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DEVELOPMENT OF IMPROVED STERILIZABLE POTTING AND ENCAPSULATING COMPOUNDS FOR SPACE APPLICATIONS

NORMAN BILOW

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DEVELOPMENT OF IMPROVED STERILIZABLE POTTING AND ENCAPSULATING COMPOUNDS FOR SPACE APPLICATIONS

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National Aeronautics and Space Administration

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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.

During the first four months of this year's program Mr. Robert B. Feuchtbaum served as principal investigator, whereas during the remainder of the program Dr. Norman Bilow, Hughes Staff Chemist, was the principal investigator. Technical assistance was also obtained from Mr. Max Bart, Dr. Abraham L. Landis, Mr. Raymond E. Lawrence, Mr. Theodore Glenn and others.

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INTRODUCTION

The purpose of this program is 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 out-gas seriously under the high vacuum of space. This may be accompanied by matrix embrittlement as well as by the 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 into first quality composite structures.

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 the previous 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.

SUMMARY AND CONCLUSIONS

Two principal classes of polymers were investigated during the course of this program. These include siloxyurethanes and epoxysilicones. With the siloxyurethanes the principal effort was placed upon the synthesis of siloxypolyols derived from trimethylolpropane and bis(hydroxymethyl) diphenyl ether. These polyols were ultimately to be used in preparing siloxyisocyanate prepolymers. However, they were evaluated to a large extent in urethane formulations made with a standard commercial isocyanate prepolymer. A study of the trimethylolpropane based siloxypolyols demonstrated that permanently stable polyol prepolymers were obtained only when the siloxane chains in the polyol were limited to an average of 2 to 2-1/2 silicon atoms. This short chain length proved too small to yield good dielectric materials. Siloxypolyols derived from bis(hydroxymethyl) diphenyl ether, however, have shown a great deal of promise as far as their dielectric properties are concerned. Further work is needed before they can be made into siloxyurethanes with good physical properties.

Research on epoxysilicones was directed toward the synthesis of bis(epoxypropoxyphenyl)tetramethyldisiloxane and bis(epoxypropylphenyl)-tetramethyldisiloxane. The first of these monomers could not be obtained due to an allylic rearrangement of the intermediate allyl phenyl ether. With the second of these compounds the synthesis proceeded successfully as far as the bis(allylphenyl) tetramethyldisiloxane intermediate, but attempts to epoxidize this allyl compound thus far have failed apparently due to an oxidative cleavage of the phenyl silicon bonds.

Several amine cured epoxy resins were also investigated, and it was noted that amines containing N-methylamino groups yield epoxies with much improved dielectric properties. This observation led to the synthesis of several N-methylaniline formaldehyde telomers which were found to yield cured epoxies with excellent dielectric properties. Work in this area is to be continued.

Most of the trimethylolpropane based siloxyurethanes which were synthesized had dielectric constants above 4.5 at ambient temperature and above 6.5 at 100°C. It was recognized, however, that these values could be markedly reduced if the silicone content of the cured polymers could be significantly increased. Although this was a principal objective of the siloxyurethane investigation this objective has not yet been achieved.

In contrast to the trimethylolpropane based polyols the bis (hydroxy-methyl) diphenyl ether based siloxy polyols have been quite promising, having exhibited ambient dielectric constants of 3.4-3.8 and dissipation factors of 1.1-1.2%.

MATERIALS SYNTHESIS

DISCUSSION

Siloxyurethanes

Various siloxypolyols were synthesized for use in the preparation of siloxyurethane polymers. These syntheses fall into several categories, namely: (1) reactions of trimethylolpropane with di- and tri-functional alkoxysilanes, (2) reactions of neopentyl glycol with alkoxysilanes, (3) reactions of decanediol with alkoxysilanes and (4) reactions of bis(hydroxymethyl)diphenyl ether with alkoxysilanes.

Siloxyurethanes have been investigated in this program because they can theoretically be designed to have dielectric properties comparable to the silicones without such disadvantages of silicones as poor adhesion, severe outgassing in high vacuum, etc. To accomplish this objective, it has become apparent that the siloxane moieties of the siloxyurethanes should constitute the major portion of the polymer. With the trimethylolpropane-based siloxypolyols, it has been concluded that "n" in the following illustration should probably be eight to ten if the polyol is to be cured with conventional isocyanate monomers such as tolylene diisocyanate or diphenylmethanediisocyanate.

$$
C_2H_5 - \underset{\underset{CH_2OH}{|}}{\overset{\overset{CH_2OH}{|}}{C}} - CH_2O \left(\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}} - O \right)_n CH_2 - \underset{\underset{CH_2OH}{|}}{\overset{\overset{CH_2OH}{|}}{C}} - C_2H_5
$$
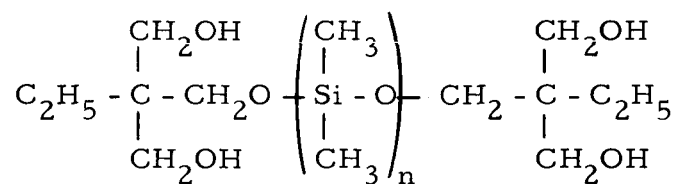
Polyols of this type were prepared by the reaction of trimethylolpropane with dimethyldiethoxysilane, diethoxytetramethyldisiloxane, diethoxyhexamethyltrisiloxane, and diethoxyoctamethyltetrasiloxane. The generalized reactions are illustrated below.

5

$$
\begin{array}{c}
CH_3 \\
| \\
C_2H_5O - Si - OC_2H_5 \\
| \\
CH_3
\end{array}
$$

$$H^+ \Big| H_2O$$

$$
C_2H_5O \left(\begin{array}{c} CH_3 \\ | \\ Si - O \\ | \\ CH_3 \end{array} \right)_n C_2H_5
$$

$$2\ C_2H_5 - C(CH_2OH)_3 \quad \Big| H^+$$

$$
\begin{array}{c}
CH_2OH \\
| \\
C_2H_5 - C - CH_2 - O
\end{array}
\left(\begin{array}{c} CH_3 \\ | \\ Si - O \\ | \\ CH_3 \end{array} \right)_n
\begin{array}{c}
CH_2OH \\
| \\
CH_2 - C - C_2H_5 \\
| \\
CH_2OH
\end{array}
$$
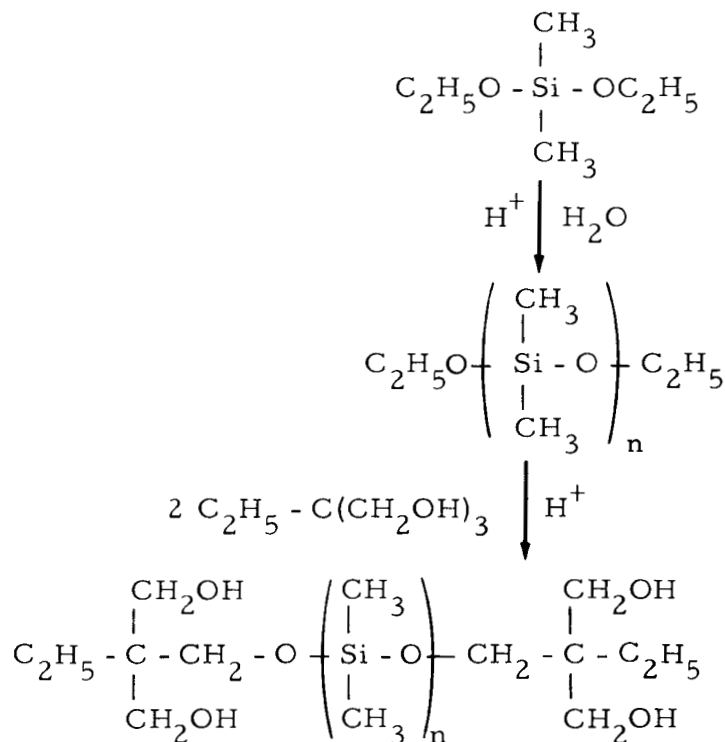
These neopentyl intermediates were selected because of their high degree of thermal stability and the potential improvement in the thermal stability of polymers derived from them. Although siloxydiols or triols could be prepared by the reaction of alkoxysiloxanes with glycols such as ethylene glycol, propylene glycol, or hydroxy termi- nated polyethers as illustrated below,

$$
CH_3O \left(\begin{array}{c} R \\ | \\ Si - O \\ | \\ R' \end{array} \right)_n CH_3 + 2\ HOCH_2CH_2OH \xrightarrow{H^+} HO - CH_2 - CH_2 - O \left(\begin{array}{c} R \\ | \\ Si - O \\ | \\ R' \end{array} \right)_n CH_2CH_2OH
$$
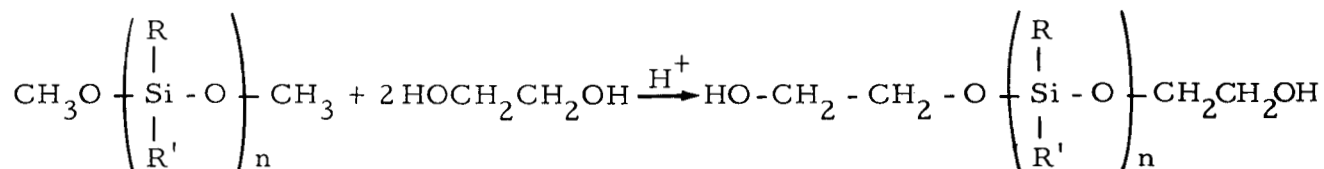
the aliphatic glycols of this type would yield polyurethanes which would tend to lack the requisite stability under thermal sterilization conditions.

Degradation is less probable at the sterilization temperature if the glycols, from which the hydroxyalkoxysiloxanes are prepared, are either neopentyl glycol or trimethylolpropane. A typical polyurethane derived from such a neopentyl glycol based siloxane is illustrated on the following page.

$$\text{---Si} \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{|}} + O - CH_2 \overset{\overset{H_3C \diagdown \diagup CH_3}{C}}{\underset{\alpha \quad \beta}{}} CH_2 - O \underset{\alpha'}{+} \overset{\overset{O}{||}}{C} - NH - R' \text{---}$$
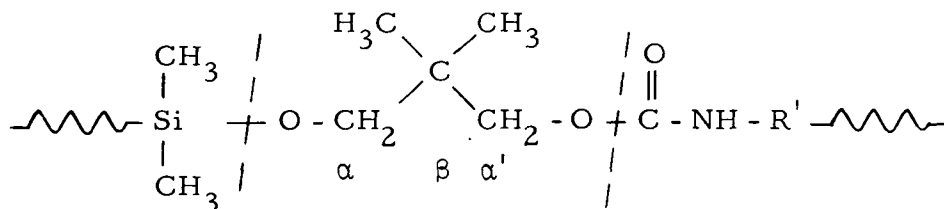
Since the carbon atom β to the siloxy oxygen atom and beta to the urethane group contains no hydrogen atoms, thermal degradation into silanols or carbamic acids followed by subsequent degradation to disiloxanes plus water or amines plus carbon dioxide respectively, is far less feasible. Thermal rearrangements can of course occur at more extreme temperatures and thus breakdown mechanisms still exist.

In actual practice the neopentylglycol based siloxypolyols which were studied extensively were obtained by the reaction of trimethylol-propane with partially hydrolyzed dimethyldiethoxysilane. The silane was hydrolyzed with the theoretical amounts of water required to produce dimers, trimers, etc. as shown below.

$$n \quad C_2H_5O - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}} - O - C_2H_5 + (n-1)H_2O \xrightarrow{H^+} C_2H_5 - O \left(\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}} - O \right)_n C_2H_5 + (2n-2)C_2H_5OH$$
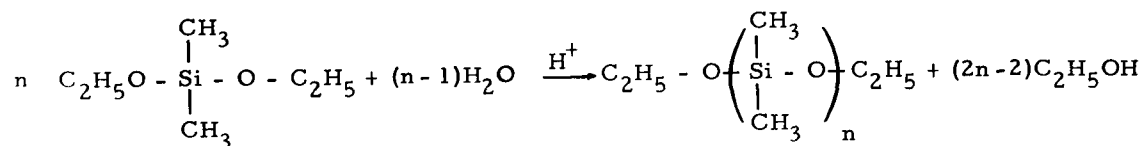
However, no attempt was made (in most cases) to separate the various siloxane isomers from the hydrolysis mixtures because it was recognized that in subsequent acid catalyzed reactions with trimethyolpropane the siloxanes would re-equilibrate into mixtures once again. Consequently, efforts were directed toward the synthesis of stable homogenous equilibrated polyol mixtures containing the maximum silicone content.

During the course of these reactions ethanol was removed continuously from the reaction mixtures until the reaction was complete. Additional catalyst was then added to the reaction mixtures and heating

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continued until total equilibration was achieved. This subsequent step was necessary to minimize the percentage of cyclosiloxanes in the siloxy polyol mixtures since cylic products are produced to a much greater extent when diluents (in this case ethanol) are present during the polymerizations.

By this process a series of siloxypolyols was produced. Of this series the only permanently homogeneous polyol was the one derived from the disiloxane. The analogous trisiloxane derivative remained homogeneous for an extended period of time (several weeks) but eventually separated into two phases. An infra-red spectra of the disiloxane polyol is presented in figure 1.

In one experiment a fractional separation of the various diethoxysiloxane isomers was carried out and it was found that only the disiloxane and trisiloxane were capable of producing homogeneous stable polyols. Polyols derived from the higher telomers always were inhomogeneous (except at $150^{\circ}C$), probably due to the presence of cyclosiloxanes; however, they were capable of yielding homogeneous isocyanate prepolymers when reacted with conventional diisocyanates such as tolylene diisocyanate. Such a reaction is illustrated as follows:
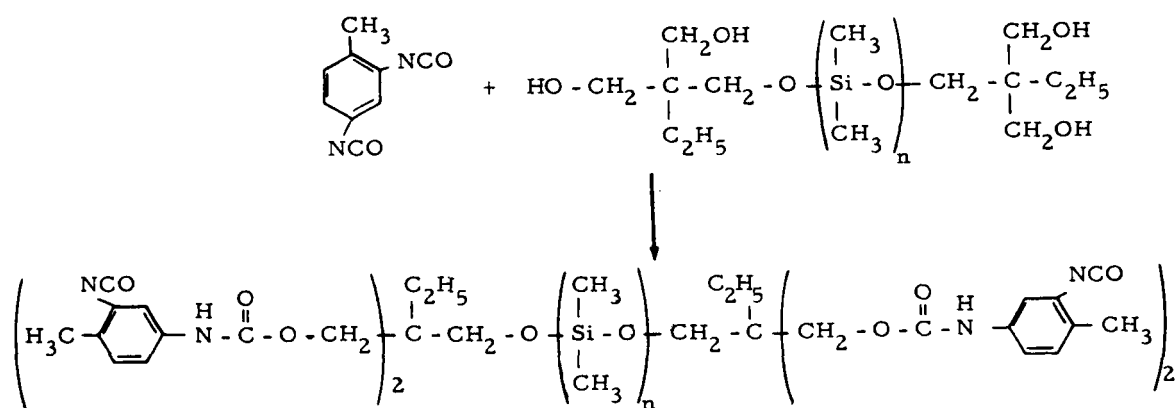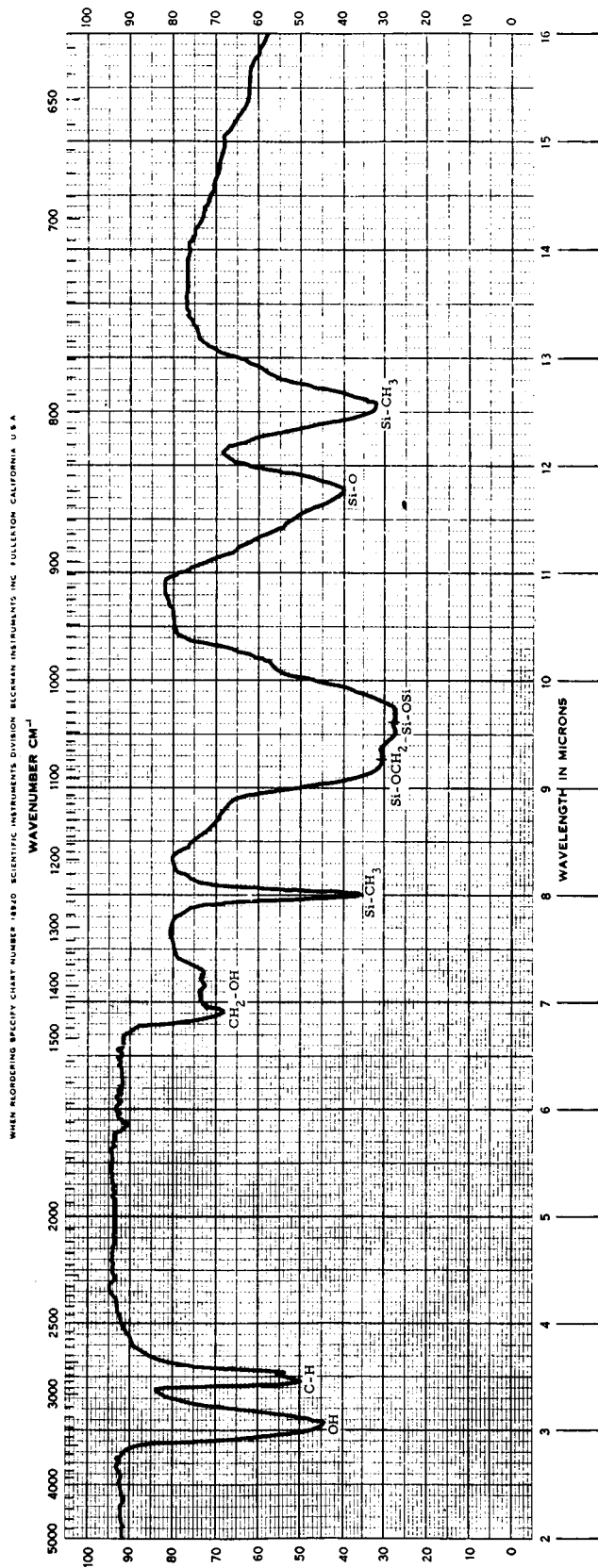
Figure 1. Infrared spectrum of siloxypolyol derived from trimethylolpropane and diethoxytetramethyldisiloxane (C1980-57).

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In evaluating the various siloxypolyols they were generally reacted with monomeric diisocyanates or with a standard isocyanate prepolymer. When the polyurethanes derived from these siloxypolyols were excessively brittle or were poor for any other reason the synthesis of isocyanate prepolymers was considered to be unwarranted except where the prepolymer was to ultimately be used with an entirely different polyol.

The major problem involved in the utilization of the isocyanate prepolymers which were prepared was their high melting points (>120°C). Attempts to formulate them with other siloxypolyols were unsuccessful, since at the isocyanate melting point the reaction mixtures cured much too rapidly. Lower melting prepolymers would most likely be obtained from analogous siloxypolyols if the siloxane chains were sufficiently long. Prepolymers with lower melting points were obtained when excess diisocyanate monomer remained in the prepolymer. However, this merely lowered the prepolymer equivalent weight and increased its reactivity, both factors which were detrimental to the preparation of homogeneous non-brittle polymers.

Another approach to the synthesis of long chain siloxypolyols involved the attempted equilibration of octamethylcyclotetrasiloxane with trimethylolpropane as illustrated below.
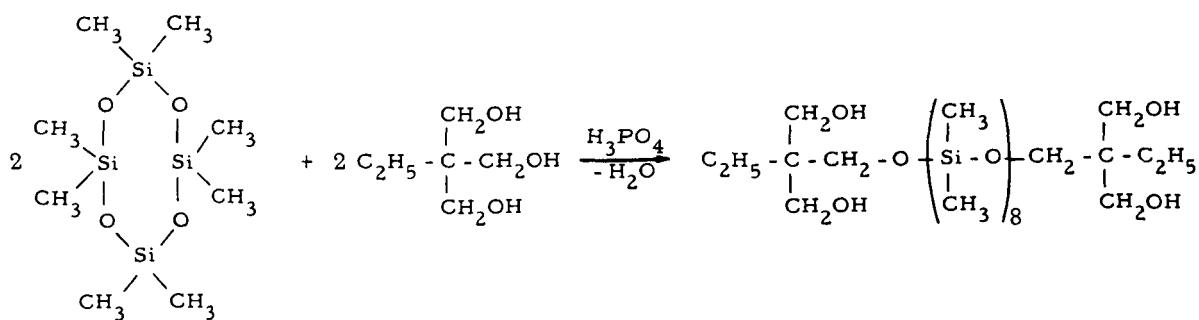
The following reactant ratios were used:

No.	Octamethyl-cyclotetra-siloxane		Methanol		Trimethylol-propane		H_3PO_4, drops	Max. Temp., °C	Time
	g	mole	g	mole	g	mole			
1	26	0.089			13	0.10	5	130	20 hours
2	20	0.068			20	0.15	5	130	20 hours
3	13	0.044			26	0.19	5	130	20 hours
4	8	0.027			32	0.24	5	130	20 hours
5	14.8	0.050	3.2	0.10	9.0	0.07	2	145	6 days
6	14.8	0.050	4.8	0.15	13.5	0.10	2	145	6 days
7	14.8	0.050	6.4	0.20	18.0	0.13	2	145	6 days

In the latter three equilibration reactions, the methanol was removed as the equilibration presumably progressed. It was initially added to permit the equilibration to proceed via methoxysiloxane intermediates.

The difficulty of producing linear siloxypolyols of the desired type can be attributed to the strong tendency for cyclosiloxanes to retain their cyclic configuration as well as to the difficulty of removing water from the reaction mixture.

Experiments have also been carried out aimed at the synthesis of siloxypolyols from neopentyl glycol. The reaction is analogous to that used for the trimethylolpropane and is illustrated below:
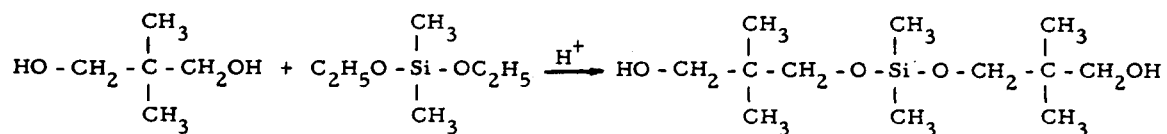
The major product of this reaction was the cyclosiloxane
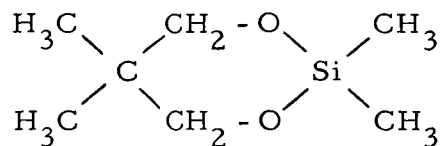
although a siloxypolyol was also obtained which had an equivalent
weight of 377. Elemental analysis of the polyol gave the following
results.

	Observed, percent	Calculated for $C_{11}H_{26}Si_2O_3$	Calculated for $C_{12}H_{28}SiO_4$
Carbon	50.20	50.3	54.6
Hydrogen	9.95	9.96	10.6
Silicon	21.18	21.20	10.6

This data, as well as the hydroxyl equivalent, demonstrated that the
product was not the desired diol but a siloxypolyol having a longer
siloxane chain. Furthermore, it explains the incompatibility of the
product with polar compounds such as trimethylolpropane and highly
functional isocyanate prepolymers. Satisfactory 4-rod test specimens
could not be obtained from this siloxypolyol. The phosphoric acid used
as catalyst for this reaction may to a large extent be responsible for
the low yield of high molecular weight product. Its removal is of
course very difficult and even trace quantities would catalyze the con-
tinuous shift in equilibrium as the cyclic byproduct was removed from
the reaction mixture. Acetic acid may be the preferred catalyst since
its removal by heat and vacuum is feasible.

In addition to the siloxypolyols derived from trimethylolpropane
and neopentyl glycol, another type of siloxypolyol has been synthesized.
More specifically, 1,3-bis(hydroxymethyl)tetramethyldisiloxane has
been prepared from trimethylchlorosilane by chlorination followed by
hydrolysis, then displacement of the chlorine atoms with acetoxy
groups and subsequent hydrolysis. The reaction sequence is illus-
trated below and follows the procedure of R. I. Akawie [Development
of Seals and Sealants for Use at Cryogenic Temperatures, NAS 8-2428,
June 1963].

$$H_3C-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{Si}}-Cl + Cl_2 \xrightarrow{h\nu} Cl-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{Si}}-Cl \xrightarrow{H_2O} ClCH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{Si}}-O-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{Si}}-CH_2Cl$$

$$HO-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{Si}}-O-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{Si}}CH_2OH \underset{H^+}{\xleftarrow{CH_3OH}} CH_3-\overset{O}{\overset{\|}{C}}-O-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{Si}}-O-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{Si}}-CH_2O-\overset{O}{\overset{\|}{C}}-CH_3$$
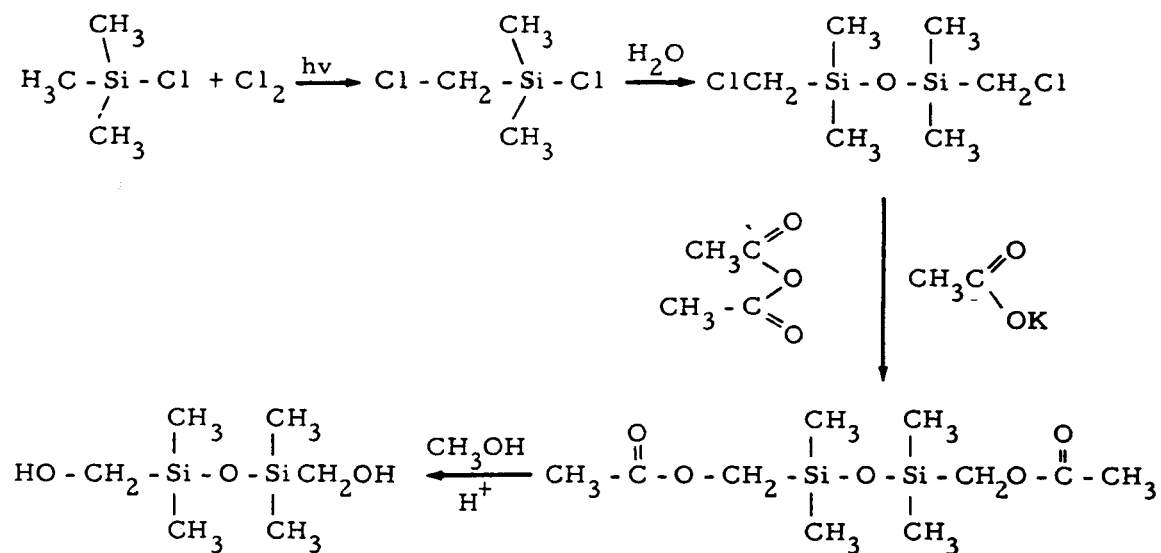
The product of this reaction sequence is to be used in subsequent equilibration experiments directed toward the lengthening of the siloxane chain. Isocyanates prepared from mixtures of this diol with siloxypolyols derived from trimethylolpropane have been evaluated. Because of the shortness of the siloxane chain moieties, the dielectric properties which were measured were in no way outstanding.

Siloxypolyols have also been prepared from trimethylolpropane and 1, 3, 5-triphenyl-1, 3, 5-trimethoxy-1,5-dimethyltrisiloxane. The first of these was prepared as follows:

$$CH_3O-\overset{\overset{\displaystyle C_6H_5}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{Si}}-O-\overset{\overset{\displaystyle C_6H_5}{|}}{\underset{\underset{\displaystyle OCH_3}{|}}{Si}}-O-\overset{\overset{\displaystyle C_6H_5}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{Si}}-OCH_3 + 3\,C_2H_5-\overset{\overset{\displaystyle CH_2OH}{|}}{\underset{\underset{\displaystyle CH_2OH}{|}}{C}}-CH_2OH$$

$$\downarrow H^+$$

$$C_2H_5-\overset{\overset{\displaystyle CH_2OH}{|}}{\underset{\underset{\displaystyle CH_2OH}{|}}{C}}-CH_2-O-\overset{\overset{\displaystyle C_6H_5}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{Si}}-O-\overset{\overset{\displaystyle C_6H_5}{|}}{\underset{\underset{\displaystyle O}{|}}{Si}}-O-\overset{\overset{\displaystyle C_6H_5}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{Si}}-O-CH_2-\overset{\overset{\displaystyle CH_2OH}{|}}{\underset{\underset{\displaystyle CH_2OH}{|}}{C}}-C_2H_5$$

$$\underset{\underset{\underset{\displaystyle C_2H_5}{|}}{HOCH_2-\overset{\overset{\displaystyle CH_2}{|}}{C}-CH_2OH}}{}$$
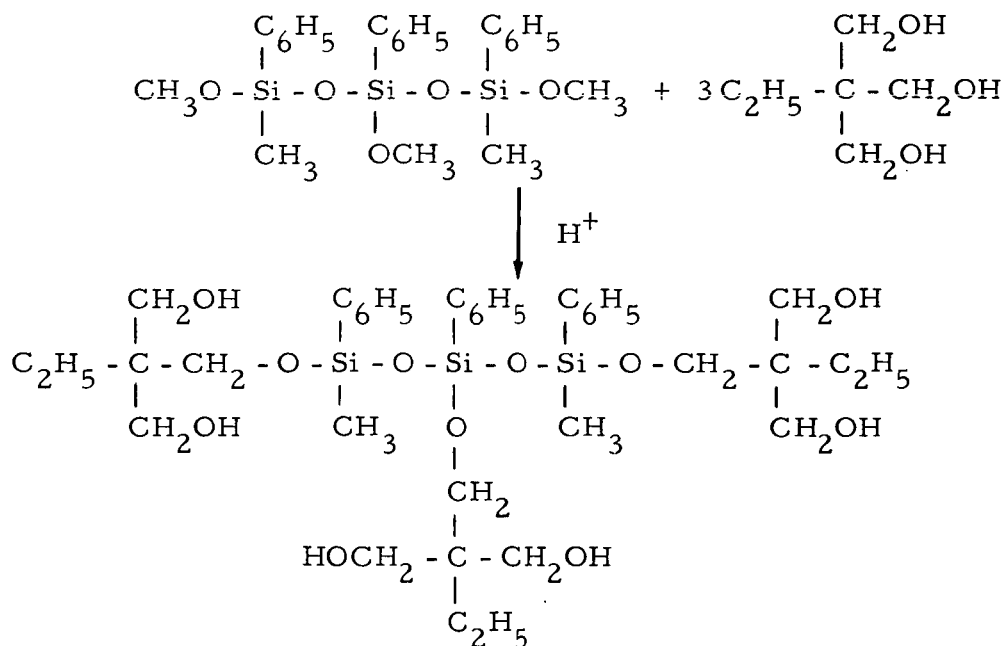
Three types of cyclic products are also possible from this reaction and are illustrated below.

$$
\begin{array}{c}
C_6H_5\!\!\diagdown \quad \underset{O}{\diagdown}\!-\!CH_2\diagdown \quad \diagup C_2H_5 \\
\qquad Si \qquad\qquad C \\
CH_3 \diagup \mid \quad O\!-\!CH_2 \quad \diagdown CH_2 \\
\qquad O \diagdown\mid \qquad\qquad\quad O \\
\qquad\quad Si \diagup \\
\qquad\diagup \quad O\!-\!Si\diagdown C_6H_5 \\
C_6H_5 \qquad\quad CH_3
\end{array}
$$

$$
\begin{array}{c}
CH_2OH \\
\mid \\
C_2H_5 - C - CH_2 - O - \underset{|}{Si} - O - \underset{|}{Si} - O - \underset{|}{Si} - CH_3 \\
\mid \qquad\qquad\quad C_6H_5 \quad C_6H_5 \quad C_6H_5 \\
CH_2OH \qquad\quad CH_3 \quad\; O \qquad\quad O \\
\qquad\qquad\qquad\qquad\qquad\quad CH_2 \quad CH_2 \\
\qquad\qquad\qquad\qquad\qquad\qquad\; C \\
\qquad\qquad\qquad\qquad\quad C_2H_5 \quad CH_2OH
\end{array}
$$

$$
\begin{array}{c}
C_2H_5 \\
\mid \\
HOCH_2 - C - CH_2OH \\
\mid \\
CH_2 \\
\mid \\
O \\
\mid \\
O - Si - O \\
CH_3 \diagup \quad\mid\quad \diagdown \; CH_3 \\
\quad Si \quad C_6H_5 \quad Si \\
C_6H_5 \diagup \; O \qquad O \diagdown C_6H_5 \\
\qquad\mid \qquad\quad \mid \\
\quad CH_2 \qquad CH_2 \\
\qquad\quad C \\
\quad C_2H_5 \quad CH_2OH
\end{array}
$$
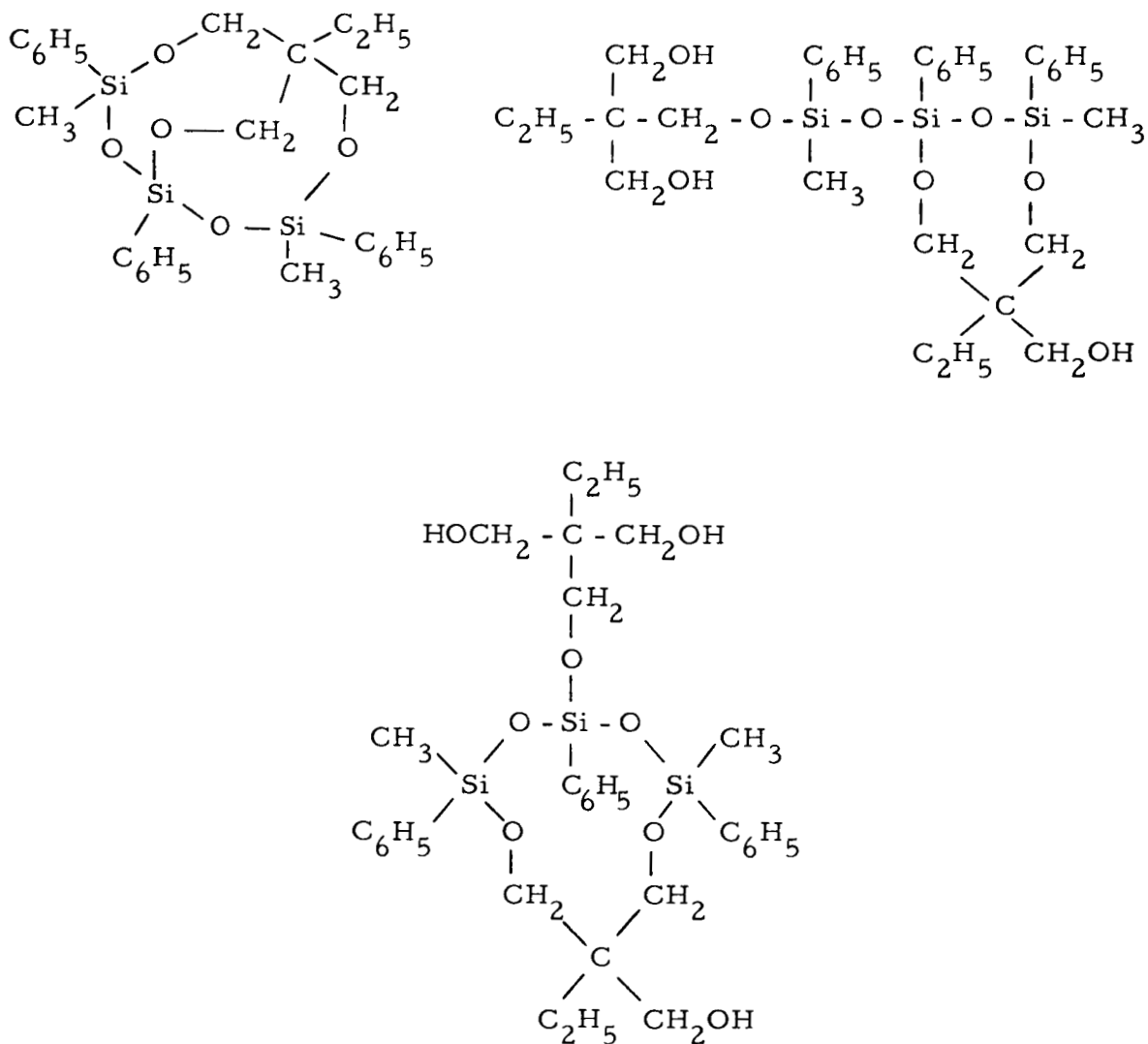
In the first example no functional hydroxymethyl groups are present and the compound is thus useless in preparing polyurethanes. Both of the other cyclic reaction products are trifunctional and consequently are suitable for polymer preparation. It should be noted here that all of these cyclic products are highly probable as indicated by Stuart-Briegleb molecular models. Syntheses of the above polyols thus had
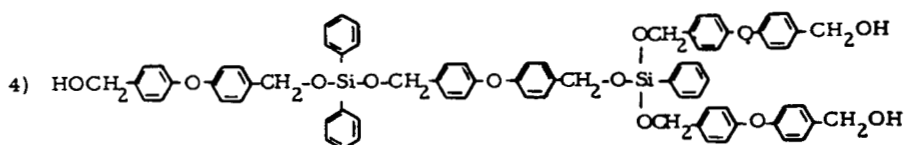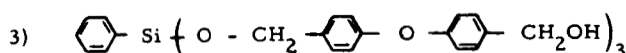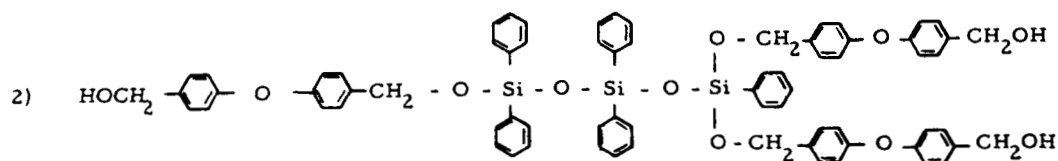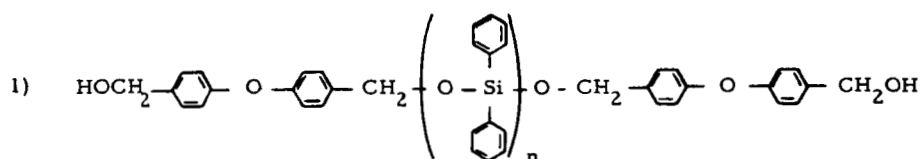
14

to be carried out using an excess of trimethylolpropane in order to limit the formation of the bicyclic intermediate. In one experiment where excess trimethylolpropane was not used, the bicyclic compound appeared to be the only product.

Two experiments were also carried out using 1, 10-decanediol as the basis for a siloxypolyol which would be useful in preparing isocyanate prepolymers. The preparations followed the following reaction sequence:

$$HO\left(CH_2\right)_{10}OH \ + \ C_2H_5O\left(\begin{array}{c}CH_3\\|\\Si-O\\|\\CH_3\end{array}\right)_2 C_2H_5 \longrightarrow HO\left(CH_2\right)_{10}O\left(\begin{array}{c}CH_3\\|\\Si-O\\|\\CH_3\end{array}\right)_2\left(CH_2\right)_{10}OH$$

A

$$A \ + \ \underset{NCO}{\overset{CH_3}{\bigcirc}}NCO \ \xrightarrow{5°C} \ H_3C\underset{NCO}{\bigcirc}NHCO_2\left(CH_2\right)_{10}O\left(\begin{array}{c}CH_3\\|\\Si-O\\|\\CH_3\end{array}\right)_2\left(CH_2\right)_{10}OCONH\underset{NCO}{\bigcirc}CH_3$$
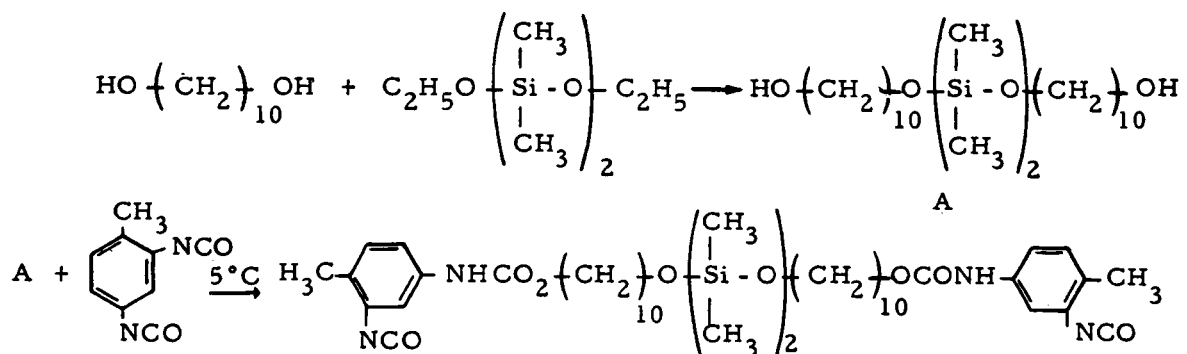
The aliphatic character of the isocyanate prepolymer was sufficiently high to yield siloxyurethanes with good dielectric properties. However, during the prepolymer preparations, it became obvious that resins prepared from these isocyanates would lack the requisite thermal stability.

The last class of siloxypolyols which was investigated and which is still under investigation is that derived from bis(hydroxymethyl)-diphenyl oxide. This diol contains small amounts of tris(hydroxymethyl)-diphenyl oxide and mono(hydroxymethyl)diphenyl oxide, but has an equivalent weight corresponding to the bis(hydroxymethyl) homologue. Structures of polyols obtained from the reaction of this diol with diphenyldiethoxysilane, phenyltriethoxysilane or a combination of both are illustrated below.
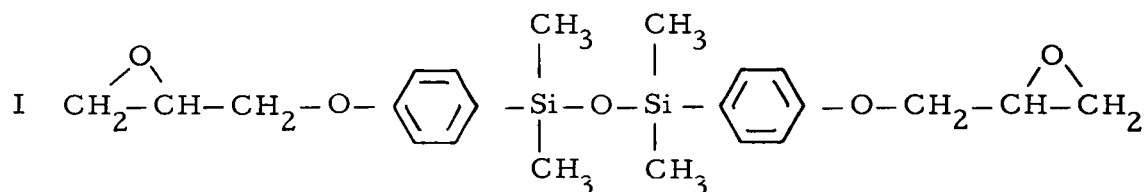
1) $HOCH_2$—⟨⟩—O—⟨⟩—$CH_2$$\left(O-Si\right)_n$$O-CH_2$—⟨⟩—$O$—⟨⟩—$CH_2OH$ (with phenyl groups on Si)

2) $HOCH_2$—⟨⟩—O—⟨⟩—CH_2—O—Si—O—Si—O—Si—⟨⟩ (with phenyl groups on Si); with $O-CH_2$—⟨⟩—O—⟨⟩—CH_2OH substituents

3) ⟨⟩—$Si$$\left(O-CH_2\text{—⟨⟩—}O\text{—⟨⟩—}CH_2OH\right)_3$

4) $HOCH_2$—⟨⟩—O—⟨⟩—CH_2-O-Si-O-CH_2—⟨⟩—O—⟨⟩—CH_2-O-Si—⟨⟩ (with phenyl and OCH_2—⟨⟩—O—⟨⟩—CH_2OH substituents)

The first of these siloxydiols is bifunctional and consequently polymer-
izes into a fusible polymer when reacted with 3, 3'-dimethyldiphenyl-
4,4'-diisocyanate. In contrast, compound 3 is too highly functional and
subsequently reacts with the above mentioned diisocyanate to give a
cured product before thorough mixing is accomplished. Compounds 2
and 4 are intermediate between 1 and 3 in their degree of functionality.
Both 2 and 4 produced brittle resins when reacted with the dimethyldi-
phenyldiisocyanate. However, with Adiprene L-315 isocyanate pre-
polymer, compound 2 produced an elastomer whereas compound 4 pro-
duced a tough rigid polymer. The latter looks most promising although
it did cure too fast to yield excellent dielectric test specimens. Never-
theless preliminary dielectric tests have been extremely promising.
Longer siloxane chain moieties may be required, however, if good
physical properties are to be achieved. Several new bifunctional polyols
are to be made containing tetraphenyldisiloxane moieties or hexaphenyl-
trisiloxane moieties and polyfunctionality will be avoided to prevent
excessive rigidity.

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These latter polyols, as well as the linear diol (1) above have an advantage over the polyfunctional polyols (2, 3, and 4) in that they are more likely to yield isocyanate prepolymers which are not excessively high melting. Linear isocyanate prepolymers derived from these polyols would, however, have to be cured with polyfunctional polyols such as the trimethylolpropane based siloxypolyols previously discussed.
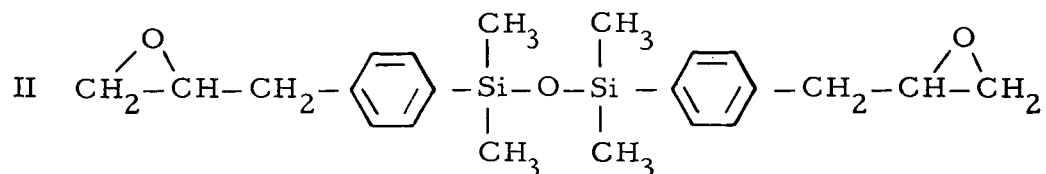
If the polyurethanes derived from diisocyanate monomers and polyfunctional polyols illustrated previously had been sufficiently tough, the polyols would be suitable for reaction with an excess of diisocyanate monomer to produce useful isocyanate prepolymers. These could then be reacted with stochiometric amounts of additional polyol at the time they were to be used in an encapsulation process.

Epoxysilicones

Several intermediates required for the ultimate synthesis of epoxysilicones have been prepared. These intermediates are precursors of 1, 3-bis(epoxypropoxyphenyl)tetramethyldisiloxane and 1, 3-bis(epoxypropylphenyl) tetramethyldisiloxane. The structures of these two compounds are illustrated below.

I $\quad CH_2\!-\!CH\!-\!CH_2\!-\!O\!-$ ⟨◯⟩ $-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}\!-\!O\!-\!\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}\!-$ ⟨◯⟩ $-\!O\!-\!CH_2\!-\!CH\!-\!CH_2$

1, 3-bis(epoxypropoxyphenyl)tetramethyldisiloxane

II $\quad CH_2\!-\!CH\!-\!CH_2\!-$ ⟨◯⟩ $-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}\!-\!O\!-\!\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}\!-$ ⟨◯⟩ $-\!CH_2\!-\!CH\!-\!CH_2$

1, 3-bis(epoxypropylphenyl)tetramethyldisiloxane

The synthetic route which was planned for the synthesis of both compounds I and II is outlined schematically as follows.

In the first of these two procedures no problems were encountered in preparing the p-bromophenyl allyl ether; however, upon distillation about 5-10 percent of the compound rearranged into o-allyl-p-bromophenol and completely inhibited the formation of Grignard reagent when the p-bromophenyl allyl ether was reacted with magnesium. It thus became necessary to remove the rearranged phenol by an alkali extraction from the unrearranged bromophenyl allyl ether. Even after this extraction was completed, however, the purified p-bromophenyl allyl ether failed to react vigorously with magnesium even when ethylmagnesium iodide was added to the reaction mixture to serve as initiator and scavenger. It thus appeared that in the highly polar environment further allylic rearrangement cannot be prevented. This explanation is substantiated by the previously reported observation that phenyl allyl ethers rearrange at a rate which is largely dependent upon the dipole moment of the medium or solvent in which they are dissolved and Grignard reagents are of course highly polar.
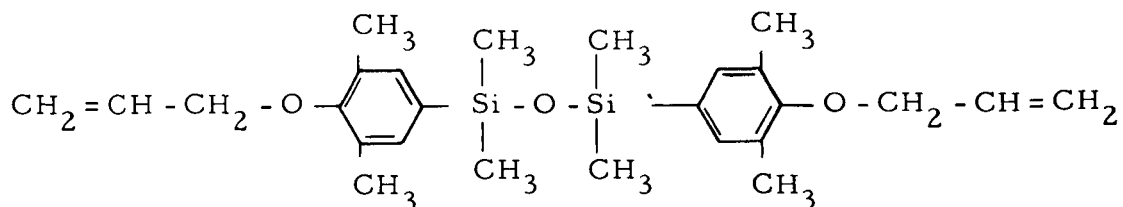
Regardless of the apparent failure of the Grignard reaction a theoretical quantity of 1,3-dichlorotetramethyldisiloxane was added to the Grignard reaction mixture, in the event that the Grignard reaction had proceeded to some extent. After treatment with water and after removal of solvent, the high boiling product was recovered by molecular distillation. An elemental analysis of this product showed that it contained only 1.32 percent Si and thus could not possibly be the desired diallyl compound.

Results of these studies suggest that 2,6-dimethyl-4-bromophenol
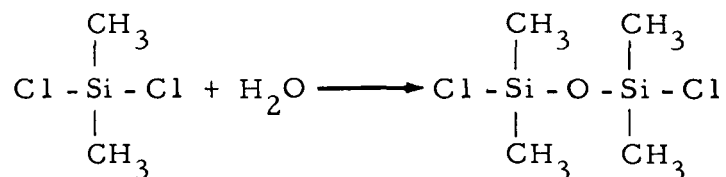

should be used in place of p-bromophenol since the allyl ether of the dimethylbromophenol should not be susceptible to rearrangement.

Subsequent efforts to prepare bis(allyloxyphenyl)tetramethyldisiloxanes
will therefore be shifted to the methylated analogue, namely

$$CH_2=CH-CH_2-O-\underset{CH_3}{\overset{CH_3}{\bigcirc}}-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-\underset{CH_3}{\overset{CH_3}{\bigcirc}}-O-CH_2-CH=CH_2$$

The dimethylbromophenol required for this synthesis has been prepared
by the bromination of 2, 6-dimethylphenol in water. Subsequent steps in
the total synthesis, however, have not been carried out.

1, 3-Dichlorotetramethyldisiloxane used in the bis(allyloxyphenyl)-
tetramethyldisiloxane synthesis was obtained from the partial hydrolysis
of dimethyldichlorosilane

$$Cl-\underset{CH_3}{\overset{CH_3}{Si}}-Cl + H_2O \longrightarrow Cl-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-Cl$$

The first five steps leading to the ultimate synthesis of 1, 3-
bis(epoxypropylphenyl)tetramethyldisiloxane (compound II) have been
carried out and have produced the compound 1, 3-bis(allylphenyl) tetra-
methyldisiloxane. The initial Grignard reaction proceeded smoothly in
ether as did the condensation of this Grignard with allyl chloride to yield
p-bromoallylbenzene. The second Grignard reaction was very slow
when carried out in ether and gave only a fair yield of the allylphenyl-
magnesium bromide. When tetrahydrofuran was used as the solvent
rather than ethyl ether the reaction proceeded vigorously and much more
efficiently. A comparison between the reaction rates of the meta isomer
and the para isomer with magnesium in ether showed that the meta-
bromoallylbenzene reacted only slightly faster and gave a slightly
improved yield of product. Reactivities of the two isomers were not
compared in tetrahydrofuran.

After condensation of the allylphenylmagnesium bromide with
ethoxydimethylchlorosilane the ethoxydimethylsilylphenylpropene was
separated from the unreacted silane by distillation. After hydrolysis,

the bis(allylphenyl)tetramethyldisiloxane was isolated by distillation
under high vacuum. Elemental analyses obtained on products of the
various experiments is presented in Table 1 below

Sample	Isomer	Solvent	Overall Yield	B.P.,°C	Pressure	Analysis, percent			n_D^{26}
						C	H	Si	
C 1961-41-3	Para	Ether	11 percent	145-160	≃2 mm	65.69	8.07	13.91	1.5043
-4						62.33	8.07	19.07	1.4979
C 1961-42-R2	Meta	Ether	15 percent	130-135	~1 mm	58.79	8.06	18.20	1.4894
-R3								19.48	1.4918
C 1961-48	Meta	Tetrahydro-furan	37 percent	120-140	2 mm <1 mm	71.14	8.14	15.22	1.5196
Calculated for $C_{22}H_{30}Si_2O$						72.20	8.26	15.35	

Table 1. Analytical data from the preparation of
bis(allylphenyl)tetramethyldisiloxane.

From the above data is is readily apparent that a high purity product
can be obtained in satisfactory yield if the reactions are carried out in
tetrahydrofuran. An infrared spectrum of this compound (C1961-48)
is presented in figure 2.

Having resolved the problem of synthesizing bis(allylphenyl)tetra-
methyldisiloxane, the final problem was to epoxidize the allyl groups.
Experiments were carried out using perbenzoic acid as the epoxidizing
agent. The reaction was carried out in a mixture of chloroform and
tert-butyl alcohol and its course was followed by periodic analysis of
aliquots of the reaction mixture. Treatment with potassium iodide
followed by titration of the liberated iodine with standard sodium thio-
sulfate yielded data on the amount of residual peracid. Reactions were
terminated after 95 percent of the perbenzoic acid was consumed. A
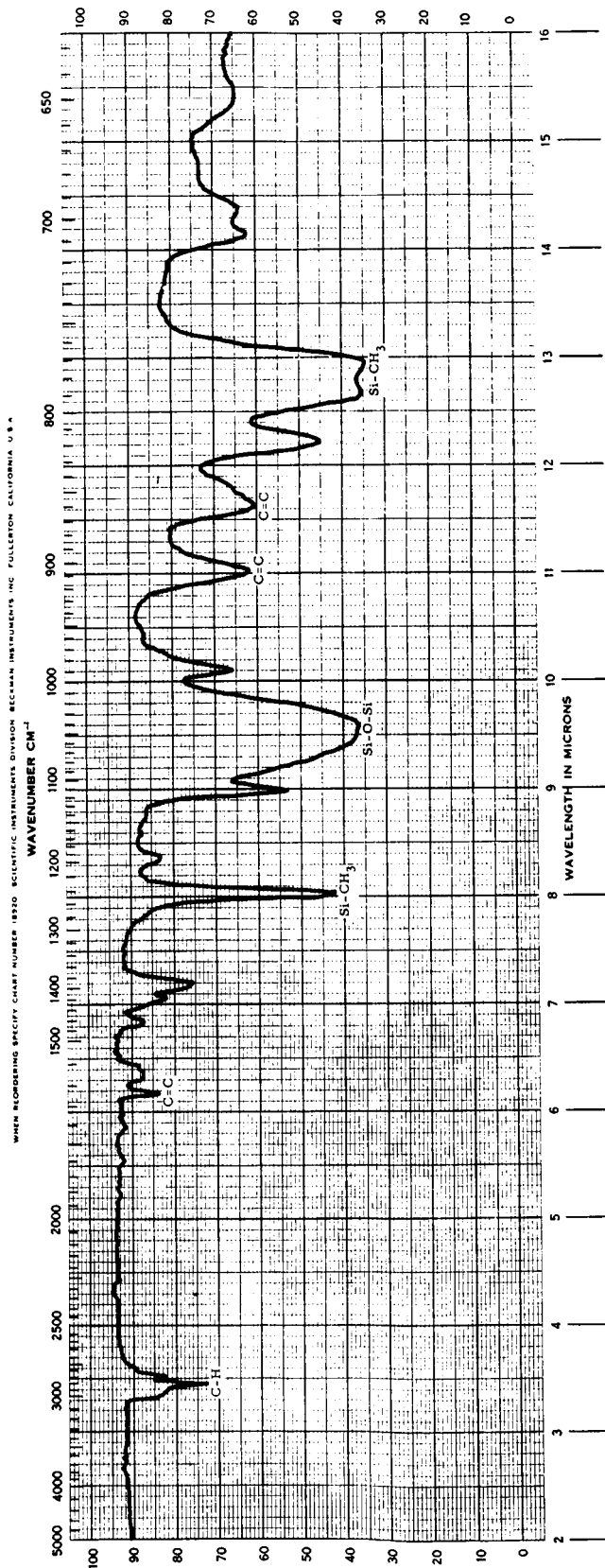typical rate curve is shown in figure 3.

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Figure 2. Infrared spectrum of bis(m-allylphenyl)tetramethyldisiloxane (C1961-42B).
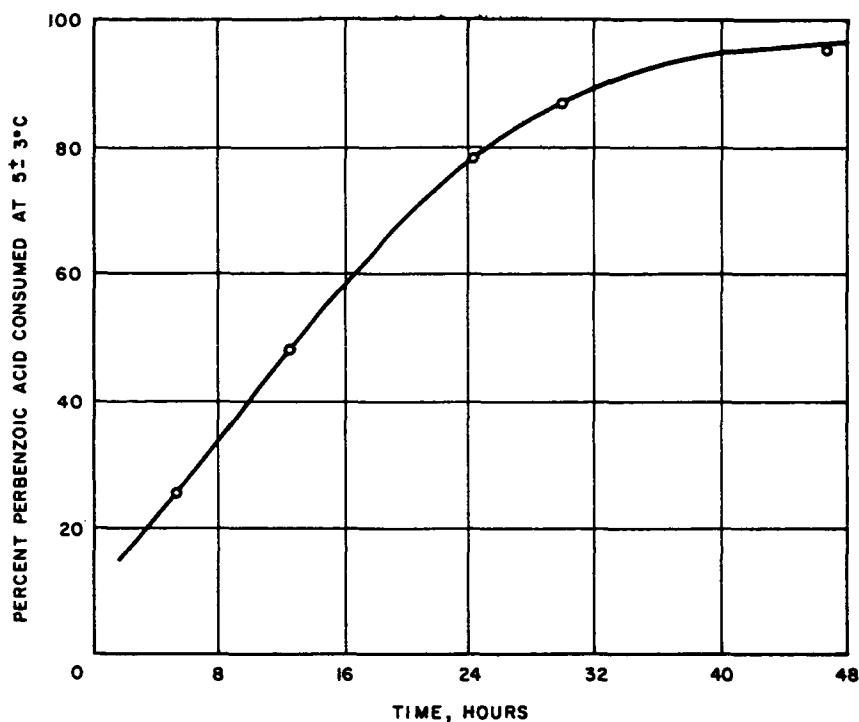
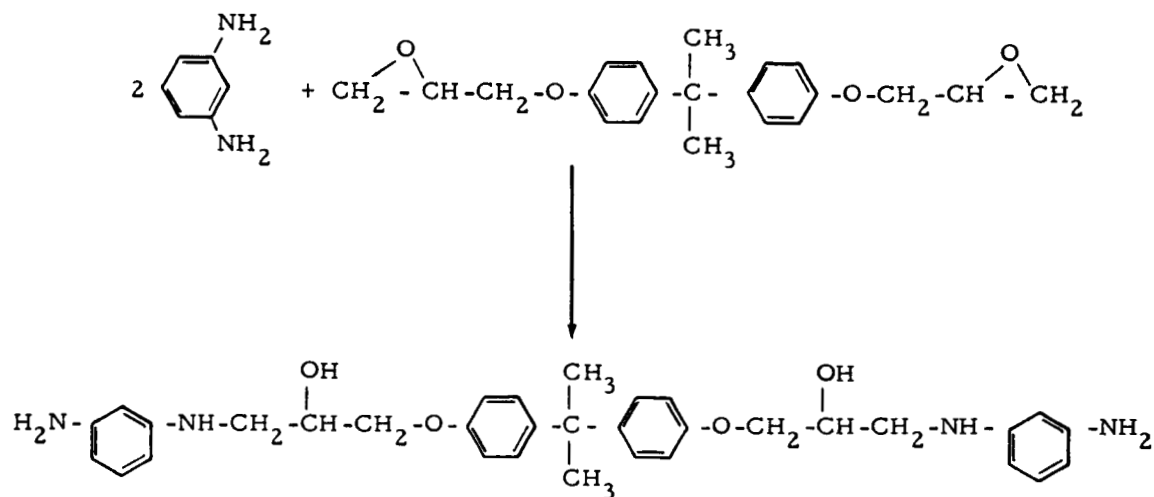Figure 3. Rate of epoxidation of bis(allylphenyl)-
tetramethyldisiloxane.

Elemental analyses of the two high boiling fractions from the
epoxidation reaction gave the following results:

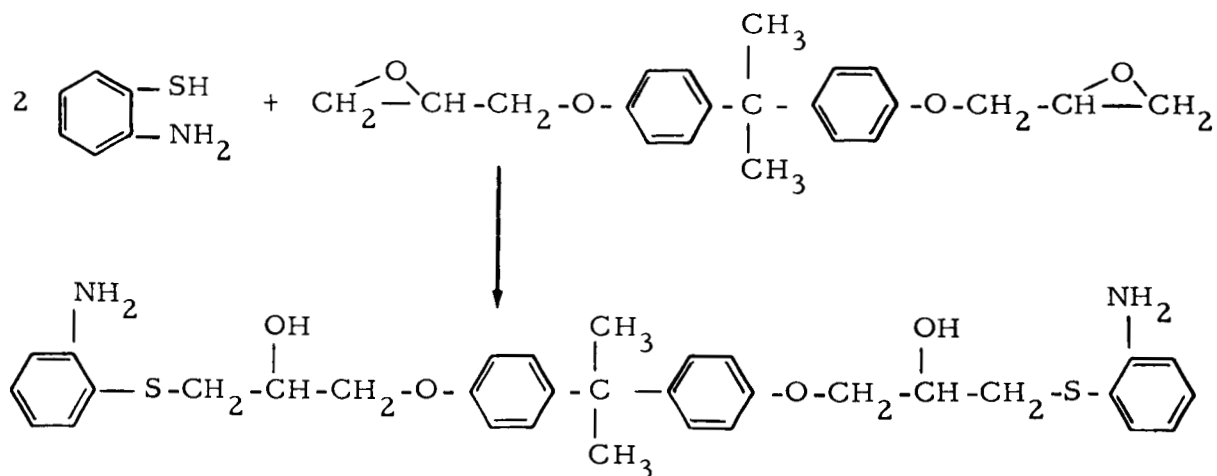|	Percent		
	C	H	Si
C 1961-49-2B	73.82	7.35	2.60
C 1961-49-2C	73.79	7.28	0.10
Calculated for $C_{22}H_{30}Si_2O_3$	66.33	7.60	14.1

From these analyses it became quite apparent that the epoxidation did
not proceed as desired. Furthermore, the virtual absence of silicon
in the high boiling product indicates that oxidative cleavage occurred
between the phenyl groups and silicon atoms of the allyl compound.
The homologous bis(allylphenyl)tetraphenyldisiloxane may be more
resistant to cleavage under the epoxidation conditions and thus warrants
examination.

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Epoxy Resins

p, p'-Bis(epoxypropoxy)-2, 2-diphenylpropane has been reacted with an excess of m-phenylenediamine to yield an adduct suitable for use as an epoxy curing agent. The reaction is illustrated below:

$$2 \; (m\text{-phenylenediamine, } NH_2, NH_2) + CH_2\text{-}CH\text{-}CH_2\text{-}O\text{-}(C_6H_4)\text{-}C(CH_3)_2\text{-}(C_6H_4)\text{-}O\text{-}CH_2\text{-}CH\text{-}CH_2 \text{ (diepoxide)}$$

$$\downarrow$$

$$H_2N\text{-}(C_6H_4)\text{-}NH\text{-}CH_2\text{-}CH(OH)\text{-}CH_2\text{-}O\text{-}(C_6H_4)\text{-}C(CH_3)_2\text{-}(C_6H_4)\text{-}O\text{-}CH_2\text{-}CH(OH)\text{-}CH_2\text{-}NH\text{-}(C_6H_4)\text{-}NH_2$$

Also prepared for use as an epoxy curing agent was the adduct of p, p'-bis(epoxypropoxy)-2, 2-diphenylpropane with o-aminobenzenethiol. This reaction is illustrated as follows:

$$2 \; (C_6H_4)(SH)(NH_2) + CH_2\text{-}CH\text{-}CH_2\text{-}O\text{-}(C_6H_4)\text{-}C(CH_3)_2\text{-}(C_6H_4)\text{-}O\text{-}CH_2\text{-}CH\text{-}CH_2 \text{ (diepoxide)}$$

$$\downarrow$$

$$(C_6H_4)(NH_2)\text{-}S\text{-}CH_2\text{-}CH(OH)\text{-}CH_2\text{-}O\text{-}(C_6H_4)\text{-}C(CH_3)_2\text{-}(C_6H_4)\text{-}O\text{-}CH_2\text{-}CH(OH)\text{-}CH_2\text{-}S\text{-}(C_6H_4)(NH_2)$$

In both of these reactions a large excess of the amine was used in order to prevent polymerization. Upon completion of the reactions excess monomers were removed by steam distillation and the water was
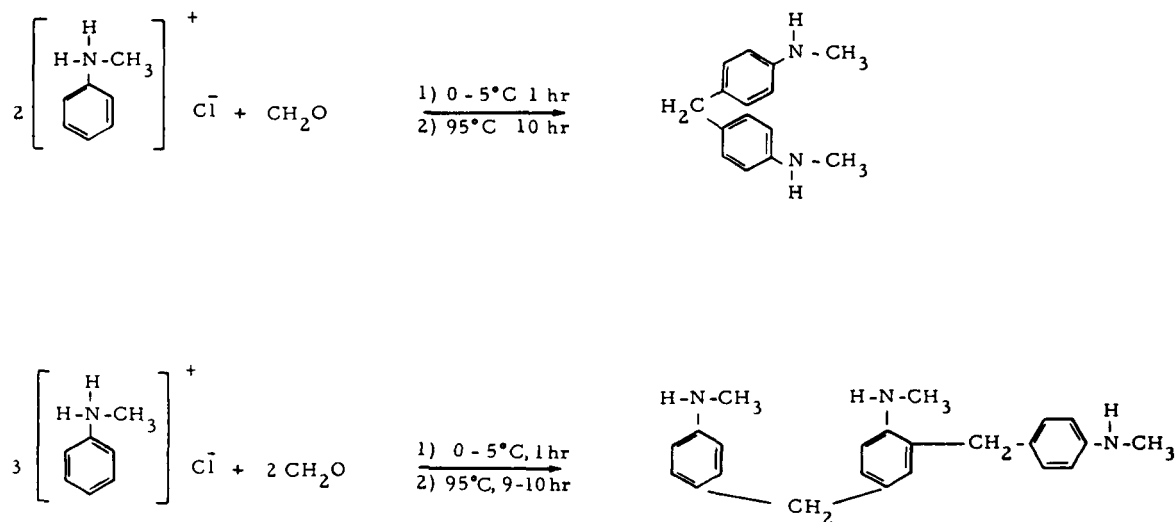
removed by heat and vacuum. It should be noted that with the o-aminobenzenethiol two modes of addition are actually possible; however, since the aminobenzenethiol can exist as a zwitterion, it is quite probable that much of the addition occurs as illustrated. To some extent, however, both modes of addition probably occur simultaneously.

The purpose of carrying out these two reactions was to obtain amine substituted prepolymers useful in formulating epoxy resins, and, through the use of molecular distillation or its equivalent, both of these amine adducts as well as the epoxy prepolymers can be freed of their volatile constituents. Cured epoxy resins obtained from these adducts would thus have little tendency to outgas in high vacuum space environments. Although somewhat incidental to the intended application, it has been noted that epoxy prepolymers cured with these adducts appear to have far greater impact strength than the chemically equivalent epoxy resins made by standard procedures. Hartshorn electrical test specimens have been prepared from mixtures of the amine adducts with additional p, p'-bis(epoxypropoxy)-2, 2-diphenylpropane. The stoichiometry of the formulations was of necessity based upon the theoretical equivalent weight of the adducts since actual equivalent weights had not been successfully obtained. Aqueous titrations have been completely unsatisfactory, whereas titrations in acetic acid have yielded equivalent weights based upon total amino groups rather than upon the total number of functional N-H groups. Dielectric properties of the epoxy resins obtained from these amine adducts were definitely superior to analogous resins made by conventional techniques.

Samples of p, p'-bis(epoxypropoxy)-2, 2-diphenylpropane were also cured with "unconventional" amines such as N, N'-diphenylethylene-diamine and bis(methylamino)diphenylsilane. In both cases 4, 4'-diaminodiphenylmethane was used simultaneously as a crosslinking agent. Results of dielectric tests on the cured resins indicated these amines to be superior to other aromatic amines such as meta-phenylene-diamine or 4, 4'-methylenedianiline alone. Since one of the characteristics which bis(methylamino)diphenylsilane and N, N'-diphenylethylene-diamine have in common is their secondary methylamino groups, it is

highly probable that the improved dielectric properties which they impart to cured epoxies can be attributed to this factor. It must of course be recognized that even primary amines are converted in part to secondary amines when they add across epoxy rings and consequently the observed improvement in dielectric properties can be attributed to physical characteristics rather than to chemical structural characteristics. However, polymerizations of epoxy compounds with primary amines produce both secondary and tertiary amino groups, but the extreme bulkiness of the secondary amino groups formed initially would tend to inhibit total conversion to tertiary groups and consequently many residual N-H groups would remain in the cured resin even when equivalent amounts of amines and epoxy compounds are reacted together.

Secondary aromatic methyl amines analogous to N-methylaniline were thus selected for further study. This selection was limited to the N-methylanilines because these compounds could be expected to yield more heat resistant epoxy polymers than do the completely aliphatic secondary amines. N-Methyl groups in these amines would be sufficiently small to minimize steric interference during the polymerization. Amines which were synthesized for this purpose include 4,4'-bis(methylamino)-diphenylmethane and a higher molecular weight analogue of this compound. Both amines were prepared by the procedures illustrated below.

$$2 \left[\underset{\text{C}_6\text{H}_5}{\text{H-N}^+(\text{H})\text{-CH}_3} \right] \text{Cl}^- + \text{CH}_2\text{O} \quad \xrightarrow[\text{2) 95°C 10 hr}]{\text{1) 0-5°C 1 hr}} \quad \text{H}_2\text{C}(C_6H_4\text{-NH-CH}_3)_2$$

$$3 \left[\underset{\text{C}_6\text{H}_5}{\text{H-N}^+(\text{H})\text{-CH}_3} \right] \text{Cl}^- + 2 \text{CH}_2\text{O} \quad \xrightarrow[\text{2) 95°C, 9-10 hr}]{\text{1) 0-5°C, 1 hr}} \quad (\text{CH}_3\text{-NH-C}_6\text{H}_3)_2\text{CH}_2\text{-CH}_2\text{-C}_6\text{H}_4\text{-NH-CH}_3$$
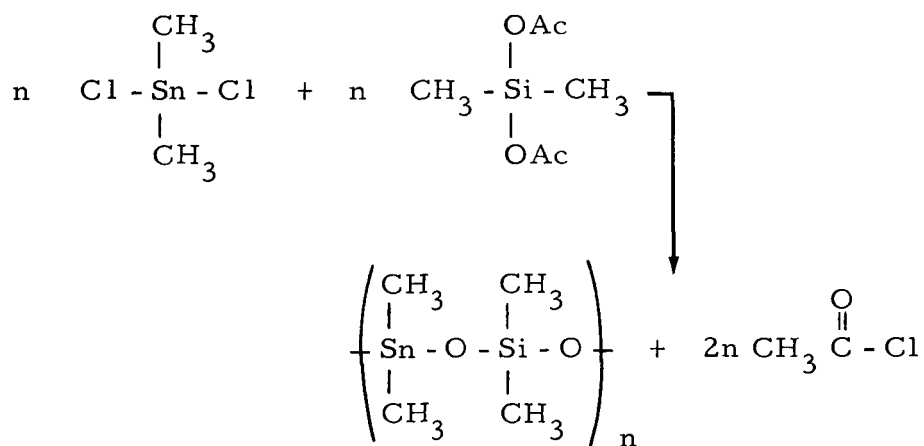
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The first of these two products was crystalline; however, a suitable recrystallization solvent could not be found. Furthermore, attempts to distill the product at 180°C and 0.01 torr have failed. This low volatility may indicate that the compound is in fact a higher telomer rather than a dimer. No attempt has been made to crystallize or distill the higher molecular weight analogue prepared by the second procedure. It will therefore be used in the form in which it was recovered. Its equivalent weight was determined by titrating the amine in glacial acetic acid using perchloric acid. A discussion of the procedure is presented in the analytical section of this report. An infrared spectrum of the higher telomer is presented in figure 4. This spectrum verifies the proposed structure of the amine and demonstrates the ortho-para substitution.

Stannosiloxane Resins

The stannosiloxane resins are a class of resins, characterized by tin-oxygen-silicon bonds in their polymer chains, which have many of the properties of the silicones. The stannosiloxanes were considered to have interesting possibilities as dielectric potting and encapsulation resins, and thus samples of these materials were synthesized for evaluation.

Stannosiloxane polymers have been prepared by two techniques, namely condensation reactions and cohydrolysis. A typical condensation reaction is illustrated below.

$$
n \quad \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Cl-Sn-Cl}} \quad + \quad n \quad \underset{\underset{OAc}{|}}{\overset{\overset{OAc}{|}}{CH_3-Si-CH_3}} \longrightarrow
$$

$$
\left(\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Sn}} - O - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}} - O \right)_n \quad + \quad 2n \ CH_3 \overset{\overset{O}{\|}}{C} - Cl
$$

The condensation proceeds as acetyl chloride is removed by distillation.
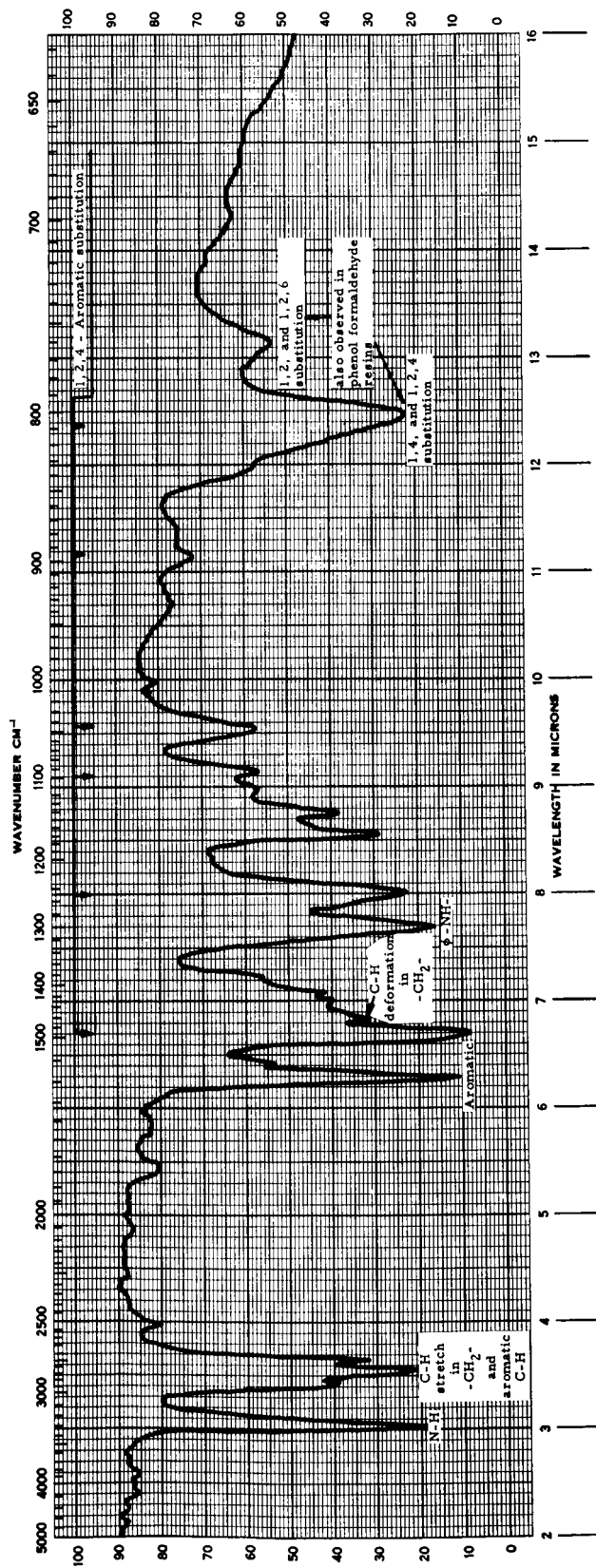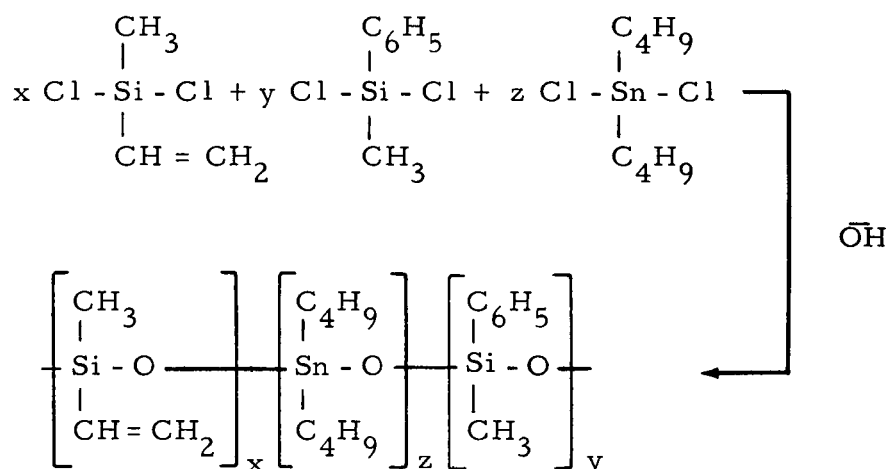
Figure 4. Infrared spectrum on n-methylaniline formaldehyde (C2425-15B).

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Generally, these alternate copolymers are hard materials with little elasticity. It has been found, however, that increasing the silicon-tin ratio decreases the viscosity of the uncured polymer and increases the elasticity of the cured material. The elasticity is also increased by introducing the tin in a random manner into the polymer chain. To accomplish this randomization an interfacial cohydrolysis process has been found to be most satisfactory. In applying this technique the monomers are dissolved in an organic solvent such as toluene or methylene chloride and are hydrolyzed in a high shear blender using an aqueous alkaline phase. The reaction can be illustrated as follows:

$$
x \; Cl-\underset{\underset{CH=CH_2}{|}}{\overset{\overset{CH_3}{|}}{Si}}-Cl \; + \; y \; Cl-\underset{\underset{CH_3}{|}}{\overset{\overset{C_6H_5}{|}}{Si}}-Cl \; + \; z \; Cl-\underset{\underset{C_4H_9}{|}}{\overset{\overset{C_4H_9}{|}}{Sn}}-Cl \quad \xrightarrow{\;\overline{O}H\;}
$$

$$
\left[\underset{\underset{CH=CH_2}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O\right]_x \left[\underset{\underset{C_4H_9}{|}}{\overset{\overset{C_4H_9}{|}}{Sn}}-O\right]_z \left[\underset{\underset{CH_3}{|}}{\overset{\overset{C_6H_5}{|}}{Si}}-O\right]_y
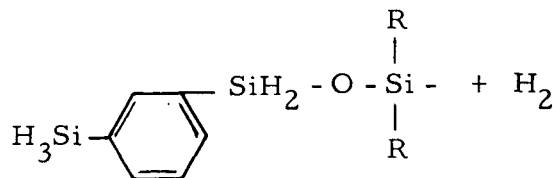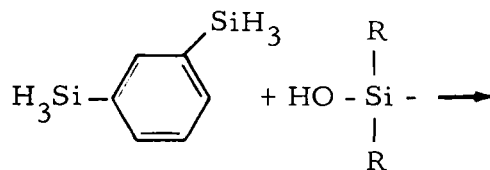$$

Polymer chains are hydroxyl terminated as has been determined by chemical and infrared evidence. This procedure also allows the introduction into the polymer of vinyl groups which serve as curing sites for peroxide or silane induced cures.

Although several stannosiloxane polymers were prepared for this study, efforts to obtain high quality cured dielectric test specimens were unsuccessful. Lower viscosity prepolymers will be required to produce usable dielectric specimens and therefore new polymer samples will have to be synthesized. Further work on these materials has been deferred until time permits its resumption.

One of the problems encountered in curing these resins with silanes is attributed to the presence of hydroxyl end groups on the polymer chains.

Hydrogen is liberated during cure and subsequently bubble-free resin specimens are not obtained. This undesirable reaction is illustrated below.

$$
H_3Si\text{-}\langle\bigcirc\rangle\!\!-SiH_3 \quad + HO\text{-}\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{Si}}\text{-} \quad \longrightarrow
$$

$$
H_3Si\text{-}\langle\bigcirc\rangle\!\!-SiH_2\text{-}O\text{-}\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{Si}}\text{-} \quad + \quad H_2
$$

The preferred cure reaction involves the addition of Si-H groups across the vinyl groups present in the polymer molecule.

Another problem that has been encountered is that at elevated temperatures bis-silylbenzene appears to reduce part of the tin present in the polymer. This has resulted in blackening of the cured resin. Peroxide cures thus far have either been ineffective in curing the stannosiloxanes or have been too rapid.

EXPERIMENTAL

Reaction of Trimethylolpropane with Triphenyltrimethoxydimethyltri-siloxane (C2425-1A)

Trimethylolpropane (30 g, 0.224 mole) was dried azeotropically with benzene (100 ml), and a solution of triphenyltrimethoxydimethyltrisiloxane (Dow Corning Sylkyd 50, 52.6 g, 0.112 mole) in benzene (50 ml) was then added along with four drops of glacial acetic acid. The slurry was heated at reflux while slowly removing the benzene-methanol azeotrope. After 8 hours the pot temperature had reached 135°C. Additional acetic acid (12 drops) was then added and heating continued

for 3 hours. After cooling, the reaction mixture was diluted with ether and washed with water. After removal of the ether by heat and vacuum an unsuccessful attempt was made to distill the product at 170°C at less than 5 mm Hg pressure. The inhomogeneity of the reaction mixture indicated that the hydroxyl-free bicyclic compound or a cyclosiloxane was a major product.

Reaction of Excess Trimethylolpropane with Triphenyltrimethoxy-dimethyltrisiloxane (C2424-1B)

A mixture of trimethylolpropane (90 g, 0.672 mole), triphenyl-trimethoxydimethyltrisiloxane (Sylkyd 50, 52.6 g, 0.112 mole) and glacial acetic acid (10 drops) was heated while stirring continuously. During the first 2 hours the temperature rose to 127°C and the reaction mixture became homogeneous. After 3-1/4 and 5-1/4 hours extra acid (4 and 6 drops, respectively) was added, and after a total of 24 hours the temperature reached 140°C and 8 g of methanol had been collected. The remaining methanol (8 g) and other volatiles were removed under vacuum (5 torr) while heating at 140°C. Upon cooling a clear viscous solution was obtained.

Curing of a Siloxypolyol with Adiprene L-167 (C2425-2B)

A mixture of a polyisocyanate (Adiprene L-167, 65 g, 0.1 eq.), siloxypolyol (C2425-1B, 6.3 g, 0.08 eq. based on theoretical equivalent weight), and triethanolamine (1.0 g, 0.02 eq.) was thoroughly blended, then degassed in vacuum without heat. It was then precured at 60°C for 3 days and post-cured at 130°C for 5 hours. The clear yellow product had the appearance of hard rubber.

Reaction of a Dimethoxypolydimethylsiloxane with Trimethylolpropane (C2425-2C)

A mixture of diethoxypolydimethylsiloxanes (C1090-53A) was prepared by the gradual addition of water (183.3 g, 10.2 mole) to a solution of dimethyldiethoxysilane (2013 g, 2263 ml., 13.6 mole) and sodium hydroxide (5.5 g). The addition was made at 40°C and upon completion the reaction mixture was heated at reflux for 30 minutes. Ethanol (100 g) was then removed by simple distillation.

A portion of the siloxane mixture (50 g), trimethylolpropane
(32 g, 0.72 eq.) and glacial acetic acid (20 drops) were heated at 125-
130°C for 8-3/4 hours without evolving ethanol. Concentrated phos-
phoric acid (2 drops, 85 percent) was then added and ethanol evolution
commenced immediately. After 25 hours 6.3 ml (0.2 eq.) of the alcohol
had been recovered. No further evolution occurred when heating was
continued at 160°C for an additional 24 hours. When the hot mixture
was placed under vacuum a small but indefinite quantity of volatiles was
evolved. After setting in a separatory funnel for several days two layers
separated. The lower layer contained primarily unreacted trimethylol-
propane and was found to weigh 35 g. Excess phosphoric acid was re-
moved from the siloxane layer (47 g) by treatment with magnesium oxide.

Reaction of Diethoxypolydimethylsiloxane with Trimethylolpropane (C1587-78 to 80)

Four different fractions of diethoxypolydimethylsiloxane were
separated from a mixture of polymerized dimethyldiethoxysilanes
(C1090-53A). The separate fractions were then reacted with trimethylol-
propane as discussed below.

Fraction 1 (10.2 g, b.p.$_{128\,torr}$ = 65-79°C), trimethylolpropane
(10.2 g), and phosphoric acid (85 percent, 1 drop) were heated at
$130 \pm 10°C$ for 6 hours during which time 1.24 g of ethanol distilled off.
To the homogeneous solution was then added magnesium oxide (0.2 g)
to neutralize the residual phosphoric acid.

Fraction 2 (18.2 g, b.p.$_{128\,torr}$ = 80-105°C), trimethylolpropane
(18.2 g) and phosphoric acid (85 percent, 1 drop) were vigorously stirred
and heated at $130 \pm 10°C$ for 6 hours. During this period 6.8 g of ethanol
was evolved, indicating a relatively efficient reaction. This reaction
mixture also became homogeneous. After cooling it was neutralized
with magnesium oxide (0.10 g), then filtered through a fritted glass
filter.

Fraction 3 (14.1g, b.p.$_{70\,torr}$ = 90-110°C), trimethylolpropane
(14.1 g) and phosphoric acid (85 percent, 1 drop) were heated at
$130 \pm 10°C$ for 6 hours. During this period only 1.2 g of ethanol was
evolved and the reaction mixture failed to become completely
homogeneous.

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Fraction 4 (14.4 g, b.p.$_{25 \text{ torr}}$ = 100-120°C), trimethylolpropane (14.4 g) and phosphoric acid (85 percent, 1 drop) were heated at 135°C for 3 hours without any apparent reaction. After reaching 150°C the evolution of ethanol commenced; however, due to overheating, the reaction product was not recovered.

Attempted Preparation of Bis(2,2-Dimethyl-3-Hydroxypropoxy) Dimethylsilane (C1587-81)

A mixture of dimethyldiethoxysilane (74 g, 0.5 mole), 2,2-dimethyl-1,3-propanediol (312 g, 3.0 mole) and Dowex 50 (acidic cationic exchange resin, 2 g) was heated at 120-125°C until 27 g of ethanol had been recovered. After 24 hours phosphoric acid (85 percent, 4 drops) was added and the temperature was allowed to rise to 150°C. The reaction was then allowed to proceed until a total of 31 g of ethanol (0.67 mole) had been collected. After cooling, the solidified mixture was mixed with crushed ice, water, and sodium bicarbonate (0.5 g). Two phases were then observed. A series of extractions with ether, 50 percent ether in hexane, and finally benzene was used to separate the siloxanes from the excess neopentyl glycol. A great deal of difficulty was encountered in separating the emulsified phases. Ether furthermore turned out to be somewhat undesirable as an extraction solvent because of its very high solubility in the aqueous phase. Thus benzene appeared to be the extraction solvent of choice. Five days were required for the final separation. After combining the various organic phases, they were again washed with water (300 ml) and dried with sodium sulfate. Excess solvents were then removed, first by heat, then by heat and vacuum. The clear product weighed approximately 40 g and would represent a 33 percent yield; however, its high equivalent weight (375) and its incompatibility with various isocyanates indicated that it was not the desired diol.

Preparation of Phenylenediamine Based Prepolymer for Curing Epoxy Prepolymers (C1587-63; 64)

To a refluxing solution of m-phenylenediamine (600 g, 5.56 mole) in dioxane (600 ml) was slowly added a solution of p,p'-bis(epoxypropoxy)-2,2-diphenylpropane (Epon X-24, 400 g, 1.18 mole) in dioxane (200 ml).

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After the addition was complete refluxing was allowed to continue for 8 hours. The reaction was carried out under an atmosphere of nitrogen. Upon completion of the reaction the dioxane was distilled off at ambient pressure. After most of the dioxane had been removed, the excess phenylenediamine was removed by steam distillation, still maintaining the nitrogen atmosphere. The viscous residue was then dried at 100°C under a pressure of 1 torr. It weighed 550 g, and melted to a viscous syrup at about 70°C.

Preparation of an Aminobenzenethiol Based Prepolymer for Curing Epoxy Prepolymers (C1587-65)

A solution of 2-aminobenzenethiol (800 g, 4.8 mole) in dioxane (600 g) was heated to reflux (105° C) under an atmosphere of dry nitrogen. A solution of p,p'-bis(epoxypropoxy)-2,2-diphenylpropane (Epon X-24, 600 g, 1.77 moles) and dioxane (200 ml) was then added at the rate of 1 drop per second. Upon completion of the addition refluxing was continued for 8 hours. Excess aminobenzenethiol was then removed by steam distillation and the product was dried with heat (125° C) and vacuum (0.1 torr). The dark amber product weighed 880 g.

Reaction of Trimethylolpropane with 1,5-Dimethyl-1,3,5-Triphenyl-1,3,5-Trimethoxytrisiloxane (C1961-24)

Trimethylolpropane (60.0 gm, 0.45 mole) and 1,5-dimethyl-1,3,5-triphenyl-1,3,5-trimethoxytrisiloxane (Sylkyd 50, 52.6 gm, 0.11 mole), were mixed together and slowly heated to 110° C. Ten drops of glacial acetic acid (approximately 0.2 gm, 0.003 mole) were added to the hot mixture while stirring continuously. The reaction flask was fitted with a distillation head and condenser so that the methanol, evolved as a side product of the reaction, could be collected by distillation (the methanol began to distill shortly after the addition of the acetic acid). After four hours of reaction, the evolution of methanol ceased. Additional glacial acetic acid (6 drops) was added to the mixture and the reaction temperature brought to 138° C, after which more methanol distilled over. After one more hour of reaction, distillation of methanol ceased again. The reaction system was then placed under vacuum and heated a total of two more hours at 140° C. More methanol was collected in a cold trap. The total amount of methanol collected during the reaction was 9.16 gm (0.29

.mole). The product, originally a clear viscous liquid, turned cloudy after standing several days. The siloxypolyol weighed 98. 8 gm.

Acid-Catalyzed Equilibration of Octamethylcyclotetrasiloxane with Trimethylolpropane (C2425-4)

Three equilibration experiments were carried out simultaneously in an effort to produce a homogeneous siloxypolyol. Ratios of reagents used in these runs were:

	I	II	III
Trimethylolpropane	9. 0 g (0.067 mole)	13. 5 g (0. 10 mole)	18. 0 g (0. 13 mole)
Octamethylcyclotetrasiloxane	14. 8 g (0. 050 mole)	14. 8 g (0. 05 mole)	14. 8 g (0. 05 mole)
Methanol	3. 2 g (0. 10 mole)	4. 8 g (0. 15 mole)	6. 4 g (0. 20 mole)
Phosphoric acid	2 drops	2 drops	2 drops

Reaction mixtures were vigorously stirred for at least 18 hours at $83 \pm 2°C$. Methanol was gradually removed by distillation, allowing the temperatures to rise gradually to 140 to 145°C over a six-day period. None of the reactions produced homogeneous solutions.

Reaction of Dimethyldiethoxysilane with Trimethylolpropane (C2425-5B)

Dimethyldiethoxysilane (b. p. 110 to 112°C, 148 g, 1. 0 mole) was added in portions to molten dry trimethylolpropane (268 g, 2. 0 mole) containing acetic acid (l g). The reaction temperature gradually rose to about 160°C. After removal of the residual volatiles at 120°C in vacuum the equivalent weight was found to be 71. Additional acetic acid (1 cc) was then added to the polyol and the mixture was reheated to 140°C for three hours. Again the volatiles (4. 3 g) were removed with heat ($110 \pm 10°C/4$ hours, then $85 \pm 5°C/16$ hours) and vacuum. The final product weighed 312 g and had an analyzed hydroxyl equivalent of 66.

Reaction of Dimethyldiethoxysilane with Trimethylolpropane (C2425-7A)

Dimethyldiethoxysilane (134 g, 0. 9 mole) was added gradually to molten trimethylolpropane (121 g, 0. 90 mole) containing acetic acid (1 g). The temperature was allowed to rise gradually to 146°C while the ethanol (82 g) was continuously removed by distillation. Residual volatiles (4 g) were then removed by heating the mixture under vacuum ($105 \pm 5°C$,

6 torr) using a rotary evaporator. The final product (152 g, 89 percent yield) was a clear homogeneous fluid and had an analyzed hydroxyl equivalent of 121.

Reaction of Trimethylolpropane with "Diethoxytetramethyldisiloxane" (C2425-7B)

Freshly distilled dimethyldiethoxysilane (103 g, 0.70 mole), water (6.0 g, 0.33 mole), and acetic acid (0.2 to 0.3 g) were mixed and ethanol (27 g) was removed by distillation. The mixture was then added to molten trimethylolpropane (74 g, 0.5 mole) and was then heated gradually to 150°C (3 hours) while additional ethanol was distilled off (33 g, 60 g total, 99 percent total). After heating under vacuum (2 torr) at 90 ±10°C for 4 to 5 hours, a small amount of volatiles (7.2 g) and the product (106 g) were recovered. The product had an analyzed hydroxyl equivalent of 102.

Reaction of Trimethylolpropane with "Diethoxyhexamethyltrisiloxane" (C2425-8A)

Freshly distilled dimethyldiethoxysilane (89 g, 0.60 mole, b.p. 110 to 112°C), water (7.2 g, 0.40 mole), and acetic acid (5 drops) were mixed and shaken together until the hydrolysis was complete (5 minutes). The solution was then added to molten trimethylolpropane (54 g, 0.40 mole) and the stirred solution was heated gradually to 150°C while distilling off ethanol (52 g, 94 percent). After the residual volatiles (7 g) were removed at 80°C (5 torr, 16 hours) using a rotary evaporator, the product weighed 90 g (95 percent yield) and had a hydroxyl equivalent of 98.

Reaction of Trimethylolpropane with "Diethoxyoctamethyltetrasiloxane" (C2425-9B)

Freshly distilled dimethyldiethoxysilane (122 g, 0.827 mole, b.p. 110 to 112°C), water (10.8 g, 0.60 mole) and acetic acid (4 drops) were shaken together for about 10 minutes until hydrolysis was complete. The solution was then added to trimethylolpropane (61 g, 0.454 mole) containing additional acetic acid (3 drops). Ethanol was gradually removed by

distillation until the pot temperature reached 150°C and 96 percent of the ethanol had been recovered (73 g). Residual ethanol, acid, and other volatiles (12 g) were then removed using vacuum (2 torr, 100 ± 10° C) and a rotary evaporator. The siloxypolyol weighed 103 g, had an analyzed equivalent weight of 121, and separated into 2 phases when cooled.

Reaction of Trimethylolpropane with "Diethoxydecamethylpentasiloxane" (C2425-8B)

Freshly distilled dimethyldiethoxysilane (74.5 g, 0.50 mole), water (7.2 g, 0.40 mole) and acetic acid (5 drops) were mixed together and shaken until the hydrolysis was complete (5 to 10 minutes). The mixture was then added to molten trimethylolpropane (27 g, 0.2 mole), and acetic acid (3 drops) was added. The temperature of the reaction mixture was gradually raised to 150°C while continuously removing ethanol (45 g, 98 percent). As soon as the temperature was allowed to drop to about 130 to 140°C the reaction mixture began to separate into two phases. Residual ethanol and other volatiles (7 g) were removed at 80°C (3 torr, 16 hours).

Preparation of a Siloxyisocyanate Prepolymer (C2425-6)

Siloxypolyol (C2425-5B, 31 g, 0.47 mole) was added to freshly distilled tolylene diisocyanate (Nacconate 80, 210 g, 1.2 mole), which contained pyridine (1 drop), over a one hour period. The mixture was heated in an oil bath (70 to 80°C) for 5 hours, then cooled and stirred overnight. Excess tolylene diisocyanate was then removed with heat (150 ±10°C) and vacuum (2 torr) using a rotary evaporator. The fusible brittle product weighed 110 g, had an isocyanate equivalent of 199, and was too reactive at its melting point to produce useful polyurethanes.

Preparation of Siloxyisocyanate Prepolymer (C2425-9A)

Siloxypolyol (C2425-8B, 52.5 g) was vigorously shaken to disperse the two phases and was then added over a 1/2 hour period to 2,4-tolylene diisocyanate (Nacconate 100, 248 g, 1.43 mole). The reactants were stirred continuously while heating in an oil bath. By the time the addition

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was completed the bath temperature was 115°C. The glassy polymer melted about 140°C and was too reactive when molten to yield useful polyurethanes.

Preparation of Siloxyisocyanate Prepolymer (C2425-10)

Siloxypolyol (C2425-9B, 30 g, 0.25 eq.) was vigorously shaken to disperse the two phases as well as possible and was then added to pure 2,4-tolylene diisocyanate (277 g, 1.59 mole). The addition required 3/4 hour and the reaction vessel was submerged in an oil bath at 90°C. The clear fluid was stirred for two hours and allowed to cool slowly. Excess isocyanate monomer was later removed under vacuum using a rotary evaporator and an oil bath heated at 160°C. Prepolymer obtained by this process weighed 101 g and was a clear glass. Monomeric tolylene diisocyanate (15 g) was then added to the prepolymer in order to reduce its viscosity and melting point. Its analyzed equivalent weight was 178. The prepolymer was hard but not brittle and softened between 100-120°C. It was, however, too reactive at its melting point to yield useful polyurethanes.

Preparation of Chloromethyldimethylchlorosilane (1961-26 and 32)

Trimethylchlorosilane (380.2 gm, 3.50 moles) was chlorinated by bubbling chlorine gas (approximately 250 gm, 3.5 moles) through the constantly stirred liquid silane for five hours at reflux temperature (56°C at start of reaction to 70°C after five hours reaction time) in the presence of a 150 watt lamp. After the removal of starting material by distillation through a Vigreux column (this distillate, probably mostly trimethylchlorosilane, came over at 57 to 62°C and weighed 112 gm), the product (chloromethyl)dimethylchlorosilane (153.8 gm, 1.08 mole) was distilled over at 112 to 115°C. (30.9 percent of theoretical.)

Another chlorination reaction was performed as per C1961-26 described above, using 1257.7 gm (11.6 moles) of trimethylchlorosilane and 628.1 gm (8.7 moles) of chlorine gas. The distillation of the (chloromethyl)dimethylchlorosilane yielded 501.7 gm (2.83 moles, 32.5 percent of theoretical) of product boiling at 112 to 115°C.

percent of theoretical), was collected by vacuum distillation (103 to 108° C, 5 torr) and hydrolyzed as before in a methanol solution of HCl (14 gm HCl gas in 500 ml absolute methanol). After removal of most of the methanol by distillation, the remaining reaction mixture was combined with that from above and the final product collected by distillation at 2 torr.

Two fractions were collected: the first boiling at 53 to 67° C (13.6 gm), and the second boiling at 67 to 95° C (52.5 gm, 0.19 mole). A hydroxyl analysis (No. C2497-6) revealed an equivalent weight of 141.5 for the high boiling fraction. Thus, this fraction was taken to be the final product, 1,3-bis(hydroxymethyl)tetramethyldisiloxane (25 percent of theoretical, based on combined molar amounts of acetate intermediate).

Preparation of p-Bromoallylbenzene (C1961-31)

p-Dibromobenzene (235.9 gm, 1.0 mole) was dissolved in absolute ether and added slowly to a mixture of absolute ether and dry magnesium (27.0 gm, 1.1 mole). The addition of the dibromobenzene was begun only after the Grignard reaction had been initiated by the addition of a few ml of ethylmagnesium bromide to the magnesium-ether slurry. Refluxing of the reaction mixture was moderated by intermittent use of an ice bath. The reaction was stirred continuously and heated at reflux for 3/4 hour after the addition was completed. Immediately following the formation of the bromophenylmagnesium bromide an ethereal solution of allyl bromide (130.0 gm, 1.08 mole, in two volumes of absolute ether) was added slowly with constant stirring. (The allyl bromide had been previously purified by fractional distillation at 70 to 71.5° C.) Again refluxing was moderated during the addition of the allyl bromide by use of an ice bath. The mixture was heated at reflux with constant stirring for a half hour after the addition was completed. The crude product was poured over crushed ice which had been acidified with HCl. After separation of the organic phase, the aqueous phase was washed several times with fresh ether, and the organic phase was washed with 6N HCl. These ether washes were combined with the previously isolated organic phase, and the ether removed by distillation.

Preparation of 1,3-Bis(hydroxymethyl)tetramethyldisiloxane
(C1961-27 to 29)

Chloromethyldimethylchlorosilane (154 g, 1.08 mole) was poured
into 1 liter of constantly stirred distilled water at room temperature, the
addition being made over a 15-second interval. The hydrolysis reaction
mixture was stirred at approximately room temperature, although the
reaction is slightly exothermic for five minutes. The product,
1,3-bis(chloromethyl)tetramethyldisiloxane, was separated from the
aqueous phase, dried over calcium carbonate, and distilled at 198 to
206°C. It weighed 66.1 gm (0.29 mole). (An undetermined amount of
distillate was spilled accidentally in removing the receiver from the still.
Hence, the percent yield could not be calculated.)

1,3-Bis(chloromethyl)tetramethyldisiloxane (78.0 gm, 0.34 mole,
preparation C1099-3) was mixed with potassium acetate (73.0 gm, 0.75
mole), glacial acetic acid (80 ml), and acetic anhydride (3 ml) and
the slurry of reactants was refluxed with constant stirring for 16 hours.
The product was poured into water and the organic phase was isolated.
It was then washed with aqueous potassium carbonate, dried over
anhydrous potassium carbonate, and distilled (120 to 132°C, 23 torr).
The product, 1,3-bis(acetoxymethyl) tetramethyldisiloxane (20.4 gm,
0.08 mole) was added to a methanol solution of HCl (3 gm HCl gas
in 100 ml absolute methanol) with constant stirring and reacted at room
temperature for 12 hours. The resulting solution was distilled to remove
low boiling solvent. Distillation was stopped at a head temperature of
70°C, and the remaining reaction mixture was added to the hydroxymethyl-
disiloxane prepared as described below.

A second batch of chloromethyldimethylchlorosilane was hydrolyzed
as before, and 56.1 gm (0.24 mole) of bis(chloromethyl)tetramethyl-
disiloxane was recovered by distillation (24.3 percent of theoretical).
The 1,3-bis(chloromethyl)tetramethyldisiloxane from two runs (122.2
gm, 0.53 mole) was combined and mixed with potassium acetate (114.3
gm, 1.17 mole), glacial acetic acid(126.1 ml), and acetic anhydride
(4.6 ml), and reacted as in the previous acetylation. The product,
1,3-bis(acetoxymethyl)tetramethyldisiloxane (104.1 gm, 0.39 mole, 74

The crude product was steam distilled, and the organic phase was taken up in ether and dried over $CaSO_4$. After removal of the ether by distillation, the p-bromoallylbenzene (112.9 gm, 0.57 mole, 57 percent of theoretical) was collected by vacuum distillation (78 to 83°C, 5 to 6 torr).

Preparation of m-Bromoallylbenzene (C1961-42)

m-Dibromobenzene (236 g, 1.0 mole) in anhydrous ether (200 ml) was added dropwise to a slurry of magnesium (27 g, 1.1 mole) in ether (400 ml). The reaction was initiated by the addition of a small amount of ethylmagnesium iodide. After the addition was completed the reaction mixture was heated at reflux for 3/4 hours. Allylbromide (130 g, 1.1 mole) was then added dropwise over a 1/2 hour period and the mixture was then maintained at reflux for a 1/2 hour period. After cautiously pouring the reaction mixture over a mixture of ice and dilute hydrochloric acid, the ether layer which separated was isolated and thoroughly washed with water. Distillation yielded 123 g (0.62 mole, 62%, B.P.$_1$ = 38-40°C) of m-bromoallylbenzene.

Preparation of Ethoxydimethylchlorosilane (C1961-40)

Absolute denatured ethanol (180.0 gm, 3.9 mole) was added with constant stirring (as rapidly as possible so as to insure even evolution of HCl gas) to dimethyldichlorosilane (507.0 gm, 3.9 mole, fractionally distilled at 70 to 71°C). The reaction was run at room temperature for a half hour and then the product was fractionally distilled through a 25-inch packed heated column at 94 to 97°C. The ethoxydimethylchlorosilane weighed 120.6 gm (22.3 percent of theoretical yield).

Preparation of 1,3-Dichlorotetramethyldisiloxane (C1961-35)

A solution of distilled water (73 gm, 4.0 moles, in 75 ml dioxane) was added, with vigorous stirring, to an ethereal solution of dimethyldichlorosilane (1035 gm, 8.0 moles) in an equal volume of absolute ether. The addition was performed by forcing the water solution into the silane solution through a capillary tube, using compressed air. The reaction was run at room temperature. The solvent loss was prevented by the

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use of a dry ice condenser. After addition of the water, which took four hours, the reaction mixture was stirred at room temperature for an additional hour. The ether was then removed by distillation, and the 1,3-dichlorotetramethyldisiloxane (156.9 gm, 0.77 mole, 9.7 percent of theoretical) was collected by fractional distillation through a 25 inch heated packed column. The final product, taken after a series of distillations, boiled at 133 to 139°C.

Preparation of 1,3-Bis(p-allylphenyl)tetramethyldisiloxane in Ether (C1961-39 to 41)

p-Bromoallylbenzene (113 g, 0.57 mole) was gradually added to a slurry of magnesium (15.5 gm, 0.62 mole) in absolute ether while stirring constantly. The reaction was initiated by the addition of ethylmagnesium iodide and was totally uncharacteristic of Grignard reactions in general. Attempts were made to speed up the reaction by the addition of small amounts of ethylmagnesium iodide and fresh magnesium intermittently over a four hour period. The dark brown reaction mixture was heated at reflux an additional 6 hours. Then the ether phase was added with constant stirring to an ethereal solution of ethoxydimethylchlorosilane (80.0 gm, 0.58 mole) by forcing the liquid slowly through a fritted glass filter into the solution of the silane in three volumes of ether. The pot mixture was then distilled to remove most of the ether and residual starting silane (3 to 22°C, 100 torr). The remaining reaction mixture, containing product and residual Grignard reagent, was then carefully acidified with dilute hydrochloric acid until the solution pH was 3. The ethereal phase was isolated and the aqueous phase was extracted with fresh ether. The combined ether layers were then washed with distilled water and dried over potassium carbonate.

After removal of the ether by simple distillation, the high boiling products were distilled under reduced pressure. Five fractions were collected; these include the following.

    I.   25-65°C, 1-2 torr, 14.9 g

    II. 65-145°C, 1-2 torr, 4.8 g

    III. 145-160°C, 1-2 torr, 10.7 g (5.1%)

IV. 160°C, 1-2 torr, 12.9 g (6.2%)

V. 160-165°C 1-2 torr, 23.2 g

Elemental analyses on III and IV are presented in Table 1 (p. 21).

Preparation of 1,3-Bis(m-allylphenyl)tetramethyldisiloxane in Tetrahydrofuran (C1961-48)

A solution of m-bromoallylbenzene (57 g, 0.29 mole) in anhydrous tetrahydrofuran (≃120 ml) was added over a 1 hour period to a slurry of magnesium (10.5 g, 0.42 mole) in tetrahydrofuran (≃200 ml). At the start of this addition a small amount of ethylmagnesium iodide was added to the magnesium slurry to initiate the reaction. Because of the vigor of the reaction, cooling was required throughout the addition. After completion of the addition, however, the reaction mixture was heated at reflux for about one hour. After setting overnight at ambient temperature, the tetrahydrofuran solution was decanted and was added dropwise to a solution of dimethylethoxychlorosilane (55 g, 0.39 mole) in tetrahydrofuran (≃100 ml). The solution was heated at reflux for 8 to 10 hours, after which the tetrahydrofuran was removed under reduced pressure. Hydrolysis of the residual product was accomplished by treatment with aqueous hydrochloric acid (6N) until the final pH was 3 and after hydrolysis the product was taken up in ether, washed with water and dried over calcium chloride. Ether was then removed under slightly reduced pressure. Fractional distillation of the higher boiling product under reduced pressure yielded 1,3-bis(m-allylphenyl)tetramethyldisiloxane (39.5 g, 37 percent). Elementary analyses on this product are presented in Table 1 (p. 21).

Epoxidation of 1,3-Bis(p-allylphenyl)tetramethyldisiloxane (C1961-49)

A solution of perbenzoic acid (8.0 g, 0.058 mole), tert-butyl alcohol (24 g) and chloroform (150 ml) was stirred for 1/2 hour at 0°C. 1,3-Bis-(p-allylphenyl)tetramethyldisiloxane (10.9 g, 0.028 mole) was then added dropwise while maintaining the reaction temperature at 0 ±4°C. Additional chloroform (25 ml) was used to rinse the residual disiloxane into the reaction flask. Stirring was then continued for 10 hours at 0 ±6°C, then at 8°C until 95 percent of the perbenzoic acid was consumed

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(47 hours). The reaction mixture was washed with 10 percent aqueous sodium hydroxide and dried over anhydrous sodium sulfate. After removal of the chloroform at atmospheric pressure the residue was distilled under vacuum. Four fractions were collected: 1) forerun, 4.8 g, 2) 0.6 g, 26°C, 0.012 torr, 3) 2.7 g, 28 to 30°C, 0.04 torr, and 4) 1.6 g, 75 to 90°C, 0.04 torr. Elemental analyses of fractions 3) and 4) were respectively 73.82 percent C, 7.35 percent H, 2.60 percent Si, and 73.79 percent C, 7.28 percent H, and 0.10 percent Si.

Synthesis of p-Bromophenyl Allyl Ether (C2425-11)

Allyl bromide (106 g, 0.876 mole) was added during a 30 minute period to a slurry of K_2CO_3 (100 g), acetone (300 ml), and p-bromophenol (152 g, 0.876 mole). The reaction was exothermic. After about 1-1/2 hours, additional acetone (100 ml) was added. Refluxing was continued for a total of 10-1/4 hours. After washing out the KBr, K_2CO_3 and acetone with water, the product was taken up in ether and dried over K_2CO_3. Distillation yielded 170 g (0.8 mole) of the p-bromophenyl allyl ether (b.p. 100 to 104°C at 2 torr). Subsequently, after extraction with 10 percent aqueous NaOH, it was noted that the product had contained about 7 percent of rearranged 4-bromo-2-allylphenol.

Attempted Synthesis of 1,3-Bis(p-allyloxyphenyl)tetramethyldisiloxane (C2425-11)

p-Bromophenyl allyl ether (170 g, 0.80 mole) was added over a 2 to 3 hour period to a slurry of Mg (20 g) in absolute ether (500 ml). The reaction was very sluggish and could not be made vigorous even by the addition of I_2 crystals or ethylmagnesium iodide. It was later noted that the bromophenyl allyl ether was contaminated with bromoallylphenol which prevented reaction by destroying Grignard reagent as it formed. However, after removal of the phenol by alkali extraction and again starting the reaction it was still not energetic even with the addition of ethylmagnesium iodide as an initiator. After 12 hours at reflux, 1,3-dichlorotetramethyldisiloxane (80 g) was added to the solution of Grignard reagent. Its addition resulted in a reaction which first appeared vigorous, but rapidly became sluggish. After washing the supernatant solution

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with dilute hydrochloric acid and drying the organic phase with K_2CO_3, the ether was removed by distillation. The final product has not been recovered yet, but a molecular distillation is planned.

Reaction of "Diethoxyhexamethyltrisiloxane" with Decanediol (C1980-46)

Dimethyldiethoxysilane (22.2 g, 0.15 mole) was partially hydrolyzed with water (1.8 g, 0.10 mole) using acetic acid (2 drops) as catalyst. The hydrolysis product, which is largely diethoxyhexamethyltrisiloxane, was then mixed with 1,10-decanediol (17.4 g, 0.10 mole) and the mixture was heated gradually to 150°C while removing ethanol by distillation. The reaction mixture was then heated at 90°C for 20 hours under a pressure of < 5 torr.

The reaction product was then diluted with ether (20 cc) and chloroform (5 cc) and was slowly added to a solution of 2,4-tolylene diisocyanate (17.4 g, 0.1 mole) in ether (10 cc) cooled to 8 ± 2°C. After the initial reaction was completed, the isocyanate prepolymer was warmed to 100°C and recovered by removal of the solvents with heat and vacuum.

Preparation of 4-Bromo-2,6-dimethylphenol (C1980-60)

2,6-Dimethylphenol (122 g, 1 mole) was dissolved in warm water (1500 ml). Bromine (160 g, 1 mole) was then added dropwise keeping the water bath temperature below 35°C. Prior to addition of the bromine the flask was wrapped with aluminum foil to exclude light. After setting overnight the water was decanted and the dark purple solid product (154 g, 76 percent) was dried under reduced pressure (≈100 torr) for 6 hours. One recrystallization yielded 61 g of tan crystals.

Reaction of Diethoxytetraphenyldisiloxane with Bis(hydroxymethyl-diphenyloxide (C1980-73)

Diphenyldiethoxysilane (55.8 g, 0.41 eq.) was partially hydrolyzed by shaking it with water (1.8 g, 0.20 eq.) and acetic acid (8 drops). To the tetraphenyldisiloxane mixture thus produced was added hydroxymethyl-diphenyloxide-14 (Dow Chemical Co., 48 g, 0.40 eq.) and the mixture was then heated at 115°C (120 torr) until ethanol evolution was virtually

complete. The pressure was then reduced to ≃2 torr and the remaining alcohol removed. The following day additional acetic acid (12 drops) was added and the mixture was heated at 130°C for 6 hours to induce total equilibration. It was then heated at 115°C for 16 hours at <1 torr. The viscous product weighed 89 g (102 percent of theoretical).

Preparation of Diphenyldiethoxysilane (C1980-59)

Diphenyldichlorosilane (139 g, 0.55 mole) was added slowly to ethanol (65 g, 1.4 mole) and the mixture was heated to reflux. Excess ethanol and HCl were removed by distillation at ambient pressure and the diphenyldiethoxysilane (139 g, 93 percent) was then distilled under vacuum (124 to 130°C, 3 torr).

Preparation of Phenyltriethoxysilane (C2425-13A)

Phenyltrichlorosilane (180 g, 0.86 mole) was added slowly to ethanol (≃125 ml) at such a rate as to avoid excessive frothing. The HCl and excess ethanol were then removed by distillation at ambient pressure and the phenyltriethoxysilane was distilled under vacuum (93 to 103°C at 3 torr).

Reaction of Bis(hydroxymethyl)diphenyloxide with Phenyltriethoxysilane and Diphenyldiethoxysilane (C2425-14A)

A mixture of hydroxymethyldiphenyloxide-14 (Dow Chemical Co., 120 g, 1.0 eq.), freshly prepared phenyltriethoxysilane (8.0 g, 0.1 eq. 93 to 103°C, 3 torr), freshly distilled diphenyldiethoxysilane (55 g, 0.4 eq.), and glacial acetic acid (10 drops) were heated at 120 ± 10°C in vacuum for several hours then at 115°C and 20 torr overnight. Ethanol distilled out of the reaction mixture during this treatment. The viscous product weighed 160 g (100 percent), and had an observed equivalent weight of 308. Its theoretical equivalent weight is 320.

Reaction of Diethoxytetraphenyldisiloxane with Bis(hydroxymethyl) diphenyloxide and Phenyltriethoxysilane (C2425-14B)

Freshly distilled diphenyldiethoxysilane (55.8 g, 0.41 eq.) water (1.8 g, 0.20 eq.) and acetic acid (2 drops) were shaken together until

the mixture became homogeneous and virtually clear. To the disiloxane
thus produced was added phenyltriethoxysilane (0.055 eq., 4.4 g,
b.p. 93 to 103°C at 3 torr), acetic acid (6 drops), and hydroxymethyl-
diphenyloxide-14 (60 g, 0.5 eq.). The reaction mixture was heated at
110 ± 10°C (at 80 ± 20 torr) until ethanol evolution ceased. Additional
acetic acid (10 drops) was then added and the reaction mixture was
heated at 130 to 135°C (80 torr) for 15 minutes and then for 3 hours at
5 torr. The viscous product weighed 105 g (105 percent) and had an
apparent equivalent weight of 286.

Reaction of Bis(hydroxymethyl)diphenyloxide with Diphenyldiethoxysilane (C2425-13B)

Diphenyldiethoxysilane (27.2 g, 0.10 mole), and hydroxymethyl-
diphenyloxide-14 (46 g, 0.20 mole) were melted together at 85°C and
acetic acid (10 drops) was then added. The reaction mixture was
gradually heated to 160°C while removing ethanol continuously. Residual
ethanol was removed under reduced pressure.

Reaction of Bis(hydroxymethyl)diphenyloxide with Phenyltriethoxysilane (C2425-13C)

Hydroxymethyldiphenyloxide-14 (48.4 g, 0.40 eq.) was melted,
mixed with phenyltriethoxysilane (16.0 g, 0.20 eq.), and acetic acid
(10 drops) was then added. The reaction mixture was gradually heated
to 130°C while removing ethanol at 120 torr. After 1/2 hour the
pressure was reduced to 80 torr and maintained at 135 degrees for 2-1/2
hours. Acetic acid (6 drops) was then added, and after mixing thoroughly
the pressure was reduced to 2 torr and the temperature was lowered to
120°C. After 4 hours the temperature was lowered to 90°C and main-
tained for ≃16 hours. The product weighed 54 g (98 percent yield).

Reaction of Diethoxytetramethyldisiloxane with Trimethylolpropane (C1980-57)

Dimethyldiethoxysilane (222 g, 1.5 mole) was hydrolyzed to the
dimer by reaction with water (13.5 g, 0.75 mole) and acetic acid (1.0 g).
The mixture was vigorously shaken for 5 to 10 minutes until it became

clear. Trimethylolpropane (202 g, 1.51 moles) was added and the mixture was gradually heated to 150°C while constantly removing ethanol. The last traces of ethanol were removed at 100°C (4 torr), using a roto-film evaporator, yielding 285 g (95 percent) of siloxypolyol.

Preparation of N-Methylacetanilide (C1961-53)

Freshly distilled N-methylaniline (54 g, 0.50 mole, b.p. 54°C at 2 torr) was dissolved in pyridine (150 ml), and acetic anhydride (53 g, 0.52 mole) was added dropwise while stirring constantly (1/2 hour). Refluxing was continued for an additional 1/2 hour. The reaction mixture was poured over a mixture of ice and hydrochloric acid, and the precipitated solid product (60 g, 80 percent) was collected by filtration. After recrystallization from water containing decolorizing charcoal, the pure dried product weighed 29.9 g and melted at 104 to 105°C (Lit. 104°C).

Preparation of N-Methylaniline-Formaldehyde Prepolymer (C1961-55)

To a solution of N-methylaniline (43 g, 0.40 mole) in concentrated aqueous hydrochloric acid (18 ml, 0.21 mole) was added dropwise an aqueous solution of formaldehyde (37 percent, 20 g, 0.25 mole) while maintaining the temperature at 0 to 5°C. Stirring was continuous during the addition, which took 30 minutes, and for 1 hour thereafter. The mixture was heated at 90 to 95°C for 10 hours, then cooled and neutralized with aqueous sodium hydroxide (8.4 g/500 ml). The yellow gum which precipitated was pressed dry, dissolved in methanol with some difficulty, then recovered by methanol evaporation, redissolved in benzene, and dried by azeotropic distillation. When the benzene-soluble product was again recovered and poured into ether a small amount of yellow powder (1.2 g) precipitated. Upon evaporation of the ether from the soluble phase a resinous product (27.5 g) was isolated. The equivalent weight of this product (96 ± 2) was determined potentiometrically by titrating an acid solution of the resin with alcoholic alkali as well as by a potentiometric titration of the amine in glacial acetic acid using perchloric acid.

Synthesis of p,p'-Bis(methylamino)diphenylmethane (C2943-2)

A solution of N-methylaniline (48 g, 0.45 mole) in concentrated aqueous hydrochloric acid (19 cc, 12 N, 0.23 mole) was cooled to 0 to 5°C, and formalin (16 g, 37 percent, 0.20 mole) was added dropwise over a 1 hour period while maintaining the temperature below 5°C. Stirring was continued for 1 hour at this temperature, and the mixture was then heated to 93°C for 9 hours. The reaction mixture was poured into a vigorously stirred alkali solution (10 percent NaOH) at 10°C, and the precipitated polymer was then taken up in benzene. After washing the aqueous phase with benzene the various benzene fractions were combined and the solvent was removed by distillation. Efforts to distill the product at 170°C (< 1 torr) have failed; however, a lower pressure distillation is planned. Upon standing at room temperature the product crystallized.

Synthesis of Stannosiloxane Prepolymer (B5202-4)

A solution of phenylmethyldichlorosilane (172 g, 0.90 mole), methylvinyldichlorosilane (14 g, 0.10 mole) and dibutyltindichloride (61 g, 0.20 mole) in toluene (650 ml) was cooled to -5°C. The toluene solution and an aqueous solution consisting of potassium hydroxide (161 g, 2.88 mole), Alconox (2.0 g) and water (550 ml) were cooled to -21°C and were added simultaneously to a laboratory blender having a jacket packed with an acetone-ice mixture. The reaction mixture was dispersed at high speed in the blender for two minutes, during which time the temperature rose to 20°C. It was then neutralized with dilute hydrochloric acid and the aqueous phase was separated and discarded. Solvent was removed from the organic phase by vacuum distillation at room temperature, yielding a light colored clear resin (171 g).

Synthesis of Stannosiloxane Prepolymer (C1090-40)

A solution of dimethyldichlorosilane (11.6 g, 0.09 mole), methylphenyldichlorosilane (17.2 g, 0.09 mole), methylvinyldichlorosilane (2.8 g, 0.02 mole), methyltrichlorosilane (1.5 g, 0.01 mole) and dibutyltindichloride (9.1 g, 0.03 mole) dissolved in 150 ml of toluene was

cooled to -10°C. The toluene solution and an aqueous solution consisting of potassium hydroxide (35.6 g, 0.64 mole), Del-O-Dex detergent (0.2 g), and water (125 ml) cooled to -21°C were added simultaneously to an ice-jacketed blender operating at moderate speed. During mixing at high speed for 2 minutes the temperature rose to 27°C. Dilute hydrochloric acid was then used to neutralize the reaction mixture, and the organic phase was then separated by centrifugation and concentrated by means of a rotary evaporator. An oily liquid (20.5 g) was collected from which a small amount of tin salts precipitated upon standing. This liquid cured to a friable elastomer by adding 0.5 g of Dow Corning QF-1-0104 (a silicon hydride) and a drop of di-tert-butyl peroxide to 5.0 g of the oil and warming gently with a hot air gun. A similar composition cured in less than one hour at room temperature. In both of the cured samples an appreciable amount of hydrogen formed, which made the resulting product porous.

Synthesis of Stannosiloxane Prepolymer (C1090-35)

A solution of dimethyldichlorosilane (24.3 g, 0.188 mole), methylvinyldichlorosilane (2.8 g, 0.02 mole) and dibutyl tin dichloride (12.5 g, 0.041 mole) dissolved in 150 ml of toluene was cooled to -16°C. This solution and an aqueous solution consisting of potassium hydroxide (35.6 g, 0.64 mole), Alconox (0.2 g), and water (125 ml) cooled to -21°C were added simultaneously to an ice-jacketed blender operating at high speed. The reaction mixture was dispersed for two minutes in the blender at high speed and the highest temperature reached was 23°C. After neutralization with dilute hydrochloric acid, the organic phase was separated in a separatory funnel, cooled in a dry ice-acetone bath and filtered through glass wool to remove ice-crystals. The solution was then concentrated using a rotary evaporator and yielded a clear resin (21 grams).

It was found that a formulation consisting of 5.0 grams of this resin, 0.15 g of bis-silylbenzene[3] (85 percent meta-isomer and 15 percent para-isomer), and one drop of di-tert-butyl peroxide cured in less than 15 minutes at 90°C, but at higher temperatures, i.e., 140°C, the polymer darkened presumably due to the reduction of tin by unreacted

silicon hydrides. The formulation also cured in air after standing for fifteen minutes.

A formulation using 5.0 grams of the resin, 0.25 g of Union Carbide Y-1524 Silicone (a silicon hydride) and one drop of di-tert-butyl peroxide cured in less than 15 minutes at 200° F. It also showed appreciable cure at room temperature in air after one and one-half hours. After standing for several days the cure did not appear to advance too much further.

Synthesis of Stannosiloxane Prepolymer (C1090-29)

A solution of methyldichlorosilane (2.35 g, 0.02 ml), dimethyldichlorosilane (15.5 g, 0.12 mole), methyltrichlorosilane (9.0 g, 0.06 mole) and dimethyltindichloride (11.0 g, 0.05 ml) in 130 ml of methylene chloride was cooled to -20°C. The methylene chloride solution and an aqueous solution consisting of potassium hydroxide (37.7 g, 0.67 mole), Alconox (0.2 g), and water (125 ml) initially at -20°C were added simultaneously to an ice-jacketed blender operating at high speed. There was a violent reaction which caused some of the reaction mixture to be thrown from the blender. Appreciable quantities of insoluble gum formed apparently due to the methyltrichlorosilane, which produced much crosslinking.

Modification of Stannosiloxane Polymers to Eliminate Hydroxyl End Groups (C1090-50)

In a 100 ml flask fitted with a magnetic stirrer were placed stannosiloxane polymer B5202-4 (39 g) and toluene (50 ml). The mixture was agitated overnight to insure complete solution of the polymer; then phenyl isocyanate (2.0 g) was added and the reaction mixture was stirred for 1 hour. Solvent and the unreacted phenyl isocyanate were then removed by using a rotary evaporator. This process reduced the viscosity of the polymer, apparently because it prevents hydrogen bonding of the terminal hydroxy groups which contribute to the viscosity of the uncured polymer.

To the treated polymer (28.0 g) was added 1,4-bis-silylbenzene (1.4 g) and a few crystals of dicumyl peroxide. The mixture was

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thoroughly mixed and placed in a 2 x 2 x 1/4-inch mold protected from the atmosphere with aluminum foil. The mold was heated for 210° F for about 25 minutes and allowed to cool overnight while being subjected to 10,000 psi pressure. The resulting polymer was friable and somewhat porous.

Synthesis of Siloxyurethane Resin (C1090-44)

Into a 500 ml three-necked flask fitted with a magnetic stirrer, glass heating mantle, thermometer and Vigreux column were placed dimethyltriphenyltrimethoxytrisiloxane ((Dow Corning Sylkyd 50; 156.7 g, 0.33 mole) and ethylene glycol (20.7 g, 0.30 ml). The reaction mixture was heated to 160°C for several hours while methanol (15.7 g, 0.49 mole) was removed by distillation. A clear homogeneous product was obtained.

To 40 grams of the above resin, 2 grams of tolylene diisocyanate and several drops of triethylamine were added. The mixture was stirred and allowed to stand in a desiccator. The mixture cured slowly. The resulting product was fairly friable and had a small amount of bubbles, probably due to traces of water present in the ethylene glycol which formed carbon dioxide upon reaction with the diisocyanate.

Synthesis of Siloxyurethane Resin (C1090-45)

Into a 250 ml flask fitted with a magnetic stirrer, thermometer, heating mantle, and Vigreux column were placed dimethyltriphenyltri-methoxytrisiloxane (Dow Corning Sylkyd 50; 110.5 g, 0.235 mole) and ethylene glycol (24.2 g, 0.470 mole). The mixture was heated slowly to 160°C during which time 15.7 grams (0.49 mole) of methanol distilled over. The mixture was then heated for an additional 2 hours.

To 40 grams of the above resin (equivalent −OH groups 0.135 mole) was added Nacconate 80, which is a mixture of 80 percent 2,4-tolylene diisocyanate and 20 percent 2,6-tolylene diisocyanate (23.5 g, or 0.135 ml), and a few drops of triethylamine. The mixture thickened upon standing. The mixture,when placed in a desiccator, cured after a day into a friable solid which had some porous structure probably due to traces of moisture which was present in the ethylene glycol.

ANALYTICAL PROCEDURES

Optimum physical and dielectric properties of siloxyurethanes or other polymers prepared in this program can generally be expected when stoichiometric amounts of the intermediate prepolymers are reacted together. Thus, in urethane formulations, for example, residual -NCO or -OH groups are to be avoided. Excess -NCO groups can be expected to be especially detrimental due to their very high dipole moments. To obviate these problems equivalent weights of newly synthesized siloxypolyols, isocyanate prepolymers, epoxy prepolymers, polyamines, etc., must be determined.

Suitable procedures are of course available for the analysis of both aliphatic hydroxyl compounds and isocyanates. The analysis of hydroxyl compounds containing siloxy groups, however, is complicated by the fact that the acetic anhydride used in conventional hydroxyl analyses can react with alkoxy silanes; thus, in an analysis involving an acetylation procedure, the acetic anhydride can displace alkoxy end groups from the siloxane to produce acetoxy groups as illustrated.

$$CH_3 - \overset{\overset{O}{\|}}{C} \overset{\diagdown}{\underset{\diagup}{}} O \; + \; RO-\underset{|}{\overset{|}{Si}}- \longrightarrow CH_3 - \overset{\overset{O}{\|}}{C} - O - \underset{|}{\overset{|}{Si}} - \; + \; RO-\overset{\overset{O}{\|}}{C}-CH_3$$
$$CH_3 - \underset{\underset{O}{\|}}{C}$$
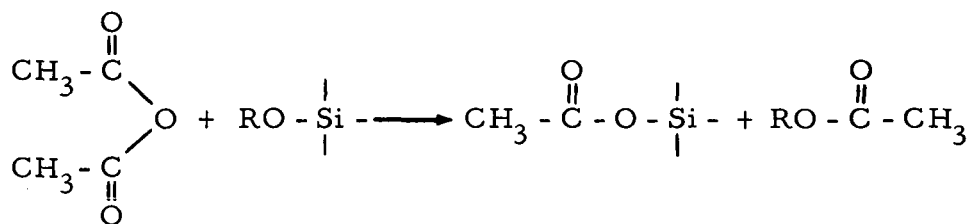
This reaction uses up 2 equivalents of acetyl group per alkoxy group.

Prepolymers and other intermediates synthesized during the course of this program were thus analyzed to determine actual equivalent weights since these values generally differed from the theoretical values. Siloxypolyols were analyzed by the procedure of Ogg, Porter, and Willits [Quantitative Organic Analysis via Functional Groups, S. Siggia, Third ed., John Wiley and Sons, Inc., 1963, New York, N.Y., p. 12-14]. A modification of the procedure was necessary, however, since the recommended acetylation period (45 minutes) proved to be

inadequate for complete reaction. The preferred acetylation period appeared to be more like 90 minutes. For a more conventional alcohol such as trimethylolpropane 45 minutes at 100°C was quite adequate, as evidenced by the following results:

Trimethylolpropane

Observed Equivalent Weight	Theoretical Equivalent Weight
45.3	44.7

In contrast to these results are those from the analysis of a siloxypolyol derived from the reaction of trimethylolpropane with 1, 5-dimethyl-1, 3, 5-triphenyl-1, 3, 5-trimethoxytrisiloxane (C2425-1B)

Acetylation Period	Observed Equivalent Weight g/eq.	Theoretical Equivalent Weight g/eq.
45 minutes	379 ± 50	
60 minutes	259 ± 50	
90 minutes	78.6 ± 0.2	79
120 minutes	74.5 ± 0.5	
180 minutes	77.0 ± 5.0	

From the above data it will be noted that not only did the first two acetylation periods produce highly erroneous results but also they produced individual results which varied widely from the mean. Results were, however, relatively consistent for acetylation periods of 90 minutes or greater. Minimum deviations from the averages were noted with the 90 minute period.

To determine the extent to which Si - O - Si groups interfere, samples of octamethylcyclotetrasiloxane were analyzed.
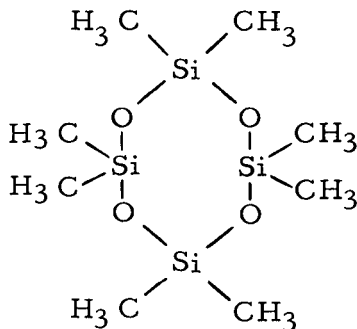
Octamethylcyclotetrasiloxane

Negative results indicated that this compound, and thus the Si - O - Si group, is not readily susceptible to cleavage during the acetylation process and consequently constitutes no problem. Furthermore, it was previously demonstrated that Si - OCH_3 groups do interfere with hydroxyl analyses because of the susceptibility of the methoxyl group to displacement by acetoxyl group. This latter evidence was obtained from an analysis of a sample of triphenyltrimethoxydimethyltrisiloxane (Sylkyd 50), which, although it has no hydroxyl groups, consumed 17.2 percent of the acetyl equivalence and thus indicated that 8.6 percent of the methoxyl groups had been displaced. Thus, although methoxyl groups do constitute a problem, data obtained on siloxypolyol C2425-1B show that acetylation periods greater than 90 minutes yield results which are very close to the results from the 90 minute acetylation period; consequently, the 2, 2-bis-(hydroxymethyl)butoxyl groups (the trimethylolpropane moieties)

$$CH_2OH$$
$$\diagdown$$
$$C_2H_5 - C - CH_2 - O -$$
$$\diagup$$
$$CH_2OH$$
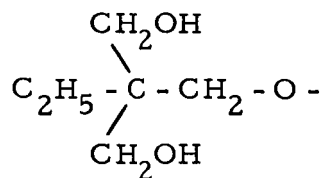
do not appear to be susceptible to displacement as are the methoxyl groups.

It should also be noted that the previously described siloxypolyol (C2425-1B) contains phenyl groups on each silicon atom of the siloxane chain and these apparently are partly responsible for the lower rate of acetylation. Homologous siloxanes derived from trimethylolpropane and dimethyldiethoxysilane apparently acetylate somewhat more rapidly, as evidenced by the data on C2425-5B presented below. Here a 70 minute acetylation period appeared to be quite adequate.
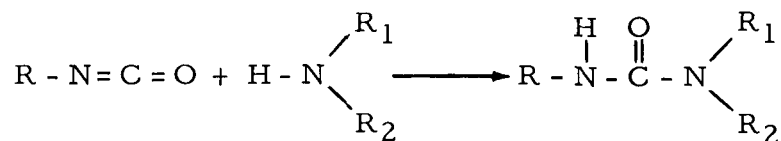
Acetylation Period	Observed Equivalent Weight
70 minutes	68.5
90 minutes	64.3
110 minutes	67.7
130 minutes	63.7
Average	66.05

After establishing a suitable reaction period, various siloxypolyols were analyzed and the results are presented in Table 2. All results are the average of at least duplicate runs.

Siloxypolyol Number	Analysis Number	Acetylation Period, minutes	Observed Hydroxyl Equivalent, g/eq.	Theoretical or Expected Hydroxyl Equivalent, g/eq.
C2425-1B	B5269-42	90	78.6	79
C2425-7A	C2497-4	90-120	121	190
C1587-81,82	C2497-1	90-120	375	132
C1961-29HB	C2497-6	90	141	97
C2425-5B	C2497-3	90-110	66.0	81
C2425-7B	C2497-5A	90	102	99
C2425-8A	C2497-5B	90	98	118
C2425-9B	C2497-7	90	121	137
C2425-8B	—	—	—	155
C-1980-45	C2497-17	90	212	
C-1980-57	C2497-26A	90	92	99
C-2425-13B	C2497-26B	90	404	321
C-2425-14A	C2497-25A	90	308	320
C-2425-14B	C2497-25B	90	453	430

Table 2. Analyzed equivalent weights of various siloxypolyols.

Several siloxyisocyanate prepolymers were also analyzed. This was accomplished by establishing their amine equivalents by determining the number of secondary amino groups which react with the available isocyanate groups. The reaction is illustrated below:

$$R-N=C=O \; + \; H-N\begin{smallmatrix}R_1\\ \\R_2\end{smallmatrix} \longrightarrow R-\underset{H}{N}-\overset{O}{C}-N\begin{smallmatrix}R_1\\ \\R_2\end{smallmatrix}$$

Isocyanate samples were reacted with an excess of the secondary amine and the unreacted amine was subsequently titrated with standard aqueous hydrochloric acid. The analytical procedure was essentially that described in a brochure from the Mobay Chemical Company and was developed for the analysis of tolylene diisocyanate. In the Hughes procedure, dipropylamine was used to replace dibutylamine and was standardized against samples of 2, 4-tolylene diisocyanate which had an equivalent weight of 88. 2 (theoretical value 87. 5). Duplicate samples of the standard varied by 0. 2 units. Isocyanates which were subsequently analyzed are indicated below in Table 3.

Siloxy Isocyanate Prepolymer	Analysis Number	Equivalent Weight	
		Observed	Theoretical
C-2425-6A (made from -5B)	C2497-11A	199	240
C-2425-10A (made from 9B)	C2497-11B	178	157
C1980-46	C2497-17	685	449
C1980-58	C2497-22	670	224

Table 3. Analyzed equivalent weights of several siloxy isocyanate prepolymers.

Polymeric amines which were synthesized during this report period were analyzed by titrating them with perchloric acid using acetic acid as the solvent, as well as by titrating the amine hydrochloride in water with alcoholic KOH. Titrations were followed using a pH meter and, in the acetic acid method, gave rather sharp end points. Typical titration curves are illustrated in Figures 5 and 6. As a standard of comparison for the perchloric acid titration, 4,4'-diaminodiphenylmethane was also titrated in acetic acid. Duplicate runs yielded equivalent weights of 96. 7 and 99. 0, or an average of 97. 9, as against a theoretical value of 99. 1. A typical titration curve is illustrated in Figure 7.
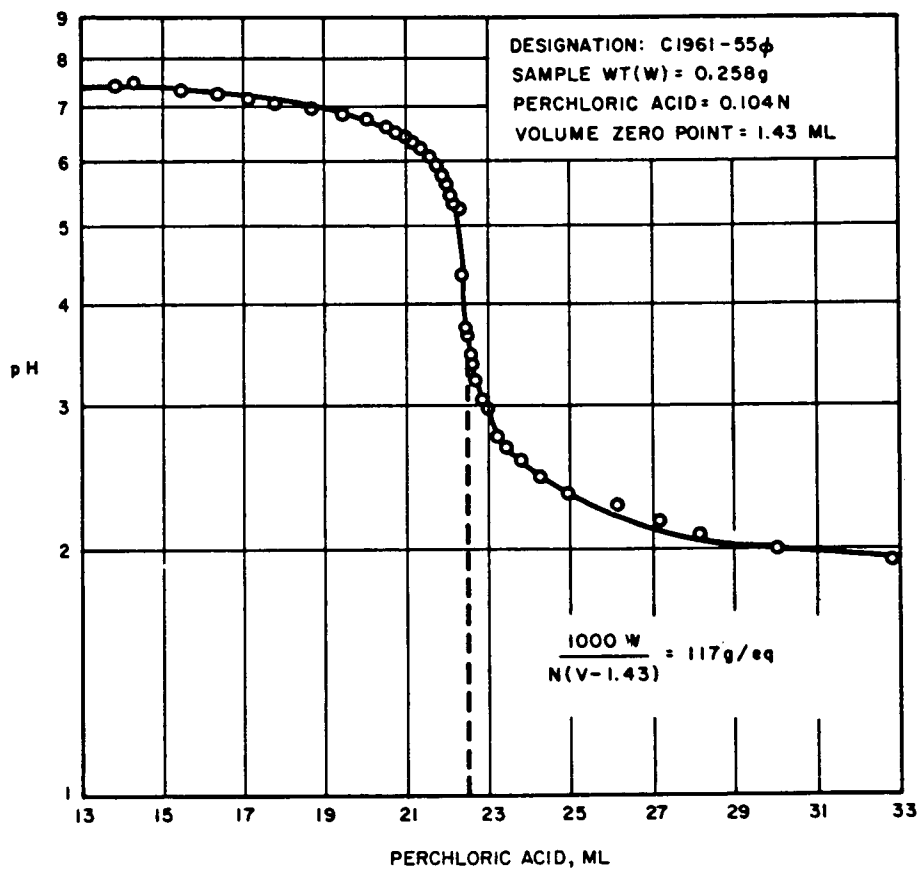
Figure 5.   pH titration curve for N-methylaniline formaldehyde in acetic acid.

DESIGNATION: C1961-55φ
SAMPLE WT(W)= 0.549g
ALCOHOLIC KOH = 0.543 N

ΔV

$$\frac{1000\,W}{N\,\Delta V} = 123\,g/eq$$

pH

VOLUME OF ALKALI, ML
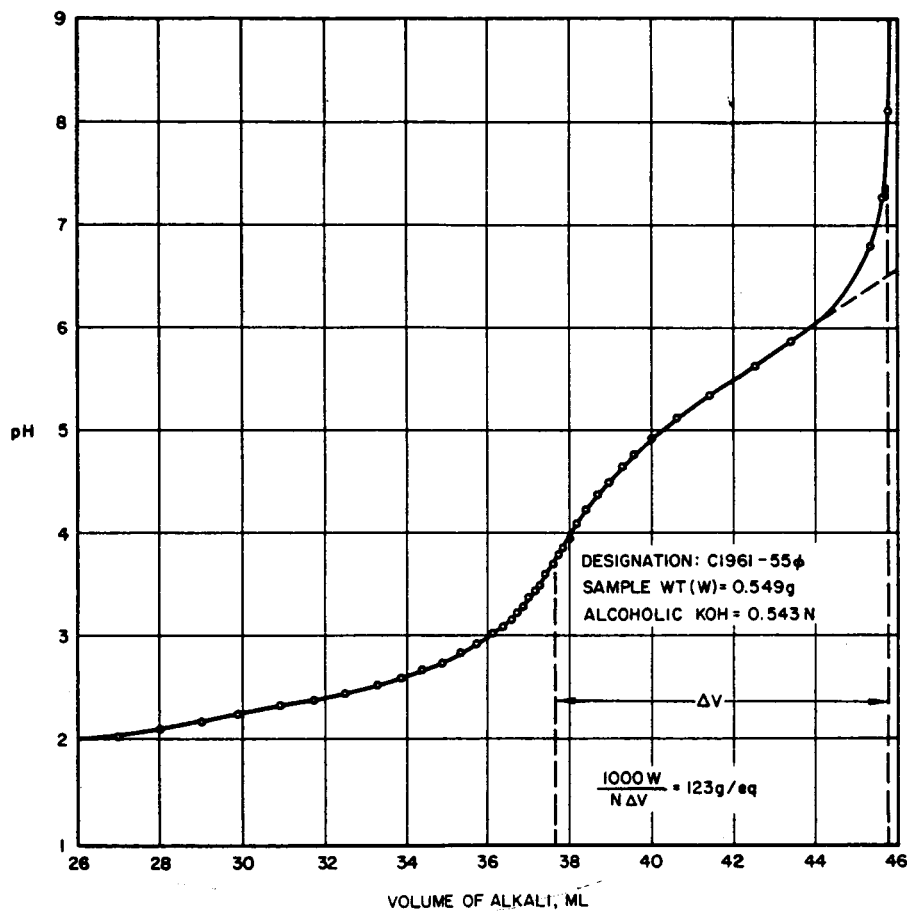
Figure 6.   pH titration curve for N-methylaniline
formaldehyde in aqueous solution.

Amine	Analysis Number	Equivalent Weight	
		Observed	Theoretical
Methylenedianiline	C2497-28A, 30A	97.8	99.1
Methylaniline formaldehyde C1961-55φ	C2497-28B, 30B C2497-27	117 [‡] 123 [‡‡]	114
Epoxy-phenylenediamine "Reactive Adduct" C1987-63, 65	C2497-29	135	139* 92.7**

[‡]Perchloric acid titration of amine in acetic acid.

[‡‡]Alkaline titration of aqueous amine hydrochloride.

*Calculated on the basis of total amino groups.

**Calculated on the basis of functional N - H groups.

Table 4. Analyzed equivalent weights of various polyamines.

ANALYSIS NO. C2497-30
ZERO POINT = 0.27 ML
PERCHLORIC ACID = 0.108 N

$$\frac{(1000)(0.2018\,g)}{(18.87)(0.108)} = 99.0\,g/eq$$

Figure 7. pH titration curve for 4,4' -diaminodiphenylmethane in acetic acid solution.

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MATERIALS EVALUATION

Dielectric tests on the various polymers were carried out using two types of specimens. The Hartshorn specimens were circular discs generally having the dimensions of 1.900-inch diameter X 0.100-inch thick. Specimens of this type were usually prepared when the resins were expected to be very rigid after cure, whereas 4-rod embedded electrode specimens were often prepared when the polymer was expected to be somewhat elastome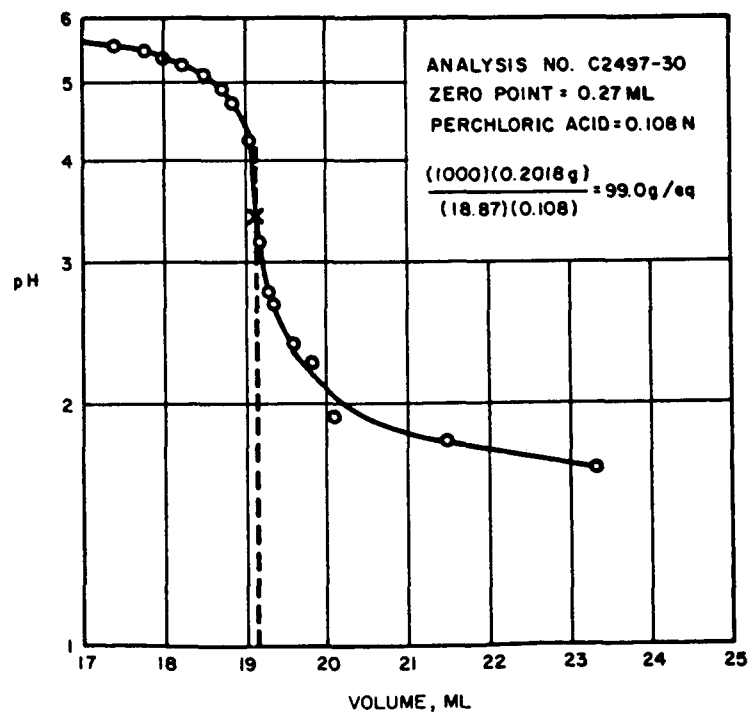ric. The latter type have the dimensions 5/8-inch diameter X 4-1/2-inch long with the brass rods 3/8 inch apart at their centers.

Hartshorn specimens are preferred for greatest precision; however, the 4-rod specimens are highly satisfactory for general screening purposes. Furthermore, Hartshorn specimens have several disadvantages in that they must be machined to precise dimensions and their surfaces must be metallized, preferably by aluminum vapor deposition. Besides being more costly, these specimens are less suitable for higher temperature tests and high vacuum tests. Four-rod embedded electrode specimens are cast to proper dimensions with the electrodes rigidly held in place during casting. These specimens are conveniently tested at temperatures of 150°C, and are highly suitable for high vacuum tests. Their principle disadvantage over the Hartshorn specimens is their requirement for larger quantities of resin.

Siloxypolyols synthesized during the course of this program were generally formulated with a standard commercial isocyanate prepolymer. The purpose of using one standard component was of course to permit the relative evaluation of the various siloxypolyols. It was intended, thereafter, to select the best siloxypolyol and use it in preparing a suitable siloxyisocyanate prepolymer. Although several isocyanate prepolymers of this type were prepared, their working characteristics were too poor to permit the preparation of good dielectric test specimens and consequently dielectric properties of siloxyurethanes prepared from these isocyanates could not be obtained.

Of all the siloxyurethanes prepared and evaluated, those derived from siloxypolyols synthesized from bis(hydroxymethyl)diphenylether were the only ones which showed a great deal of promise. The investigation of this type of polyol was initiated near the end of the annual report period and consequently results of subsequent work should prove very interesting. Dielectric constants of 3.38 and 3.86 as well as dissipation factors of 1.20 and 1.16 percent were marked improvements over the usual dielectric constants of 5 ± 0.5 and dissipation factors of 4-8 percent generally noted with other siloxyurethanes.

Although a considerable effort has been made to synthesize several epoxysilicone monomers the desired compounds have not yet been obtained. One epoxysilicone, namely 1,3-bis(epoxypropoxypropyl)-tetramethyldisiloxane, was evaluated since it was available commercially (Dow Corning Syl Kem 90). Its structural characteristics were, however, not those of interest, partly because it was completely aliphatic, but also because it contained labile hydrogen atoms β to the ether oxygen atoms. Polymers obtained from this epoxysilicone monomer showed no special promise.

A series of epoxy resins, which were prepared from a standard high purity epoxy monomer [2,2-bis(epoxypropoxyphenyl)propane, Shell Epon X-24] along with various types of amine curing agents, were evaluated. Two of the amines were simply amine terminated adducts of the X-24 with m-phenylenediamine and with aminobenzenethiol. The technique of using amine terminated prepolymers rather than monomeric amines as curing agents was investigated because the prepolymers could be thoroughly outgassed in high vacuum, thus eliminating the potential problems of outgassing in aerospace environments. As a result of this procedural change not only was the outgassing problem resolved for the most part, but also dielectric and physical properties of the cured resins were superior to properties of the analogous resins obtained by conventional mixing procedures.

The standard epoxy compound was also cured with amines such as 4,4'-diaminodiphenylmethane, mixtures of bis(methylamino)-diphenylsilane with 4,4'-diaminodiphenylmethane, mixtures of

N, N'-diphenylethylenediamine with 4, 4'-diaminodiphenylmethane, and telomeric N-methylaniline formaldehyde. Probably the most significant observation made was that every amine which contained N-methylamino groups produced epoxy resins with dielectric constants below 4. 0 (3. 4 to 3. 9) at ambient temperature and with other good dielectric properties. [Dielectric constants of 3. 8 have also been obtained at 100° C, but this data is due to be reported in a subsequent report.]

During the course of work on the siloxyurethane resins derived from trimethylolpropane, it was noted that high temperature postcures (150° C) were very useful in attaining minimum dielectric constants.

Another rather interesting observation which was made on these polysiloxyurethanes was the reversal of the order of dissipation factors (at 100° C) when specimens were cured at 74° C instead of at 150° C. This observation is shown graphically in Figure 8.
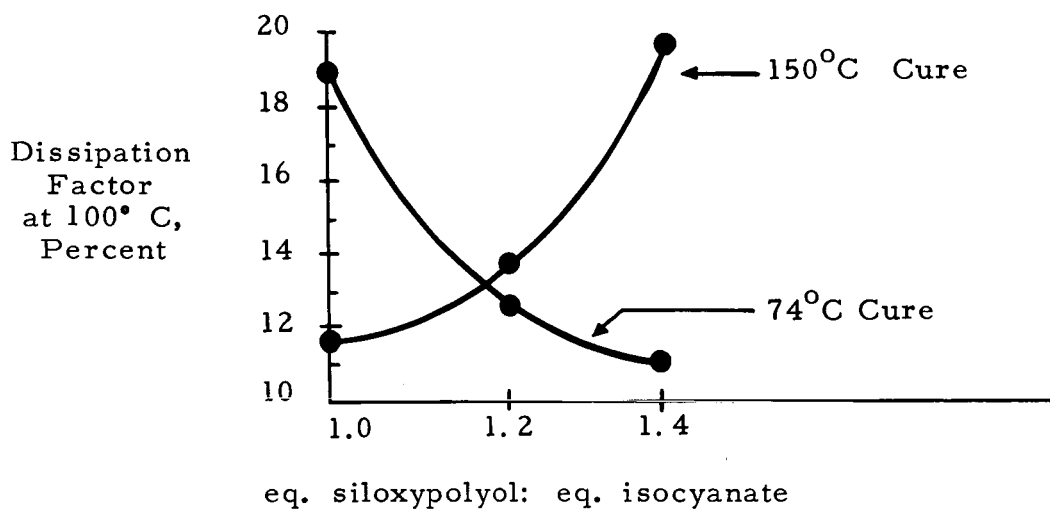
Figure 8. Dissipation factors of siloxyurethanes cured at various temperatures.

It was also noted that tests carried out at 100° C tend to yield results which exhibit a much wider spread than is observed with ambient temperature tests, and consequently illustrate the effect of composition changes quite profoundly. In a series of tests designed to demonstrate the significance of the silicone content of siloxypolyols, rather interesting trends were noted. These results are graphically illustrated in Figures 9 and 10.
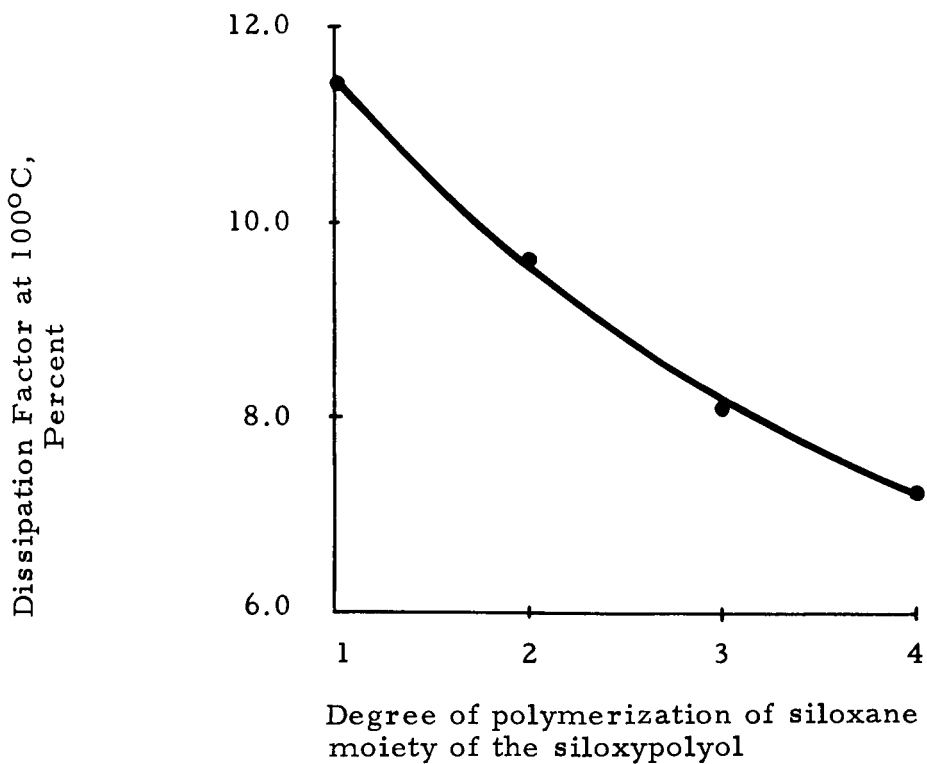
Figure 9. Variation of dissipation factors of siloxyurethanes with varying siloxane chain lengths.

Figure 10. Variation of insulation resistance with varying siloxane chain lengths.

The composition of siloxyurethane dielectric specimens which were prepared during this program are presented in Table 5 and compositions of epoxy and epoxysilicone test specimens are presented in Table 6 whereas dielectric test results are presented in Tables 7 and 8.

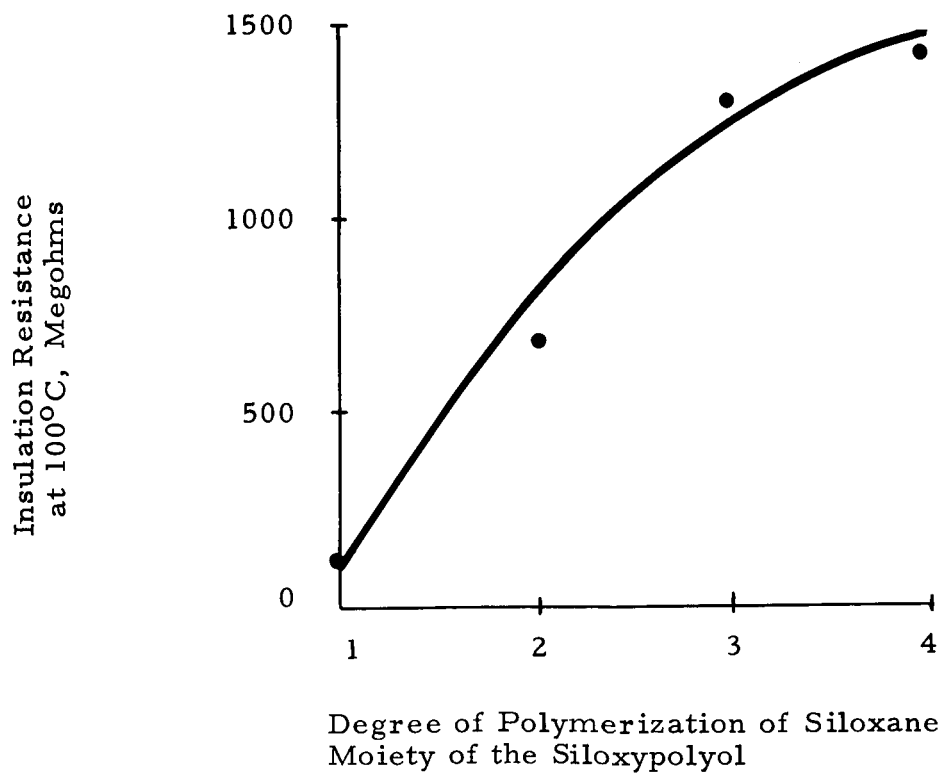| Specimen Number | Composition | | | | | | | Cure Conditions | | Comments |
| | Siloxypolyol | | | | Isocyanate | | | | | |
	Designation	Weight, g	Eq.	Derived From	Designation	Weight	Eq.	Time, hours	Temperature, °C	All 4-Rod
C2435-1 and 2	C2425-1B	15.8	0.20	G+H	A'	80.0	0.18	20 3	74 100	Clear, yellow tint, tough, flexible
-3 and 4	C2425-1B	9.9	0.13	G+H	B'	81.0	0.13	20 3	74 100	Clear, yellow tint, tough, flexible
-5 and 6	G	6.75	0.17		A'	75.0	0.17	6	100	Clear, yellow tint, tough, flexible
-S2	C2425-1B	7.9	0.10	G+H	A'	44.5	0.10	17 3	83 100	Clear, yellow tint, tough, flexible
-S3	C2425-1B	8.1	0.10	G+H	A'	44.5	0.10	17 3	83 100	Clear, yellow tint, tough, flexible
-SA1	C1587-79-2	8.3	0.10	G+I	A'	44.5	0.10	17 3	83 100	Clear, yellow tint, tough, flexible
-SC1 -SC1'	C2425-5B	6.6	0.10	G+J	A'	44.5	0.10	15 4	74 150*	Clear, yellow tint, tough, flexible
-SC2 -SC2'	C2425-5B	8.1	0.12	G+J	A'	44.5	0.10	15 4	74 150*	Clear, yellow tint, tough, flexible
-SC3 -SC3'	C2425-5B	9.2	0.14	G+J	A'	44.5	0.10	15 4	74 150*	Clear, yellow tint, tough, flexible
-SD1	C2425-7A	12.1	0.10	G+J	A'	44.5	0.10	15 4	74 150	Clear, tough, flexible, yellow tint
-SE1	C2425-7B	10.2	0.10	G+K	A'	44.5	0.10	15 4	74 150	Tough, semi flexible, yellow tint, translucent
-SF1	C2425-8A	10.2	0.105	G+L	A'	44.5	0.10	16 2 3 4	74 85 100 150	Tough, semi flexible, translucent
-SG1	C2425-9B	12.0	0.10	G+M	A'	44.5	0.10	16 2 3 4	74 85 100 150	Tough, semi flexible, translucent
C1980-41C	C2425-7B	15.4	0.15	G+K	C'	26.1	0.30			Reject Bubbles—foamed
	F'	13.3	0.15							
-41D	C2425-7B	20.6	0.20	G+K	A'	133	0.30	64 8 Vacuum	85 150	Translucent, yellow tint, tough, semi flexible
	F'	8.9	0.10							

Table 5. Composition of siloxyurethane dielectric test specimens.

Specimen Number	Composition → Siloxypolyol				Isocyanate			Cure Conditions		Comments
	Designation	Weight, g	Eq.	Derived From	Designation	Weight	Eq.	Time, hours	Temperature, °C	All 4-Rod
C1980-42	C2425-7B	15.4	0.15	G+K	D'	39.6	0.30			Reject Poor specimen
	F'	13.3	0.15							
-49	E'	9.7	0.10		A'	44.5	0.10			Reject Failed to cure
-51-5A	C2425-7A	6.0	0.05	G+J	A'	66.7	0.15	16	100	Reject Failed to cure
	E'	9.7	0.10							
-63-1	C2425-14A	15.4	0.05	N+O	A'	22.2	0.05	3 16	74 64 N_2	Reject Bubbles, tough elastomer
-63-2	C2425-14B	20.2	0.045	N+O+P	A'	22.2	0.05	3 16 4	74 64 N_2 64 vac	Reject Bubbles, failed to cure
-63-3	C2425-14A	30.8	0.10	N+O	D'	13.2	0.10			Reject Very brittle, also voids
-63-4	C2425-14B	40.4	0.09	N+O+P	D'	13.2	0.10	Same as above, very brittle – reject		Reject Very brittle, also voids
-64-5	C2425-14A	10.2	0.033	N+O	A'	22.2	0.05	16 16	74 N_2 90 vac	Very flexible, tough and clear
	C2425-14B	6.8	0.015	N+O+P						
-64-6	C2425-14A	15.4	0.050	N+O	D' A'	5.25 4.45	0.04 0.01	Same cure as above, tough but somewhat brittle, clear		Tough and clear, but somewhat brittle
-64-7	C2425-14B	20.2	0.045	N+O+P	D' A'	5.25 4.45	0.04 0.01	Same cure as above		Very brittle
-65-8	C2425-13B	14.2	0.035	N+P	D'	6.6	0.05	4 16	74 N_2 90 vac	Very brittle
	C1980-57	0.9	0.01	G+K						
-65-10	C2425-13B	16.2	0.04	N+P	D'	4.6	0.035	16 16	68 100 vac	Slightly brittle
	C1090-57	1.0	0.01		A'	7.0	0.016			

*This second higher temperature post cure was carried out after the first set of electrical tests was completed.

Code: A' – Adiprene L-315

B' – Adiprene L-167

C' – 2,4-Tolylene diisocyanate

D' – Nacconate 200 (National Aniline)

E' – 1,3-bis(hydroxymethyl) tetramethyldisiloxane

F' – 1,10-decanediol

G – Trimethylolpropane

H – Sylkyd 50 (Dow Corning Corp.)

I – Diethoxypolydimethylsiloxane

J – Dimethyldiethoxysilane

K – "Diethoxytetramethyldisiloxane"

L – "Diethoxyhexamethyltrisiloxane"

M – "Diethoxyoctamethyltetrasiloxane"

N – Bis(hydroxymethyldiphenyloxide)

O – Phenyltriethoxysilane

P – Diphenyldiethoxysilane

Table 5 (continued). Composition of siloxyurethane dielectric test specimens.

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Specimen Number	Composition						Cure Conditions		Specimen Type	Comments
	Amine			Epoxy						
	Designation	Weight	Eq.	Designation	Weight	Eq.	Time, hours	Temperature, °C		
7, 8	E	54.7	0.59	G	100	0.59	12 16	28 121	I	Dark amber tough rigid
9, 10	E F	50.0 100	0.54 0.68	G	206	1.21	16 16	28 74	I	Dark amber tough rigid
11, 12	F	87	0.59	G	100	0.59	12 16	28 85	I	Dark amber tough rigid
C1980-40A	A	16.2	0.60	G H	51.0 54.3	0.30 0.30	16 5 7-1/2	25 75 121	J	Rigid, tough AMBER CLEAR
-40AV	A	16.2	0.60	G H	51.0 54.3	0.30 0.30	16 5 3-1/4 4-1/2	25 75 121 150 vac.	J	Rigid, tough AMBER CLEAR
-40B	A	16.2	0.60	G H	34.0 72.4	0.20 0.40	16 5 7-1/2	25 75 121	J	Rigid, tough AMBER CLEAR
-40BV	A	16.2	0.60	G H	34.0 72.4	0.20 0.40	16 5 3-1/4 4-1/2	25 75 121 150 vac.	J	Rigid, tough AMBER CLEAR
-50-1	B	12	0.10	G	15.4	0.09	24 24	74 N$_2$ 125 vac.	I	Colorless tough elastomer
-50-2	B	6.0	0.05	H	9.1	0.05	24	74	I	Failed to cure
-50-3	B A	6.0 2.7	0.05 0.10	H	27.0	0.15	24 24	74 N$_2$ 125 vac.	I	Elastomer color-less
-51-4	B A	6.0 2.7	0.05 0.10	G	23.1	0.136	24 24	74 N$_2$ 125 vac.	I	Yellow tint tough elastomer
-52	C	10.0	0.20	G	34.0	0.20	16 6	74 N$_2$ 110 vac.	I	Tough rigid hard clear
-56-1-4	C D	1.68 7.0	0.034 0.066	G	15.4	0.09	4 17 48	70 N$_2$ 80 N$_2$ 90 N$_2$	I J	Tough rigid clear yellow
-65-9	D C	7.0 1.7	0.066 0.034	G	15.4	0.09	32 Al$_2$O$_3$ filled	65 N$_2$	I J	White rigid tough.

Code:　A — m-phenylenediamine
　　　　B — bis(methylamino)diphenylsilane
　　　　C — 4,4'-diaminodiphenylmethane
　　　　D — N,N'-diphenylethylenediamine
　　　　E — Amine terminated m-phenylenediamine-Epon X-24 prepolymer C1587-63, 4
　　　　F — Amine terminated m-aminobenzenethiol-Epon X-24 prepolymer C1587-65
　　　　G — Epon X-24 (Shell Chemical Co.)
　　　　H — Epoxysilicone Syl Kem 90 (Dow Corning Corp.)
　　　　I — Discs 1.9-inch diameter × 0.100-inch thick
　　　　J — Four-rod embedded electrode

Table 6.　Composition of epoxy and epoxysilicone dielectric test specimens.

Specimen Number	Dielectric Constant 1 kc		Dissipation Factor Percent		Insulation Resistance Megohms- 500 VDC	
	25°C	100°C	25°C	100°C	25°C	100°C
1, 2	4.59	7.68	3.40			
3, 4	7.54	9.02	8.79			
5, 6	4.66	7.14	4.99			
C2435-S2	4.75	7.41	3.51	10.6		
-S3	4.86	7.98	4.13	9.3		
-SA1	5.30	8.15	6.36	10.4		
-SC1	5.60	8.23	6.87	18.5	6.5×10^5	26
-SC1'	5.00	7.37	4.43	11.4	3×10^5	150
-SC2	5.15	8.18	5.20	12.2	4.5×10^5	32
-SC2'	5.10	8.18	4.58	13.3	5×10^5	95
-SC3	5.15	8.34	5.41	11.2	2.0×10^5	30
-SC3'	5.06	8.45	4.60	19.8	2×10^5	30
-SD1	5.46	7.93	6.85	10.5	2×10^5	140
-SE1	5.18	6.88	5.72	9.6	3×10^5	700
-SF1	5.60	6.76	4.49	8.1	8.5×10^5	1300
-SG1	4.66	5.74	5.00	7.2	5×10^5	1400
C1980-41D	5.25	4.02	7.37	6.4	6×10^5	200
-51-5	7.47	9.98	10.08	34.49	4.5×10^3	7
-64-5	4.67		6.96			
-64-6	3.38		1.20			
-65-10	3.86		1.16			

Table 7. Dielectric properties of various siloxyurethane resins.

Specimen Number	Dielectric Constant 1 kc		Dissipation Factor Percent		Insulation Resistance Megohms-500 VDC		Volume Resistivity Ohm Cm	
	25°C	100°C	25°C	100°C	25°C	100°C	25°C	100°C
7, 8	4.31		1.57		$> 1 \times 10^7$		5.0×10^{14}	
9, 10	4.05		0.92		$> 1 \times 10^7$		$> 4.7 \times 10^{14}$	
11, 12	4.00		0.60		$> 1 \times 10^7$		4.5×10^{14}	
C1980-40A	4.83	6.35	1.12	.5.08	$> 5 \times 10^7$	3×10^4		
-40AV	4.80	5.11	1.06	.1.00	5×10^6	1.6×10^3		
-40B	4.84	5.62	0.87	3.35	5×10^7	9×10^2		
-40BV	5.18		0.78	.1.31	1×10^7	1×10^5		
-50-1	3.36	5.47	1.03	.9.09	2.8×10^3		$.1.4 \times 10^{11}$	2×10^{10}
-50-3	5.54		5.40		5.6×10^4		2.2×10^{11}	
-51-4	3.70		1.55		3.6×10^4		2×10^{11}	3.1×10^{11}
-52	4.39	5.00	0.90	3.91			7.3×10^{13}	4.3×10^{12}
-56	3.71*	4.26*	0.47*	2.63	$> 1 \times 10^7$	8×10^5	7.4×10^{13}	3.8×10^{12}
-65-9	6.30*	6.66	1.6*	1.88	8×10^5	9×10^4		

* = average results from 4-rod specimens and Hartshorn specimens.

Table 8. Dielectric properties of various epoxy and epoxysilicone resins.