	3×10^4	2.0
-44-13	5.5	13.0	8.3	85	2×10^4	2.0
-45-14	5.5	13.4	8.3	85	2×10^4	2.0
-45-15	9.0	-	12.4	-	1×10^2	-
-45-16	9.0	-	11.4	-	1×10^2	1.0

Table 4-4. Dielectric properties of various siloxyurethane test specimens.

Code	Composition	Quantity g.	Eq.	Comments
C-2425-23-2	A*	4.1	0.04	Homogeneous mixture, hard tough state at room temperature (not usable)
	C-2425-21-1	3.6	0.02	
C-2425-23-4	A*	1.7	0.0136	Homogeneous mixture, hard and brittle at room temperature
	C-2425-21-2	3.0	0.007	
C-2425-24-9	A*	2.50	0.02	Homogeneous mixture, semi-soft, would not flow at room temperature
	C-2425-21-6	6.34	0.01	
C-2425-24-10	A*	2.50	0.02	Homogeneous mixture, fluid at room temperature
	C-2425-21-5	4.98	0.01	
*A = diphenylmethane-4, 4'-diisocyanate				

Table 4-5. Data on the preparation of various siloxy isocyanate prepolymers.

Polymethyl(hydroxymethylphenyl)siloxane was prepared by the chloromethylation of polymethylphenylsiloxane following the method of Pepper,[1] et al., followed by hydrolysis with aqueous base. The starting polysiloxane was prepared from trimethyltriphenylcyclotrisiloxane using sulfuric acid as the catalyst and using the procedure of Patnode and Wilcox[2] to prepare linear polymer having a chain length of about 25 MeφSiO units. A hydroxymethyl derivative was also prepared from the trimeric cyclosiloxane using the method of Pepper. Infrared spectra indicated the presence of hydroxymethyl groups in both the trimeric and polymeric methylphenylsiloxanes. Preliminary curing experiments with an isocyanate prepolymer, Adiprene L-315, resulted in a cure in two hours at 155°F with the polymeric siloxane and in six hours with the trimeric siloxane in a hot air oven. Further work on these materials was however never undertaken.

A possible limitation of the chloromethylation procedure of Pepper, which employs chloromethyl methyl ether with $SnCl_4$ catalyst, is that polysiloxanes are degraded significantly and the degree of chloromethyl group substitution is greater in the degraded portion of the product. This is readily separable from the relatively unaltered portion of the product by differential solubility in methanol. A hydroxymethylated methylphenylsiloxane of about 30 repeating units with a hydroxymethylphenyl at about each sixth siloxy unit would probably be useful for the preparation of siloxyurethane polymers. The result of this experiment indicates that the desired hydroxymethylated siloxane would be prepared best by employing a polymeric siloxane with a degree of polymerization of several hundred for the chloromethylation reaction, and subsequently fractionating the product by differential solubility or molecular distillation to isolate the desired portion of product.

Equivalent weights of several of the siloxypolyols synthesized in this program are presented in Table 4-6 below.

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[1] K. W. Pepper, J. Chem. Soc., 1953, p. 4097.

[2] W. Patnode and F. F. Wilcox, J. Amer. Chem. Soc. 68, p. 358 (1946).

Sample Number	Number of Samples	Acetylation Period, hour	Observed Equivalent Weight	Expected Equivalent Weight
C2425-21-1(2b)	7	1-1/2	351	289
C2425-21-4	3	1-1/2	1049	
C2425-21-5	3	2	1129	
C2425-37-2	6	1-1/2	644	357
C2425-37-2	2	2-1/2	419	
C2425-37-2	2	4	429	
C2425-37-3	2	2-1/2	318	289
C2425-37-3	2	3	295	

Table 4-6. Results of analyses of various siloxypolyols.

Hydroxyl equivalents were determined by the procedure previously described in the second annual summary report.[1] It appeared, however, that in some cases the hydroxyl esterification periods recommended previously (1-1/2 hours) were inadequate for the siloxypolyols derived from bis(hydroxymethyl)diphenyloxide and thus longer esterification periods (2.5-4.0 hours) sometimes had to be used. Reaction periods were determined by the time required to reach relatively constant values.

EXPERIMENTAL

Reaction of "Diethoxytetraphenyldisiloxane" with Trimethylolpropane (C1980-74A)

Trimethylolpropane (13.4 g, 0.3 eq.), water (0.9 g, 0.1 eq.) and acetic acid (5 drops) were melted together and mixed thoroughly. Diphenyldiethoxysilane (27.2 g, 0.2 eq.) was then added and the mixture was stirred continually while removing ethanol (9.0 g, 0.19 eq.) under

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[1] N. Bilow, op. cit.

reduced pressure. The reaction temperature was gradually raised to 170°C and maintained for 1/2-3/4 hour. A white product was obtained.

Reaction of "Diethoxyhexaphenyltrisiloxane" with Trimethylolpropane (C1980-74B)

Trimethylolpropane (13.4g., 0.3 eq.), water (1.8g., 0.2 eq.), and acetic acid (6 drops) were melted together and diphenyldiethoxysilane (40.8g., 0.3 eq.) was then added. The reaction temperature was maintained at 115°C (≃5 torr.) for about 18 hours while the volatiles, mainly ethanol, were collected (19.4g.). A brown nonhomogeneous glassy product was obtained which weighed 48.0g. (92 percent of theoretical).

Reaction of "Diethoxyoctaphenyltetrasiloxane" with Trimethylolpropane (C1980-75B)

Trimethylolpropane (13.4g., 0.3 eq.) water (2.7g., 0.3 eq.) and acetic acid (8 drops) were melted together and then diphenyldiethoxysilane (54.4g., 0.4 eq.) was added. The agitated mixture was heated to 118°C while ethanol was removed under reduced pressure (100 torr). Additional acetic acid was added (5 drops) and heating was continued overnight at 120°C. A total of 19g. (0.4 mole) of ethanol was recovered. The product had a green color and was opaque.

Reaction of Trimethylolpropane with "Diethoxytetraphenyldisiloxane" (C2942-18A)

Diphenyldiethoxysilane (54.4g., 0.2 mole) was added to a molten solution of trimethylolpropane (17.9g., 0.133 mole), water (1.8g., 0.1 mole) and acetic acid (5 drops). The reaction mixture was gradually heated to 135 ± 5°C while gradually reducing the pressure to about 5 torr. After the ethanol evolution ceased, additional acetic acid (3 drops) was added and heating continued for 6 hours at the same temperature and pressure. The nonvolatile siloxypolyol (54g.) had a theoretical equivalent weight of 278. Recovered ethanol weighed 19.8g. (105 percent of theoretical).

Reaction of Trimethylolpropane with "Diethoxyhexaphenyltrisiloxane" (C2942-18B, 18D, 30D)

Diphenyldiethoxysilane (81.7g., 0.3 mole) was added to a molten mixture of trimethylolpropane (17.9g., 0.133 mole), water (3.6 ml, 0.20 mole), and acetic acid (7 drops). The temperature was gradually raised to 130°C and the pressure lowered to below 5 torr. After ethanol evolution appeared to cease additional acetic acid (3 drops) was added and the reaction continued for 5-1/2 hours. The recovered ethanol (27.0g.) was about 97 percent of theoretical. The remaining cooled product was a white translucent glass.

(C2942-18D) Repetition of this experiment was carried out with 54.4g. (0.2 mole) of diphenyldiethoxysilane, 2.7 ml (0.15 mole) of water, 8.95g. (0.06 mole) of trimethylolpropane and 5 drops of acetic acid. In this case 18.2g. of ethanol (98 percent) was isolated. The polyol was dissolved in tetrahydrofuran, filtered, and recovered by heat and vacuum. Its theoretical equivalent weight was 476.

A third preparation (C2942-30D) was carried out as in C2942-18B above. In this case 26.6g. of ethanol was evolved (96 percent of theoretical). The polyol (71g.) was dissolved in chloroform, filtered through a Millipore filter and reconcentrated by heat (160°C) and vacuum (<5 torr). The cooled product was a hard brownish translucent glass.

Preparation of Diphenyldiethoxysilane (C2942-13)

Absolute ethanol (250g., 5.4 moles) was added dropwise to diphenyldichlorosilane (506g., 2 moles) over a 30 minute period. The resultant two-phase mixture was then distilled, first at ambient pressure to remove excess ethanol and hydrogen chloride then at reduced pressure (2 torr) to remove the diphenyldiethoxysilane (B.P. 123-130°C, 375 ml.)

Reaction of Diphenyldiethoxysilane with Water and Bis(hydroxymethyl)-diphenyloxide [2:1:2 Molar Ratio, C1980-73]

Freshly distilled diphenyldiethoxysilane (55.8g., 0.41 eq.), water (1.8g., 0.20 eq.), and acetic acid (8 drops) were shaken until homogeneous. Bis(hydroxymethyl)diphenyloxide (hydroxymethyldiphenyloxide-14,

48 g, 0.40 eq.) was then added and the mixture was heated to 115°C in a rotary evaporator. Ethanol (14.5g., 0.32 mole) was removed while gradually reducing the pressure to 2 torr. Additional acetic acid (12 drops) was then added and the mixture was heated at 130°C for 6 hours at ambient pressure, then at 115°C and 1 torr for 16 hours. The resulting equilibrated product weighed 89g. (102 percent of theoretical).

Reaction of Diphenyldiethoxysilane, Water and Bis(hydroxymethyl)-diphenyloxide [3:2:1 Molar Ratio, C2942-9]

A mixture of freshly prepared diphenyldiethoxysilane (82g., 0.60 eq.), bis(hydroxymethyl)diphenyloxide (24.2g., 0.2 eq.), water (3.6g., 0.4 eq.) and glacial acetic acid (5 drops) was heated at 120°C with continuous stirring for 1/2 hour at ambient pressure. Heating was then continued for two additional hours as the pressure was gradually reduced to about 1 torr. Additional acetic acid (10 drops) was then added and heating continued for 7 hours at 110°C at ambient pressure then at 110°C and 57 hours at ≃1 torr. The clear nonvolatile product weighed 87.1g., whereas the ethanol which was collected in a cold trap weighed 23g. (83 percent of theoretical).

Reaction of Diphenyldiethoxysilane with Water and Bis(hydroxymethyl)-diphenyloxide [3:2:1 Molar Ratio, C2942-10]

A mixture of diphenyldiethoxysilane (82g., 0.30 mole) and bis(hydroxymethyl)diphenyloxide (24.2g., 0.1 mole) were melted together. Water (3.6g., 0.2 mole) and acetic acid (5 drops) were added. The reaction mixture was then heated at 120°C for 1/2 hour while ethanol was removed by distillation. Partial vacuum (100 torr) was then applied and the reaction mixture was heated further at 120°C for about 18 hours.

Siloxypolyols from Bis(hydroxymethyl)diphenyloxide (C2425-18 through 21)

The following procedure was used in the preparation of a series of approximately fourteen siloxypolyols from bis(hydroxymethyl)-diphenyloxide and methylphenyldiethoxysilane. Reactant ratios used in ten of these preparations are tabulated in the discussion section of this report (Table 4-2).

Weighed samples of bis(hydroxymethyl)diphenyloxide were heated to their melting points and, while stirring continually, methylphenyldiethoxysilane was gradually added along with several drops of acetic acid. The reaction flask was then connected to a rotary evaporator and heated at 100°C for 19 hours while maintaining the pressure at about 5 torr. In all cases the total volatiles weighed slightly more than the theoretical amount of ethanol expected. Reaction products were then recovered and analyzed. Several of the products were heterogeneous when cold but became homogeneous upon heating.

Preparation of Methylphenyldiethoxysilane (C2425-22)

Absolute ethanol (110g., 2.2 moles) was gradually added to methylphenyldichlorosilane (191g., 1.0 mole) with constant stirring. The mixture was then heated to reflux while allowing the hydrogen chloride to boil off. Excess ethanol was then removed by vacuum distillation (b.p. 29-33°C at 35 torr) and the methylphenyldiethoxysilane was distilled at 120-123°C (35 torr). A yield of 198g. (0.94 mole, 94 percent) was obtained.

Polyurethane Preparations (C2425-23, 24, 25, 26, 27)

All polyurethanes derived from the bis(hydroxymethyl)diphenyloxide based silosypolyols were prepared by mixing reactants at ambient temperature or at the minimum temperature required to insure homogeneity.

Isocyanate Prepolymers (C2425-23-2 and 4 and 24-9 and 10)

Isocyanate prepolymers were all prepared by mixing molar equivalent amounts of the bis(hydroxymethyl)diphenyloxide based siloxypolyols with twice the stoichiometric amount of diphenylmethane-4, 4'-diisocyanate. Mixtures were maintained at the lowest possible temperature at which homogeneous mixtures could be obtained.

Preparation of Polymethylphenylsiloxane (C2222-8)

The procedure employed in the preparation was a sulfuric acid catalyzed polymerization involving cleavage of a cyclotrisiloxane under

anhydrous conditions similar to the method of Patnode and Wilcox[1] for the synthesis of polydimethylsiloxanes with about forty repeating units in chain length.

Methylphenylcyclotrisiloxane, 80 grams, was dissolved in 50 ml of redistilled, vigorously dried ethyl ether. Then a solution of 8 ml of sulfuric acid in 50 ml of dry ether was added dropwise with vigorous stirring. In spite of the slow addition of the catalyst acid solution, a slight turbidity formed in the reaction mixture. The reaction mixture was stirred overnight at ambient temperature with a drying tube attached. A very marked increase in viscosity occurred. Then another 50 ml of ether was added, also 30 ml of water, and stirring continued for one hour. The aqueous layer was then separated and the ether layer washed repeatedly with 30 ml portions of water and then left over anhydrous K_2CO_3. Ether was then removed under vacuum. Heat was then applied and the temperature slowly raised to 150°C under vacuum, and continued until beads of condensate appeared in the neck of the flask. The viscous product increased in turbidity after solvent removal and was redissolved in acetone. Celite filter aid was added and the solution centrifuged. Solvent was again removed under vacuum, leaving a clear, colorless oil.

Chloromethylation of Polymethylphenylsiloxane (C2222-6, C2222-7, C2222-9, C2222-11)

Several experiments were carried out in order to choose adequate reaction conditions for the chloromethylation of methylphenylsiloxanes using chloromethyl ether with stannic chloride catalyst. It was found necessary to employ a solvent, hexane, for these reactions because the reaction is uncontrollable when chloromethyl ether and catalyst are added to bulk siloxane, and highly colored by-products characteristic of Friedel-Crafts reactions are produced. In the procedure which gave the most nearly favorable result, minimal amounts of chloromethyl ether and catalyst were used and temperature was controlled with a water bath in the early stages, as described in the following representative reactions.

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[1] W. Patnode and D. F. Wilcox, J. Am. Chem. Soc. 68, 358 (1946).

Polymethylphenylsiloxane, 70 grams, and chloromethyl ether, 8 grams, were mixed in a dry flask, and a mixture of chloromethyl ether, 4 grams, and anhydrous stannic chloride, 0.5 ml, was added dropwise with vigorous stirring. When the flask warmed, it was placed in an icebath and stirring continued for 30 minutes. The bath was then removed. After about one hour of stirring without cooling the flask had warmed to 45°C and a reddish color developed. At this point, 100 ml of methanol was added and the reaction mixture stirred overnight. The mixture was then placed in a separatory funnel and the oil and alcohol layers separated. Fifty ml of water was added to the alcohol layer and a second oil layer separated. To the first oil fraction 50 ml of ethyl ether and 5 ml of concentrated NH_4OH were added and the mixture stirred for 24 hours. It was then washed with water, separated, and ether removed from the oil under reduced pressure. Some turbidity was observed; consequently the oil was diluted with 50 ml of acetone and 50 ml of ethyl ether and centrifuged. The solution was decanted and washed with water and separated. The aqueous layer was then washed with ether and a third oil fraction recovered by evaporation of the ether solution under reduced pressure. Following hydrolysis of the second oil fraction (methanol soluble) by stirring with concentrated NH_4OH, washing and removal of residual solvent, infrared spectra of all three oil fractions were run. The bulk of the recovered siloxane, from which methanol-soluble and then acetone-ether-soluble oils had been removed, contained neither CH_2OH nor CH_2Cl groups, as determined from the IR spectrum. The two soluble oil fractions, which were somewhat lower in bulk viscosity than the starting polymethylphenylsiloxane, both showed significant OH absorption attributable either to CH_2OH or to $-R_2SiOH$ end groups, and detectable absorption attributed to unhydrolyzed CH_2Cl groups. The combined weight of the latter two fractions was 17 grams, about 25 percent of the total recovered material.

Chloromethylation of Polymethylphenylsiloxane (C2222-11)

Polymethylphenylsiloxane, 40 grams, and 35 ml of hexane were stirred in a flask and a mixture of chloromethyl ether, 8 grams, and

stannic chloride, 0.3 grams, was added dropwise from a funnel. After the addition of the chloromethyl ether and catalyst, the reaction mixture warmed to about 35°C. The mixture was allowed to stir at ambient temperature over a weekend, with drying tube attached. A slight amber color developed during the reaction period. The volatiles were removed under reduced pressure without heat. Then 100 ml of acetone and 5 ml of concentrated NH_4OH were added and the mixture stirred for 24 hours. The mixture was then washed several times with water and the oil layer separated. Residual volatiles were removed under reduced pressure and the product dried over anhydrous Na_2CO_3 for several days. The first product gave a refractive index n_D^{25} of 1.5303, compared to 1.5475 for the starting siloxane. The IR spectrum showed some OH absorption. The intensity of the absorption band was, however, not consistent with the expected degree of substitution, one hydroxymethyl group per three methylphenylsiloxy repeating units. The product had a noticeable odor suggestive of benzyl alcohol. When mixed in equal parts with an isocyanate prepolymer, Adiprene L315, a fair cure was obtained in two hours at 155°C.

5. EPOXY AND SILICONE RESINS

Several epoxy and silicone resins were formulated during the course of this program which do not fit into the various discussions previously presented. These resins were formulated strictly from commercial products and thus entailed no synthesis effort. The composition of these resins is presented in Table 5-1 and their dielectric properties are presented in Table 5-2.

Code	Composition	Weight g.	Eq.	Filler	Cure Schedule	Comments
C1980-81-2	Epon X-24 (Shell Chemical)	15.4	0.09	Eccospheres	74°C - 16 hrs	White, tough
	N, N'-diphenylethylenediamine	7.0	0.066	R	4 hrs at 100°C	vacuum fill
	4, 4'-diaminodiphenylmethane	1.7	0.034			
-78-5	"Molecularly distilled"*	100		Eccospheres	125°C - 24 hrs	Cracks
	R-7501 silicone (Dow Corning)			R	in N_2 – 48 hrs	
	Dicumylperoxide	2			at 145°C	
-80R1	"Molecularly distilled"*	100		Eccospheres	122°C - 48 hrs	Cracks
	R-7501 silicone			R	in N_2	
	Dicumylperoxide	2			+24 hrs at 150°C	
-84-1	Epon X-24	17.8	0.105	Eccospheres R	74°C - 16 hrs	Tough
	N, N'-diphenylethylenediamine	7.0	0.066		85°C - 5 hrs	white
	4, 4'-methylenedianiline	1.7	0.034			
-84-2	Epon X-24	17.8	0.105	Alumina spheres (pre-dried 1 hr at 100°C)		Tough
	N, N'-diphenylethylenediamine	7.0	0.066		74°C - 52 hrs	white
	4, 4'-methylenedianiline	1.7	0.034			

*The term "Molecularly distilled" refers to silicone resin which was run through a thin film moleclar still at about 150°C and 10^{-3} to 10^{-4} torr to remove volatile constituents amounting to about 50 percent of its initial weight.

Table 5-1. Composition of several epoxy and silicone resins.

Code C1980-	Dielectric Constant at 1KC		Dissipation Factor, Percent		Insulation Resistance, Megohms at 500 VDC	
	25°C	100°C	25°C	100°C	25°C	100°C
-78-5	4.05	3.15	11.0	13.2	$\simeq 7 \times 10^4$	4×10^4
-80R1	3.12	2.96	4.13	9.64	5×10^5	1×10^4
-81-2	4.46	6.08	10.55	33.43	4×10^5	6×10^2
-84-1	4.2	7.1	13.0	43	6×10^5	3×10^2
-84-2	5.5	5.6	0.33	0.78	2×10^6	6×10^4

Table 5-2. Dielectric properties of several epoxy and silicone resins.

APPENDIX

This appendix was prepared to provide detailed procedures of experiments which did not appear to warrant presentation in the general discussions. The reason for this is that they do not represent optimum methods or techniques and in many cases are essentially duplicates of those included in the discussion. They do nevertheless represent work carried out under this program, and served to guide the investigators in the course of their studies.

This information may also be of value to the chemist who wishes to verify the conclusions which have already been drawn.

Preparation of m-Allylbromobenzene (C2425-17)

A solution of m-dibromobenzene (236 g, 1 mole) in anhydrous ether (150 ml) was added dropwise to a slurry of magnesium (26 g, 1.1 moles) in anhydrous ether (400 ml). The reaction was initiated with a small amount of ethylmagnesium iodide. Because of the vigor of the reaction part of the ether was lost. Upon completion of the addition the mixture was heated at reflux for one hour, then stirred for 4 hours. After setting overnight, freshly distilled allyl bromide (B.P. 69-70°C, 136 g, 1.1 moles) was added at such a rate as to keep the reaction under control. When this addition was completed the reaction mixture was heated at reflux for 2-1/2 hours. It was then poured over a mixture of ice and hydrochloric acid (≈25 ml), the ether layer was then separated, and the aqueous layer was extracted with ether several times. After combining the ether layers, they were washed with water then dried over Na_2SO_4 and filtered. Ether was then removed by simple distillation and the allylbromobenzene was recovered by fractional distillation at reduced pressure (35 torr). Five fractions were recovered, namely, I. 5.4 g, 58-68° C; II. 68-115°C, 2.1 g; III. 116-7°C, 68.5 g; IV. 117-8°C, 68.5 g; and V. 118°+, 8 g; residue unweighed. The final pot temperature was 215°C and the total yield of product (146 g) was 74 percent of theoretical.

Epoxidation of Bis(allylphenyl)tetramethyldisiloxane with Trifluoroperacetic Acid (C1961-57)

To a suspension of hydrogen peroxide (90 percent, 2.4 ml, 0.082 mole) in pre-cooled methylene chloride (15 ml at 0-5°C) was slowly added trifluoroacetic anhydride (21 g, 0.10 mole). Stirring was maintained throughout while maintaining the temperature below 3°C. After completion of the addition stirring was maintained for 15 minutes.

The peracid solution was then transferred to a dropping funnel and added over a one hour period to a cold slurry of anhydrous K_2CO_3 (34 g, 0.25 mole, dried at 70°C, 16 hours, <5 torr), meta-bis-(allylphenyl)tetramethyldisiloxane (10 g, 0.027 mole), and methylene chloride (60 ml). After the addition was completed the reaction mixture was heated to reflux and stirred for an extra half hour. Inorganic salts were filtered off and washed with methylene chloride. The combined CH_2Cl_2 layers were concentrated and the viscous product was distilled in a molecular still. The volatile fraction (3.6 g, 33 percent of theoretical, $n_D^{25} = 1.5291$) was collected at 3.5×10^{-3} torr at an outside wall temperature of approximately 130-145°C. It contained 12.16 percent Si (14.1 percent theoretical). The nonvolatile fraction weighed 7.3 g.

Attempted Epoxidation of Bis(allylphenyl)tetramethyldisiloxane with Perbenzoic Acid in the Presence of K_2CO_3 (C1961-59)

Tertiary-butyl alcohol was removed from a solution of perbenzoic acid in t-butyl alcohol by evaporation under reduced pressure (<5 torr). The evaporation was conducted using an oil bath heated to 30°C. Recovered perbenzoic acid (15 g, 0.11 mole) was then dissolved in anhydrous chloroform (60 ml) and the solution was transferred to a separatory funnel.

The perbenzoic acid solution was then gradually added to a slurry of m-bis(allylphenyl)tetramethyldisiloxane (10 g, 0.027 mole), finely powdered anhydrous potassium carbonate (34 g, 0.25 mole), and alcohol-free chloroform (60 ml). A reaction temperature of less than 8°C was maintained throughout the addition. Stirring continued at 10°C or less

while periodic peracid analyses were carried out. After 2 hours 85 percent of the peracid appeared to have been consumed whereas 99 percent appeared to have been consumed after 3-1/2 hours. After the chloroform was removed by simple distillation the high boilers were distilled by molecular distillation at 2×10^{-3} torr. The largest fraction (3.8 g) had a refractive index of $n_D^{25} = 1.5213$, whereas two smaller fractions (0.4 g and 0.3 g) were also collected which had refractive indices of $n_D^{25} = 1.5186$ and $n_D^{25} = 1.5158$, respectively. The nondistilled portion weighed 2.9 g. Wall temperatures of the still gradually rose from 70°C to 130°C. Infrared spectra of these volatile fractions demonstrated that they were the unreacted allyl compound.

Synthesis of Dimethylethoxychlorosilane (C2425-49)

Absolute ethanol (208 g, 4.5 moles) was slowly added to freshly distilled dimethyldichlorosilane. The solution was then gradually heated to reflux while allowing hydrogen chloride to escape. The solution was then fractionally distilled through a Podbielniak column. After unreacted dimethyldichlorosilane was removed, four fractions were collected, to wit: I. unweighed (75-78°C), II. 114 g (78-88°C), III. 150 g (88°C) and IV. 30 g (88-90°C).

1,3-Bis(m-allylphenyl)tetramethyldisiloxane (C2425-51)

A mixture of water (20 cc) and acetic acid (1 cc) was gradually added to m-allylphenyldimethylethoxysilane (147 g, 0.67 mole, $n_D^{23} = 1.5028$) while agitating vigorously. The mixture was placed in a separatory funnel and the lower aqueous phase was separated. The upper phase (126 g) was distilled at 1.3 torr yielding 107.9 g of product (b.p. 155°C, $n_D^{24} = 1.5199$). This yield represents 0.293 mole or 88 percent of theoretical.

A second portion of the m-allylphenyldimethylethoxysilane (27 g, $n_D^{23} = 1.5040$) was hydrolyzed with a mixture of water (5 ml) and glacial acetic acid (1/2 ml). After the reaction was complete the organic phase was separated (23.5 g) and was distilled at 1.3 torr.

Synthesis of 1,3-Bis(p-epoxypropylphenyl)tetramethyldisiloxane (C2425-54)

A solution of trifluoroacetic anhydride (53.4 g., 0.254 mole) and methylene chloride (76 ml) was added dropwise to a stirred mixture of hydrogen peroxide (8.22 g., ≃ 90 percent, 0.22 mole) in methylene chloride (50 ml). The temperature was maintained at -10° to +3°C. Stirring continued for 1/2 hour after the addition was completed.

The per acid solution thus obtained was then added dropwise to a slurry of dry potassium carbonate powder (86 g., 0.62 mole), methylene chloride (122 ml), and 1,3-bis(p-allylphenyl)tetramethyldisiloxane (23.7 g., n_D^{23} = 1.5206 and 22.6 g., n_D^{23} = 1.5193, total 46.3 g., b.p.. 135 ±5°C at 0.015 torr, 0.127 mole, 0.254 eq.). The reaction temperature was again maintained at -3 ±7°C. The total addition time was 1 hour. Overnight the pot temperature gradually rose from 5°C to 18°C. The crude product weighed 50.4 g. Its infrared spectrum showed that it had some OH groups due to the slight difficiency of anhydride. Molecular distillation of the product has yet to be carried out.

Preparation of 1,3-Bis(m-epoxypropylphenyl)tetramethyldisiloxane via Perbenzoic Acid (C1961-61)

The perbenzoic acid was recovered from a 25 percent solution in t-butyl alcohol by evaporation under vacuum. The resulting solid was taken up in 20 ml dry methylene chloride.

A preparation was planned substituting sodium bicarbonate in place of potassium carbonate to remove acid from the reaction mixture. Accordingly, the bicarbonate was finely ground, and dried 48 hours in a vacuum oven at ≥130°C. However, this preparation was abandoned in favor of the trifluoroperacetic acid epoxidation.

Preparation of Dimethylethoxychlorosilane (C1961-63)

Absolute ethanol (184.3 g., 4.0 mole) was added to a mixture of dimethyldichlorosilane (516.3 g., 4.0 moles) in pyridine (316.4 g., 4.0 moles). The product was taken up in petroleum ether, and

insoluble salts were removed by filtration. The filtrates were distilled through a packed column, and a 93-96°C fraction was collected weighing 215.7 g. (40 percent yield).

Preparation of Phenylmethylethoxychlorosilane (C1961-65)

Absolute ethanol (120 g., 2.6 moles) was added to a mixture of phenylmethyldichlorosilane (470 g., 2.5 moles) in pyridine (208 g., 2.6 moles). The product was taken up in petroleum ether, and the insoluble salts were removed by filtration. A simple distillation was performed to remove solvent (197-210°C). The crude product weighed 404.5 g. (80 percent yield). Fractional distillation has not been carried out.

Preparation of m-Allylphenylmagnesium Bromide (C1961-66)

m-Bromoallylbenzene (107 g., 0.54 mole) in 150 ml anhydrous tetrahydrofuran was cautiously added to a slurry of dry magnesium turnings (14.1 g., 0.58 mole) in tetrahydrofuran (200 ml). The reaction was initiated by a few grams of freshly prepared ethylmagnesium bromide. After completing the addition, the reaction mixture was heated at reflux for 3/4 hour.

Preparation of m-Allylphenyldimethylethoxysilane (C1961-67)

Freshly prepared allylphenylmagnesium bromide solution was decanted into an addition funnel and added dropwide to a solution of dimethylethoxychlorosilane (150 g., 1.08 mole) in additional tetrahydrofuran (200 ml). The mixture was then heated at reflux for 2 hours. The product was taken up in petroleum ether. Then the precipitated salts were removed by filtration, washed with naphtha, and the filtrates were combined. After evaporation of the solvent, the crude product was distilled at reduced pressure:

Fraction	Pressure	Temp.	Weight	Refractive Index at 24°C	Elemental Analysis		
					% Carbon	% Hydrogen	% Silicon
F1	2 torr	90°C	11.0 g.	1.4919	68.55 obs. (70.95 theory)	9.07 obs. (9.16 theory)	12.19 obs. (12.7 theory)
F2	0.25 torr	60°C	17.8 g.	1.4900			
F3	0.03 torr	45°C	28.3 g.	1.4949			
F5	10^{-3} torr	100°C	5.7 g.	1.5212			

(Infrared spectrograms were run on all fractions)

Hydrolysis of Remaining m-Allylphenyldimethylethoxysilane (C1961-69)

The two remaining fractions of the silane prepared in C1961-67 (fractions F2 and F3) were hydrolyzed as follows (the water used in both hydrolyses was acidified slightly with one drop of glacial acetic acid per 10 ml water):

F2: Water (0.6 g., 0.033 mole) was added to m-allylphenyldimethylethoxysilane (10 g., 0.045 mole), and the mixture was stirred at room temperature overnight. After removal of ethanol and residual water by distillation, the crude product weighed 7.9 g., and had a refractive index of 1.5218.

F3: Water (2.5 g., 0.092 mole) was added to m-allylphenyldimethylethoxysilane (28 g., 0.126 mole), and the mixture stirred at room temperature overnight. After removal of ethanol and residual water by distillation, the crude product weighed 23.5 g.

Since both hydrolyses appeared cloudy, even after removal of residual water, the two runs were combined, and re-distilled under vacuum. A two-phase distillate (7.6 g.) was collected in the cold trap. The combined products weighed 23.8 g.

Preparation of 1,3-Bis(m-epoxypropylphenyl)tetramethyldisiloxane (C1961-71)

Trifluoroperacetic acid was prepared freshly by dropwise addition of trifluoroacetic anhydride (21 g., 0.10 mole) in dry ethylene chloride (30 ml) to a cold slurry of 98 percent hydrogen peroxide (2.4 ml, 0.08 mole) with constant stirring. The temperature was kept at 0-5°C with an ice bath. This fresh peracid was added dropwise, with constant stirring, to a cold slurry of potassium carbonate (34 g., 0.25 mole) (which had been finely ground and dried under vacuum at 100°C overnight) and bis(m-allylphenyl)tetramethyldisiloxane (10 g., 0.055 eq) in dry methylene chloride (60 ml). Again, the temperature was kept below 5°C by use of an ice bath.

Precipitated salts were removed from the reaction mixture by filtration, washed with methylene chloride, and the combined filtrates were distilled at 1 atmosphere to remove solvent. The crude product weighed 13.9 grams after evaporation of the methylene chloride (theoretical weight = 13.8 g.).

The following three fractions were obtained by vacuum distillation at 10^{-3} torr:

Fraction	Weight	Refractive Index	Elemental Analysis		
			% C	% H	% Si
F1	1.5 g.	1.5239	68.17	7.74	14.51
F2	1.6 g.	1.5251	66.57	7.69	14.15
F3	3.0 g.	1.5215	-	-	-

Preparation of 1,3-Bis(m-epoxypropylphenyl)tetramethyldisiloxane C1961-72

Trifluoroperacetic acid was freshly prepared by dropwise addition of trifluoroacetic anhydride (48.3 g., 0.23 mole) to a cold suspension of 98 percent hydrogen peroxide (5.5 ml, 0.19 mole) in 30 ml pre-cooled dry methylene chloride. The reaction was kept below 5°C by use of an ice bath. The peracid was then transferred to a dropping funnel and added dropwise, with constant stirring, to a cold slurry of finely powdered

anhydrous potassium carbonate, which had been dried overnight in vacuum at ≥110°C (82 g., 0.58 mole), and bis(m-allylphenyl)tetramethyldisiloxane (23 g., 0.127 mole) in 125 ml dry methylene chloride. The reaction temperature was kept below 0°C during addition, and allowed to reach room temperature slowly. It was stirred overnight. After removal of the solid salts by filtration, and subsequent washing of the salts with fresh solvent, the filtrates were combined and the solvent evaporated off. The crude product was a dark amber, viscous resin. This product was run through a molecular still at 10^{-3} torr and 150°C still surface temperature. 5.4 grams of a straw-colored liquid was collected, which had a refractive index of 1.4950. The infrared spectrogram showed the presence of a considerable amount of hydroxyl groups.

Preparation of p-Allylphenyldimethylethoxysilane (C1961-73)

The p-allylphenyl Grignard was prepared by the dropwise addition of p-bromoallylbenzene (143 g., 0.73 mole) in anhydrous tetrahydrofuran (200 ml) to a slurry of dry magnesium turnings (19 g., 0.78 mole) in anhydrous tetrahydrofuran (300 ml). The reaction was initiated by the addition of freshly prepared ethylmagnesium iodide. The mixture was heated at reflux for 3/4 hour after the addition was completed. The freshly prepared p-allylphenylmagnesium bromide was decanted into a dropping funnel and added dropwise, with constant stirring, to dimethylethoxychlorosilane (200 g., 1.44 mole) in anhydrous tetrahydrofuran (200 ml). After addition, the reaction mixture was heated at reflux one hour.

The crude product was taken up in petroleum ether. The salts were removed by filtration, washed with fresh solvent and refiltered, and the filtrates were combined. After evaporation of solvent, the crude product weighed 121 grams (67 percent of theoretical). It has a refractive index of $n_D^{23} = 1.4969$.

A vacuum distillation at 0.5 torr was performed on the crude product and the following fractions were obtained.

Fraction	Temp. Range	Weight	Refractive Index (24°C)
C1961-73 F1	47- 60°C	18.4 g.	1.4945
C1961-73 F2	60- 85°C	74.4 g.	1.4925
C1961-73 F3	85-120°C	24.1 g.	1.4962

Attempted Preparation of 1,3-Bis(p-epoxypropylphenyl)tetramethyldisiloxane (C1961-74)

Trifluoroperacetic acid was freshly prepared as before, from trifluoroacetic anhydride (7.3 g., 0.034 mole) added to 98 percent hydrogen peroxide (0.9 ml, 0.031 mole). The peracid was then added dropwise, with constant stirring, to a cold slurry (0-5°C) of finely powdered anhydrous potassium carbonate (12 g., 0.085 mole) and bis(p-allylphenyl)tetramethyldisiloxane (3.5 g., 0.019 mole) in 30 ml dry methylene chloride. The addition of the peracid was made much more slowly than in Preparation C1961-72. The reaction mixture was stirred overnight as before, and the crude product worked up as in C1961-72. Again, the crude product was a dark amber, viscous polymer. Accordingly, no further work was done on this product.

Preparation of Bis(m-epoxypropylphenyl)tetramethyldisiloxane (C1961-75)

Trifluoroperacetic acid was prepared by dropwise addition of trifluoroacetic anhydride (60.7 g, 0.29 mole) in 80 ml dry methylene chloride to a cold suspension of 98 percent hydrogen peroxide (10.4 g, 0.29 mole) in dry methylene chloride (60 ml). The peracid was transferred to a dropping funnel and added dropwise, with constant stirring, to a slurry of bis(m-allylphenyl)tetramethyldisiloxane (47.7 g, 0.13 mole) and finely powdered anhydrous potassium carbonate (104 g, 0.75 mole) in 130 ml dry methylene chloride. The reaction mixture was kept below 5°C during addition by use of an ice bath. The mixture

was allowed to warm up to ambient temperature, and stirred overnight. The crude product was separated from solids by filtration, and the solids were washed with fresh solvent. Combined filtrates (which had a pH of approximately 6) were distilled at ambient pressure to remove solvent and residual low boilers. After high vacuum evaporation at 50°C (10^{-3} torr) the product weighed 38 g (74 percent of theoretical), and had a refractive index of 1.5252 at 23°C.

Attempted Repurification of bis(p-epoxypropylphenyl)tetramethyldisiloxane (C1961-78, C2425-54)

The crude product (weighing 50.4 g) was vacuum distilled, on a small molecular still, yielding the following fractions:

Fraction	Pressure (torr)	Still Temp. (°C)	Refr. Index	Weight (grams)
F1	5×10^{-4}	85-100	1.5157	1.6
F2	5×10^{-4}	125	1.5162	2.2
F3	10^{-4}	90-100	1.5034	5.2
F4	10^{-4}	110-135	1.4997	2.8
Pot res.		≥135	1.5106	23.6

Reaction of bis(m-epoxypropylphenyl)tetramethyldisiloxane with Trifluoracetic Acid, for Comparison of IR Absorptions (C1961-79)

A 0.119 N solution of trifluoroacetic acid in methylene chloride was prepared by addition of water (0.054 g, 0.00297 mole) to trifluoroacetic anhydride (0.626 g, 0.00297 mole) in 5 ml dry methylene chloride. The resulting acid was transferred quantitatively to a 50 ml volumetric flask, and brought to 50 ml volume with methylene chloride. 10.40 ml (0.00125 eq) of the acid solution were added with constant stirring to bis(m-epoxypropylphenyl)tetramethyldisiloxane (1.00 g, 0.005 eq., C1961-75). The mixture was stirred for 24 hours at 50°C. The product was purified by evaporation of low boilers at 65-70°C at 5×10^{-4} torr. Refractive index at 23°C was 1.5132, and the product weighed 0.80 g after purification.

Preparation of p-Bromoallylbenzene (C2425-56)

A solution of p-dibromobenzene (1180 g, 4 mole) in absolute ether was added gradually to a slurry of magnesium (106 g, 4.4 mole) in ether. After the reaction was completed, a solution of allyl chloride (385 g, 5.0 mole) in ether was added dropwise. The vigorous reaction proceeded smoothly all through the addition and for about a half hour thereafter, but it eventually went out of control. Control was reestablished only after massive losses had occurred. The mixture ultimately was washed with acidified water and the ether phase collected. After removal of ether by distillation the allylbromobenzene was distilled under reduced pressure. It should be noted however that much unreacted dibromobenzene remained which solidified in the product and had to be removed by decantation. Two fractions of product were finally isolated

I 183 g (B. P.$_{14}$ = 94-96°C, n_D^{22} = 1.5517)

II 96 g (B. P.$_{14}$ = 96-98°C, n_D^{22} = 1.5536)

Yield calculated on the basis of these two fractions was 279 g, 1.42 mole or 35.5 percent.

Preparation of p-Bromoallylbenzene (C1961-88)

Solid p-dibromobenzene (589.9 g, 2.5 mole) was added with vigorous stirring to a slurry of dry magnesium (68.1 g, 2.8 mole) in two liters of anhydrous ether containing 50 g of the p-dibromobenzene. The reaction was initiated with a few grams of freshly prepared ethylmagnesium iodide. Then the reaction was kept at even reflux with an ice bath. After addition of the p-dibromobenzene, the reaction mixture was stirred at reflux for three quarters of an hour, and then allyl bromide (338.8 g, 2.8 mole) in two volumes of dry ether was added dropwise with constant stirring. Again even reflux was maintained by use of an ice bath. The reaction mixture was stirred at reflux for one half hour after the addition of the 3-bromopropene. Next

the reaction mixture was poured over acidified ice water (pH approximately 3), and the organic phase was separated in a separatory funnel. The aqueous phase was shaken with fresh ether, and the ether phases were then combined. They were then washed with fresh salt water. Ether was then removed by simple distillation and the high boilers were then distilled, yielding 297.0 g of product boiling at 86-94°C at 6-8 torr. (60 percent of theoretical).

Preparation of Dimethylethoxychlorosilane (C1961-87)

A mixture of anhydrous ethanol (184.3 g, 4.0 mole) and pyridine (100 g, 1.26 mole) was added dropwise, with constant stirring, to a mixture of dimethyldichlorosilane (516.3 g, 4.0 mole) and pyridine (216.4 g, 2.74 mole). An even reflux was maintained by use of an ice bath. The reaction mixture was stirred another half hour at reflux. One liter of hexane was added to the reaction mixture, and the solids were separated out by filtration and washed with fresh hexane. Filtrates were combined and starting materials and solvent were distilled off at ambient pressure.

Preparation of bis(m-epoxypropylphenyl)tetramethyldisiloxane (C1961-84)

Trifluoroperacetic acid was prepared by the dropwise addition, with constant stirring, of trifluoroacetic anhydride (79.8 g, 0.381 mole) in dry methylene chloride (100 ml) to a cold suspension of 92.9 percent hydrogen peroxide (11.2 g, 0.306 mole) in 70 ml of dry methylene chloride. During addition the reaction mixture was kept below 5°C by use of an ice bath. The peracid solution was transferred to a dropping funnel and added dropwise, with constant stirring, to a cold slurry of bis(m-allylphenyl)tetramethyldisiloxane (50.2 g, 0.137 mole) and finely powdered dry potassium carbonate (185 g, 1.334 mole) in 150 ml of dry methylene chloride. Again, the reaction temperature was kept below 5°C by use of an ice bath. The mixture was allowed to come to room temperature, and then heated at reflux for one half hour. The mixture was stirred overnight at ambient temperature. Crude

product was then separated by filtration, the solids were washed with fresh methylene chloride, and the filtrates were combined. The pH of the filtrates was 4; thus, they were stirred two hours with fresh potassium carbonate, which brought the pH up to 6. After filtering out the solids as before, the solvent was removed by distillation and the high boilers were distilled under vacuum, yielding the following fractions.

2F2: 80-84°C at 10^{-4} torr; 7.0 g net; $n_D^{25} = 1.5119$

2F3: 84-95°C at 10^{-4} torr; 11.6 g net; $n_D^{25} = 1.5170$

A higher boiling fraction of the product, weighing 8.8 g net, was taken up in three volumes of methylene chloride and stirred for twenty-four hours at reflux in the presence of potassium carbonate (15 g). After separation and repurification of this product, IR analysis showed that the impurities remained.

Preparation of bis(p-epoxypropylphenyl)tetramethyldisiloxane (C1961-86)

Trifluoroacetic anhydride (21.0 g, 0.0999 eq) in dry methylene chloride (20 ml) was added dropwise, with constant stirring, to a cold suspension of 92.9 percent hydrogen peroxide (3.2 g, 0.0873 eq) in dry methylene chloride (20 ml). The temperature during addition was kept below 5°C by use of an ice bath. After the addition was completed the mixture was stirred for fifteen minutes.

The resulting peracid solution was then transferred to a dropping funnel and added dropwise, with constant stirring, to a slurry of bis(p-allylphenyl)tetramethyldisiloxane (16.0 g, 0.0873 eq) and finely powdered dry sodium carbonate (31.8 g, 0.3 eq) in dry methylene chloride (100 ml). During the addition of the peracid, the reaction mixture was kept at gentle reflux by use of an ice bath. After addition, the mixture was stirred another half hour at reflux.

The crude product was separated by filtration, and the solids were washed several times with fresh methylene chloride. Filtrates were combined with the crude product and fresh sodium carbonate

(10.6 g, 0.10 eq) was then added. The slurry was stirred at reflux for fifteen minutes. The product was again separated by filtration, and the solids were rewashed with fresh methylene chloride. (The filtrates had a pH of approximately 6 after both separations.) The crude product was then allowed to stand 48 hours over anhydrous magnesium sulfate. High vacuum distillation yielded three fractions as follows:

C1961-86 F1: 75-108°C at 10^{-4} torr; net = 1.4 g; n_D^{24} = 1.4990

C1961-86 F2: 108-115°C at 10^{-4} torr; net = 8.1 g; n_D^{24} = 1.5068

C1961-86 F3: >115°C at 10^{-4} torr; net = 2.9 g; n_D^{24} = 1.4968

Preparation of Phenyltris(ethylamino)silane (D1151-7A)

A solution of redistilled phenyltrichlorosilane (106 g, 0.50 mole) in anhydrous ether (100 ml) was added dropwise to a solution of anhydrous ethylamine (≈ 225 g, 5 mole) in anhydrous ether (500 ml) maintained at -10°C to 0°C. After setting for several days the mixture was filtered, and the filtrate distilled to remove ether and excess amine. High boilers were then distilled at 3 torr to yield 54.5 g of phenyltris(ethylamino)silane boiling at 110 ± 1°C. The yield represents 46 percent of theoretical.