A STUDY OF POLYMERS CONTAINING
SILICON-NITROGEN BONDS

Annual Summary Report for the Period
May 4, 1966 to June 3, 1967

GEORGE C. MARSHALL SPACE FLIGHT CENTER
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Huntsville, Alabama

Project 1710, Report 25

Robert E. Burks, Jr.
Joseph L. Greene, Jr.
Organic Section

FOREWORD

This report was prepared by Southern Research Institute under Contract NAS 8-20190, "A Study of Polymers Containing Silicon-Nitrogen Bonds," for George C. Marshall Space Flight Center of the National Aeronautics and Space Administration. The work was administered under the technical direction of the Propulsion and Vehicles Engineering Laboratory, Materials Division of the George C. Marshall Space Flight Center with Dr. Lindsey M. Hobbs acting as project manager.

TABLE OF CONTENTS

TABLE OF CONTENTS
(continued)

TABLE OF CONTENTS
(continued)

TABLE OF CONTENTS
(continued)

ABSTRACT

Methods of preparing poly[1,4-bis(oxydimethylsilyl)-benzene diphenylsilane] in molecular weights up to 400,000 were improved, and the polymer was studied as a source of high-temperature elastomers and pressure-sensitive adhesives. Elastomers with tensile strengths up to 550 psi were prepared, but better curing and filling methods are needed. A poly-silphenylene amine, poly(tetramethyl-p-silphenylene methylamine), was studied as a source of protective coatings and resilient foams. The polysilphenylene amine pigmented with aluminum formed coatings on titanium, stainless steel, and mild steel that underwent no visible change at 540°C in several hundred hours. Foams made by crosslinking the polysilphenylene amine with pentaerythritol had good thermal stability for resilient polymers, but they also had poor strength.

An epoxy resin cured with bis(methylamino)diphenylsilane was prepared for evaluation as a heat-barrier, but the results are not yet available. The same resin was found to have good thermal stability as an adhesive for lap joints of aluminum.

Several areas were explored as sources of new types of polymers that might be useful for aerospace technology. Poly-vinyl alcohol, fully silylated at the hydroxyl groups, had much better thermal stability than the original polymer; but even so, its physical properties were not good enough at either high or low temperatures to warrant further study. Diisocyanates were polymerized with silylamines, which catalyzed cyclization of isocyanate groups to isocyanurates. The resulting polymers had some useful physical properties at ordinary temperatures but not at high or low temperatures. Attempts were made to form ladder polymers or linear polymers of high thermal stability by partial hydrolysis followed by condensation of tri- and tetra-functional silylamines, but only insoluble and infusible solids were formed. The reaction of bis(methylamino)diphenylsilane with ketones was studied briefly, and it was found to be essentially a condensation-dehydration of the ketone.

The current literature on silicon-nitrogen chemistry was reviewed and summarized.

-vii-

A STUDY OF POLYMERS CONTAINING
SILICON-NITROGEN BONDS

I.   STATUS OF THE RESEARCH PROGRAM

The study of silicon-nitrogen chemistry was undertaken in a search for routes to new types of polymers that perform satisfactorily at low temperatures or that are exceptionally stable to radiation and high temperatures. Emphasis has recently been placed on development of the newly-found materials that are most promising for applications in aerospace technology. Previous work in this program was performed for the Army Ballistic Missile Agency[1] and the National Aeronautics and Space Administration.[2,3,4,5,6]

A polysilphenylene ether, poly[1,4-bis(dimethylhydroxy-silyl)benzene diphenylsilane], is being developed as an elastomer for applications requiring stability to heat and radiation. This polymer is prepared from a silicon-nitrogen compound. Known methods of curing the polymer are not satisfactory, because they require excessively high temperatures and cannot be used for curing thick layers. The elastomers being prepared presently are relatively weak compared to commercial elastomers, although they have better thermal stability. The polymer has a glass-transition temperature of 0°C, which makes it unsuitable for low-temperature applications, but structural variants of it have lower glass-transition temperatures as well as good thermal stability. The primary goal of future research planned for this type of polymer is to find a better curing system.

A polysilphenylene amine is being considered as a coating agent for applications requiring stability at 540°C or above. It remains to be determined whether some critical factors, such as erosion resistance and type of protection afforded the substrates, will be good enough to justify its selection for aerospace applications. Exploratory research on coatings is not planned for the future, and only a small amount of evaluation work is anticipated.

Silylamines are capable of curing epoxy resins to polymers with high thermal stability. Bis(methylamino)diphenylsilane cures Epon 828 to a tough rigid polymer that has good flexural strength and good shear strength in adhesives after exposure to

-1-

325°C for 2 hours. The cured epoxy also was found to have some merit in heat barriers. This silylamine-epoxy combination is recommended for additional evaluation, but none is planned for the current program.

Heptamethyldisilazane was found to catalyze trimerization of isocyanates to isocyanurates, and this reaction forms polymers with both aromatic and aliphatic diisocyanates. Some of the polymers are tough and have good tensile strength at ordinary temperatures, but they appear to be similar to polyisocyanurates prepared with other catalysts already being investigated for aerospace use. Consequently, additional work in this area is not recommended at the present time.

Other subjects investigated did not lead to materials with encouraging properties. A new type of polymer made by silylation of polyvinyl alcohol had much better thermal stability than the original, but its softening point was too low and it was brittle at moderately low temperatures. Attempts to form soluble and fusible linear or ladder polymers by controlled hydrolysis-condensation of tri- and tetrafunctional silylamines were not successful. Bis(methylamino)diphenylsilane was found to react rapidly with ketones to form octaphenylcyclotetrasiloxane in high yield, but the reaction was shown to be merely a base-catalyzed dehydration of the ketones without any features that could be developed as routes to polymers.

II. DISCUSSION OF RESULTS

Polysilphenylene ethers are made by the diol-diaminosilane reaction,[7] which is a highly versatile method of forming silicon-oxygen polymers with selected structural features. Poly[1,4-bis(oxydimethylsilyl)benzene diphenylsilane] is the polymer that has received the main emphasis in this program.

1,4-bis(dimethylhydroxy-
silyl)benzene

bis(methylamino)-
diphenylsilane

poly[1,4-bis(oxydimethyl-
silyl)benzene diphenylsilane]
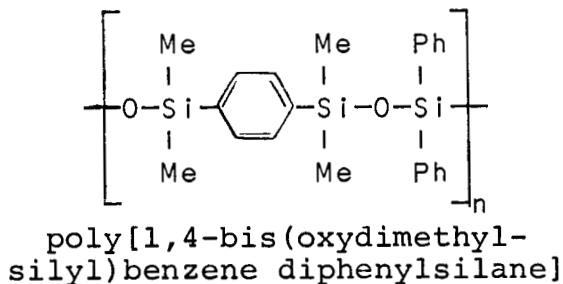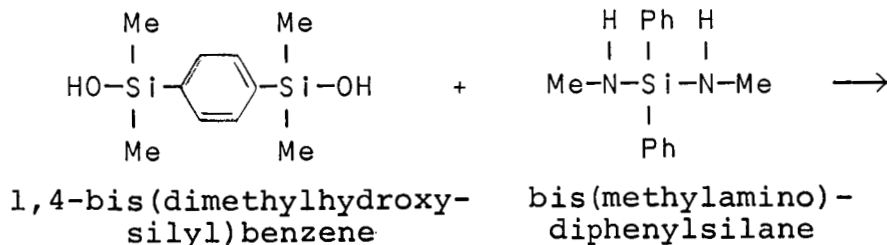
Poly[1,4-bis(oxydimethylsilyl)benzene diphenylsilane] can be converted to an elastomer that has good radiation and thermal stability, but it is not a candidate for low-temperature applications. A similar polymer with methyl groups in place of phenyl has a glass-transition temperature of -63°C. The thermal stability of silphenylene elastomers is demonstrated by the fact that they remain compressible appreciably longer at 350°C in air than other elastomers that are known to be presently available, the main obstacle to their utilization being a lack of satisfactory curing methods. During the past year, improvements have been made in methods of preparation of silphenylene polymers and these polymers have been converted to elastomers with tensile strengths of 550 psi and elongations of 210%. Silphenylene polymers of low molecular weight, 50,000 to 100,000, have desirable qualities as thermally stable pressure-sensitive adhesives. The shear strength of the pressure-sensitive adhesive in lap joints was increased by adding small amounts of a triaminosilane crosslinking agent. Some inquiries are planned to determine if the adhesive will be useful in aerospace or commercial applications.

Polysilphenylene amines have some desirable qualities as thermally stable resilient foams and protective coatings. The low strength of the foams and the lack of a satisfactory means of preparing them with uniform density discourage further work. However, aluminum-pigmented silphenylene amines adhere to titanium, stainless steel, and mild steel through several hundred hours of heating in air at 540°C (1000°F). No failure was detected during the exposure periods up to the time the experiments were discontinued. Coatings 1-2 mils thick can be applied easily, but the quality of the protection afforded by the coatings has not been studied in detail. The coating inhibits rusting on mild steel. On the other hand, 0.1 to 0.2-mil coatings on titanium failed to prevent embrittlement during exposure to sodium chloride at 550°F for 1000 hours.

Some additional work was done on the curing of epoxy resins with silylamines. The best combination found was Epon 828 and bis(methylamino)diphenylsilane. Samples of this combination filled with glass fiber, potassium titanate, and glass microballoons were submitted for heat-barrier trials in comparison with similar samples cured with Nadic Methyl Anhydride. The same epoxy-silylamine combination, unfilled, had good thermal stability as an adhesive for aluminum at 325°C.

Several subjects were explored as possible routes to new types of polymers obtainable by making use of the unique chemical properties of silylamines. Polyvinyl alcohol was silylated quantitatively by treatment with bis(trimethylsilyl)acetamide.

The resulting polymer, which had the repeating unit $-CH_2-CH(OSiMe_3)-$, was soluble in non-polar solvents, and it had better thermal stability than the original polyvinyl alcohol. However, it had a low softening point, 52-55°C, and it was rigid at 25°C, so it was not promising for space applications. Attempts were made to hydrolyze and polymerize silylamines simultaneously to form linear polymers of silica or ladder polymers related to phenylsilsesquioxane, but the products were insoluble and infusible solids. The polymerization of aliphatic and aromatic diisocyanates with silazanes was studied to extend information previously obtained. The isocyanate polymers are either rigid or flexible depending on the nature of the diisocyanate. They have good strength properties at room temperature but are not exceptionally stable thermally and have glass-transition temperatures that make them unattractive for use at low temperatures. The reaction of ketones with bis(methylamino)diphenylsilane was studied to determine whether it might be developed into a route to polymers, but it was shown to be essentially a condensation of the ketone catalyzed by the amine.

The literature on silicon-nitrogen chemistry was reviewed continuously, and the publications that appeared during the contract year are summarized in the last section of this report.

III. POLYSILPHENYLENE ETHERS

A. Discussion

1. Poly[1,4-bis(oxydimethylsilyl)benzene diphenylsilane]

a. Elastomers

The polysilphenylene ethers, as experimental elastomers, have good thermal and radiation stability but poor tensile properties. In the past year, methods of preparing poly[1,4-bis(oxydimethylsilyl)benzene diphenylsilane] were improved to produce polymers with molecular weights consistently in the range of 200,000-400,000. This polysilphenylene ether, which is called the diphenylsilane-silphenylene ether, was filled with silica and cured with peroxides to form elastomers with tensile strengths up to 550 psi and elongations up to 300% (Table I). However, the filling and curing methods, which were closely related to those currently in use for silicone rubbers, were unsatisfactory, because samples frequently contained fissures or bubbles. Furthermore, the elastomers were evidently not adequately crosslinked, because they were readily swelled by organic solvents. Triaminosilanes are capable of crosslinking the polysilphenylene ethers to some extent, but a detailed study of crosslinking reactions, including a search for better crosslinking agents, is needed.

Table I. Preparation and Properties of Silphenylene Elastomers from Poly[1,4-bis(oxydimethylsilyl)benzene diphenylsilane]

Starting material, Polymer 4480-	Premilling treatment	Estd MW[a]	Cab-O-Sil, % by weight	Peroxide Name	% by wt	Curing conditions Press mold Time, hr	Temp, °C	Post-cure Time, hr	Temp, °C	Properties Tensile strength, psi	Elongation at break, %	Appearance	Designation, Elastomer 4480-
47	hydrolysis	100,000	13	TBPB[b]	1.0	0.75	150	40 / 64	300-310 / 300-310	250 / 200	250 / 170	brown, cloudy / brown, cloudy	111-2
47	hydrolysis	100,000	13	BzP[c]	1.0	0.75	150	20 / 44	300-310 / 300-310	225 / 190	300 / 220	brown, cloudy / brown, cloudy	111-3
81	hydrolysis	240,000	13	TBPB	1.0	0.75	150	24 / 54	300-310 / 300-310	460 / 245	180 / 140	brown, cloudy / brown, cloudy	117-2
81	hydrolysis, end-capping	240,000	0	TBPB	1.0	0.75	150	16	300-310	-	-	contained air bubbles	123-1
81	hydrolysis, end-capping	240,000	13	TBPB	1.0	0.75	150	24 / 30 / 46	300-310 / 300-310 / 300-310	400 / 440 / 440	140 / 190 / 160	contained very small air bubbles	123-2
65	hydrolysis, end-capping	180,000	13	BzP	1.0	0.75	150	24	300-310	125	280	contained air bubbles	127-1
65	hydrolysis, end-capping	180,000	20	TBPB	1.0	0.75	150	24	300-310	265	260	contained fissures	127-2
65	hydrolysis, end-capping	180,000	13	TBPB	1.0	0.75	150	24	300-310	150	230	irregular, rough	127-3
65	hydrolysis, end-capping	180,000	13	TBPB	1.0	0.75	163	16 / 24	300-310 / 300-310	260 / 375	60 / 60	contained air bubbles	133-1
65	hydrolysis, end-capping	180,000	13	TBPB	1.0	0.75[d]	177	16 / 24 / 30	300-310 / 300-310 / 300-310	500 / 540 / 550	280 / 210 / 210	contained very small air bubbles	133-3
65	hydrolysis, end-capping	180,000	13	TBPB	1.0	0.17	177	16	300-310	280	80	contained air bubbles	137-1
65	hydrolysis, end-capping	180,000	13	TBPB	1.0	0.75[e]	177	16 / 36	300-310 / 300-310	230 / 505	310 / 180	irregular on surface	141-1
57	none	265,000	13	TBPB	1.0	0.75[d]	177	16 / 24 / 30	300-310 / 300-310 / 300-310	275 / 265 / 310	90 / 80 / 80	irreg. on surf., contained air bubbles	143-1
57	hydrolysis	265,000	13	TBPB	1.0	0.75[d]	177	16 / 24 / 30	300-310 / 300-310 / 300-310	385 / 435 / 440	240 / 220 / 200	contained air bubbles	143-2
57	hydrolysis, end-capping	265,000	13	TBPB	1.0	0.75	177	16 / 24 / 30	300-310 / 300-310 / 300-310	355 / 480 / 510	300 / 250 / 220	contained air bubbles	143-3
49	hydrolysis	385,000	13	Si-N[f]	0.5[g]	0.75	177	16	320-340	-	-	contained air bubbles	151-A
49	hydrolysis, end-capping	385,000	13	TBPB	1.0	0.75	177	24	300-310	540	220	very few bubbles	151-B

a. Estimated from solution viscosity measurements according to the data in Reference 8.

b. TBPB is t-butyl perbenzoate.

c. BzP is benzoyl peroxide.

d. After 10 min preheating at 177°C.

e. After 20 min preheating at 177°C.

f. Phenyltris(dimethylaminol)silane.

g. Equivalence ratio of polymer to agent, 1:12.

The diphenylsilane-silphenylene ethers have a glass-transition temperature about 0°C. Hence, they are not candidates for applications requiring resilience at low temperatures. However, lack of utility at low temperatures is not a new problem with high-temperature elastomers.

b. Preparation of polymer

Preparation of the diphenylsilane-silphenylene ethers is accomplished by condensation of two monomers, bis(methylamino)-diphenylsilane and 1,4-bis(dimethylhydroxysilyl)benzene. Condensation occurs through the diol-diaminosilane reaction.[7]
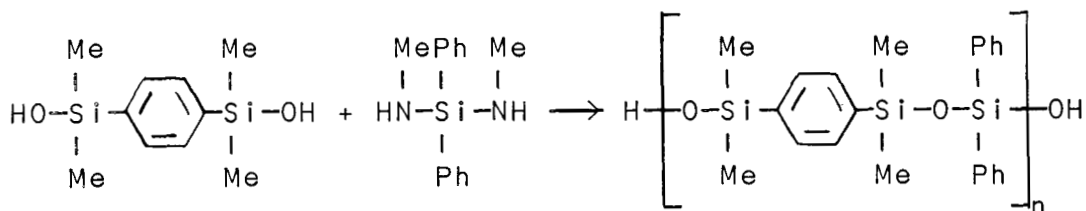
High purity of monomers is essential for successful polymerization, and considerable effort was required to develop satisfactory methods of synthesis and purification. Bis(methyl-amino)diphenylsilane is prepared from diphenyldichlorosilane and methylamine, and it is purified by distillation.

$$Ph_2SiCl_2 + MeNH_2 \longrightarrow MeN\!-\!\underset{\displaystyle Ph}{\overset{\displaystyle Ph}{Si}}\!-\!NMe$$

Ph, 82% yield
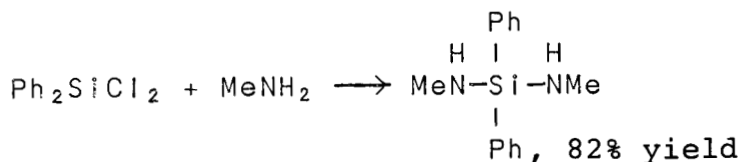
bis(methylamino)diphenyl-
silane

Melting point is used as a criterion of the purity of bis-(methylamino)diphenylsilane. A fraction is rejected unless it is at least about 90% solid at 21.7°C. 1,4-Bis(dimethylhydroxy-silyl)benzene is prepared by a modified Grignard Reaction followed by hydrolysis of the silphenylene chloride.

$$Br-\langle\bigcirc\rangle-Br \xrightarrow{Mg+Me_2SiCl_2} Cl-\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Si}}-\langle\bigcirc\rangle-\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Si}}-Cl \xrightarrow{H_2O}$$

Me, 46% yield

1,4-bis(dimethylchloro-silyl)benzene

$$HO-\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Si}}-\langle\bigcirc\rangle-\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Si}}-OH$$

Me, 75% yield
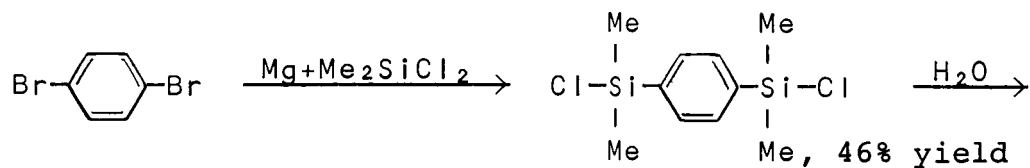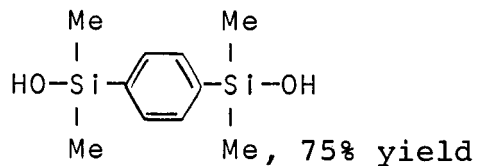
1,4-bis(dimethylhydroxy-silyl)benzene

Unless the hydrolysis reaction is carried out rapidly at high dilution it produces no monomer but only partially polymerized product. Yields of about 75% are now obtained consistently. The most striking feature of the reaction is the superiority of carbon tetrachloride over all other solvents tried for recrystallization. Diol that melts at 136-137.5°C, which is pure enough for polymerization, is obtained after two recrystallizations from carbon tetrachloride.

The diol-diaminosilane reaction requires precise stoichiometry if high molecular weights are to be reached. To check our ability to control molecular weight by stoichiometry, a polymerization was run with high-quality diol and diamine, but with 0.7% excess diol. This was the amount calculated to provide a silanol chain-stopped polymer with a molecular weight of 60,000. The molecular weight actually obtained was estimated to be 115,000, according to data obtained in an earlier study of the relation between viscosity and molecular weight.[8]

c. Pressure-sensitive adhesives

The sticky character of the raw polymer suggested that it might be useful as a thermally stable pressure-sensitive adhesive. One current need for pressure-sensitive adhesives is in the space-electronics industry for assembling circuits printed on polyimide film. The components after assembly must endure high temperatures without evolving combustible gases. A thermally stable pressure-sensitive adhesive might also have applications in other industries. Only a small amount of evaluation has been

done, but the results have been encouraging. The polymer was doctored without difficulty onto mild steel, aluminum, polyimide film, and paper. It even adhered to Teflon but less tenaciously than to other materials. Two strips of paper coated with a polysilphenylene ether with a molecular weight of 115,000 and pressed together showed a peel strength of 4.8 lb/in. For comparison, Scotch "Magic" tape had a peel strength from itself of 2.7 lb/in.

Tris(dimethylamino)phenylsilane was used to crosslink a polysilphenylene ether with a molecular weight of 50,000 in a series of experiments with different amounts of the aminosilane. The polymer alone was doctored onto two aluminum strips, and when the two strips were pressed together by hand, the resulting lap joint had a shear strength under tensile loading of 16 psi. Addition of a stoichiometrically equivalent amount of the amino-silane raised the shear strength to 21 psi at room temperature after the joint had been cured at 130°C for 2 hours. The data of Table II show that a maximum shear strength of 60 psi was obtained with 6 times the stoichiometric amount of aminosilane. Because of the exploratory nature of these experiments, the data show only that the system is capable of modification by cross-linking with a triaminosilane in such a way as to improve shear strength. Crosslinking has the undesirable effect of reducing tack, but it probably also reduces the loss of strength at elevated temperatures. The joints were capable of recombination after being sheared, and a shear strength of 200 psi resulted from recombining under higher pressures.

Table II. Effect of Crosslinking on Shear Strength
of Silphenylene Pressure-Sensitive Adhesives

(Polymer molecular weight, 50,000)

Equivalence[a] ratio of agent to polymer	Shear strength of lap joint under tensile loading, psi
0	16
0.3	17
1	21
2	23
3	35
6	60
10	50

a. A mole of agent, tris(dimethylamino)phenylsilane, is
    3 equivalents, and a mole of polymer is 2 equivalents.

This particular silphenylene ether is not expected to remain adhesive at high temperatures, because previous experiments on curing have shown that it melts as it is heated and then becomes rubbery when held at temperatures up to 350°C in air.[9] The polymer endures an exceptional amount of heating before it becomes rigid. The elastic state is reached in 50-150 hours at 250°C in air. Heating the elastomer for 16 hours at 350°C in air hardens the polymer (Figure 1), and hardening proceeds more slowly in nitrogen.[10]

d. Effect of hydrolysis and end-capping on thermal stability and milling characteristics

It was considered possible that residual amino groups in the polysilphenylene ethers might interfere with crosslinking by peroxides, and it was also possible that capping of the silanol ends of the chains might improve the thermal stability by preventing decomposition by mechanisms that require initiation at chain ends. Consequently, a study was made of the advantages of premilling treatments including hydrolysis and end-capping. Both hydrolysis to remove silylamine residues and end-capping with trimethylsilyl groups improved the ease of milling by reducing the stickiness. End-capping was accomplished by treatment of the polymer with bis(trimethylsilyl)acetamide:

$$\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{-\bigcirc\!\!-Si-OH}} \ + \ \underset{}{Me_3Si-\overset{\overset{Me_3Si-O}{|}}{N=C-Me}} \ \longrightarrow \ \underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{-\bigcirc\!\!-Si-OSiMe_3}} \ + \ \underset{}{Me-\overset{\overset{O}{||}}{C}-\overset{\overset{H}{|}}{N}-SiMe_3}$$
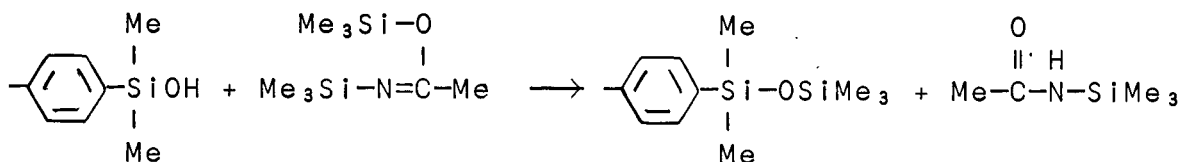
Change in durometer hardness as the elastomers were heated at 350°C was used as the measure of thermal stability. For comparison, Viton A was observed under identical conditions, and it can be seen from the data in Table III and Figure 1 that both hydrolysis and end-capping improved thermal stability. Data on the premilling treatments and the physical properties of the resulting elastomers are in Table I. Data on changes in durometer hardness are in Figure 1 and Table III. Viton A was much harder initially and reached a durometer hardness of 99 in about 8 hours at 350°C while the silphenylenes required 15 hours or more to reach the same hardness.
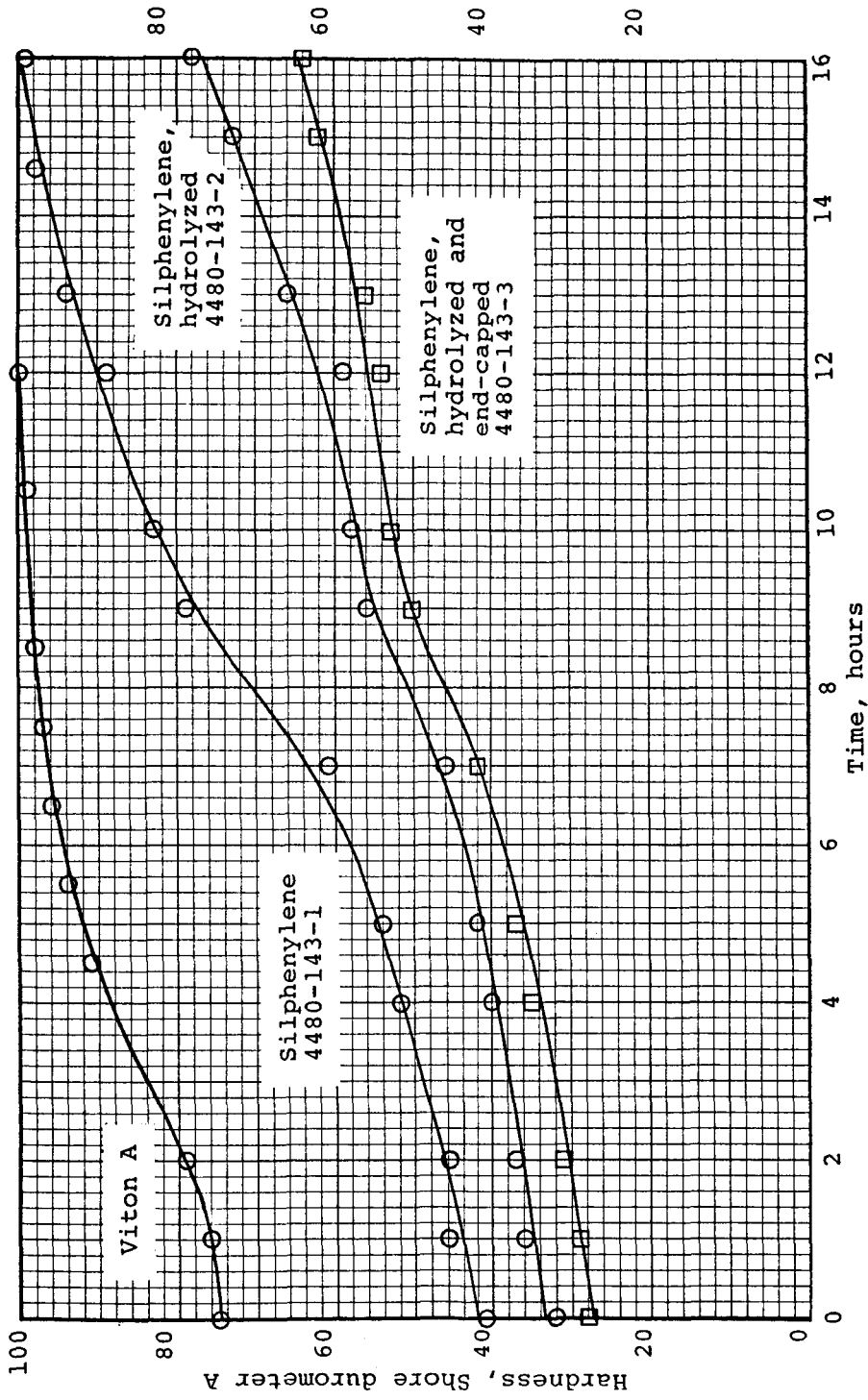
Figure 1. Changes in Hardness of Elastomers at 350°C in Air

Table III. Hardness of Elastomers after Exposure to Air at 350°C in Air
(Durometer hardness, Shore "A")

Exposure time, hr	143-1	111-2	117-2	Elastomer 4480- 143-2	123-2a	123-2	143-3	Viton A
Treatment	none	hydrolyzed	hydrolyzed	hydrolyzed	hydrolyzed, capped	hydrolyzed, capped	hydrolyzed, capped	
$\bar{M}_w{}^b$	265,000	100,000	240,000	265,000	240,000	240,000	265,000	
0	41	50	47	32	49	49	28	75
1	46	53	51	36	51	51	29	76
2	46	53	55	37	53	54	31	79
3	—	55	59	—	—	56	—	—
4.0	52	56	68	40	—	57	35	—
4.5	—	—	—	—	61	—	—	91
5.0	54	57	71	42	—	58	37	—
5.5	—	—	—	—	63	—	—	94
6.5	—	57	75	46	65	58	42	96
7.0	61	—	—	—	—	—	—	—
7.5	—	—	—	—	67	—	—	97
8.5	—	58	77	—	—	60	—	—
9.0	79	—	—	56	74	—	51	98
10.0	83	—	—	58	—	—	53	—
10.5	—	—	—	—	84	—	—	99
12	89	—	—	59	89	—	55	100
13	94	—	—	66	—	—	57	—
15	98	—	—	73	—	—	62	—
16	99	—	—	78	—	—	64	—

a. Heated in the furnace with Viton A, see text for discussion.
b. Estimated from solution viscosity correlated with $\bar{M}_w$ from light scattering.

Elastomer 4480-123-2, which was hydrolyzed and end-capped, was heated in two experiments to determine the rate of hardening. In one, the sample was adjacent to Viton A in the furnace, and it hardened at a slightly higher rate than the other silphenylenes, which were not heated with Viton A. The Viton emitted enough corrosive material to etch the aluminum sheet on which it rested. In a third experiment, for which data are not given in Table III, Viton A and a silphenylene were heated in contact with each other in a closed test tube, and both the Viton A and the silphenylene were drastically degraded. Evidently, gaseous products evolved by the Viton accelerated degradation of both materials.

e. Crosslinking with aminosilane

Work in progress indicates that the diphenylsilane-silphenylene ethers can be crosslinked to some extent by treatment with tris(dimethylamino)phenylsilane. The tackiness of samples heated with the aminosilane was decreased, but it is too early to know whether the reaction will be satisfactory for curing elastomers.

f. Quantity of polymer available

The contract stipulated that 250 g of the diphenylsilane-silphenylene ether should be made available for milling and curing studies at George C. Marshall Space Flight Center. The materials prepared are listed in Table IV.

2. Poly[1,4-bis(oxydimethylsilyl)benzene dimethylsilane]

Poly[1,4-bis(oxydimethylsilyl)benzene dimethylsilane] was prepared to determine the effect on glass-transition temperatures of substituting methyl for phenyl groups as R in the formula
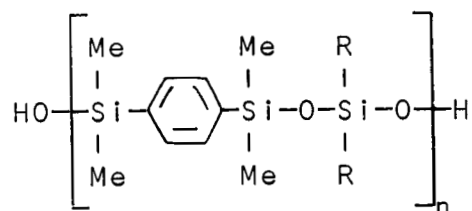
The dimethyl-silphenylene ether was prepared by the reaction:
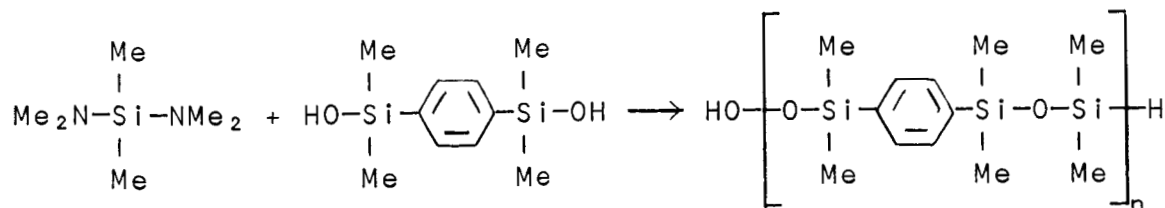
Table IV. Molecular Weights of Various Preparations of
Poly[1,4-bis(oxydimethylsilyl)benzene diphenylsilane]

Polymer 4480-	Amount, g	Inherent viscosity,[a] dl/g	Estd MW[b]
25	15.9	0.83	410,000
47	15.9	0.30	100,000
49	15.8	0.80	385,000
57	35.8	0.62	265,000
65	44.5	0.43	180,000
73	47.7	0.19	51,000
75	14.5	0.62	260,000
79	43.6	0.63	270,000
81	31.5	0.61	250,000
	265.2		

a. Inherent viscosity measured in tetrahydrofuran at
    30°C at 1 g/deciliter.

b. Estimated from solution viscosity measurements
    according to the data in Reference 8.

The raw polymer had a glass-transition temperature of -63°C.
Hence, substitution of methyls for phenyls in the $-SiR_2O-$ group
reduced the glass transition temperature by 63°C. The inherent
viscosity of the polymer was 0.62 dl/g, and its molecular weight,
$\overline{M}_w$, was 160,000 as determined by light scattering. Attempts to
cure it with peroxides resulted in a soft, resilient polymer
that could be crumbled with the fingers. No satisfactory method
of incorporating the peroxide was found. Because of the soft,
tacky nature of the polymer at room temperature, an attempt was
made to add the peroxide to a benzene solution of the polymer.
Foaming occurred during subsequent heating to cure the polymer.

3. Attempt to prepare copolyethers of diorganosilanols and
    dimethylbis[4-(dimethylhydroxysilyl)phenoxy]silane

Because of the continuing need for polymers with improved
low-temperature properties, an attempt was made to prepare polymers
with a structure that contained elements favorable to both low-
and high-temperature performance.

$$\begin{array}{ccccccc} & Me & & Me & & Me & R \\ & | & & | & & | & | \\ -Si & -\underset{}{\bigcirc}- & O-Si-O & -\underset{}{\bigcirc}- & Si-O-Si-O \\ & | & & | & & | & | \\ & Me & & Me & & Me & R \end{array}$$
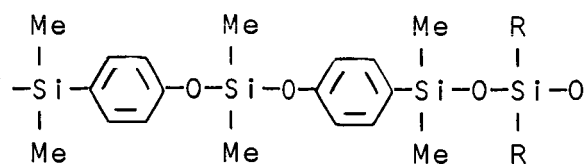
High-temperature properties would be favored by phenylene groups in the main chain and by having R = phenyl. Low-temperature properties would be favored by the large amount of Si-methyl. The following scheme of reaction was planned:

1. $(EtO)_2SiMe_2$ + Br-$\bigcirc$-OH $\longrightarrow$ EtOH + Br-$\bigcirc$-O-$\overset{\overset{Me}{|}}{\underset{\underset{Me}{|}}{Si}}$-O-$\bigcirc$-Br

2. Br-$\bigcirc$-O-$\overset{\overset{Me}{|}}{\underset{\underset{Me}{|}}{Si}}$-O-$\bigcirc$-Br $\xrightarrow[\text{Me}_2\text{SiCl}_2]{\text{Mg}}$

Cl-$\overset{\overset{Me}{|}}{\underset{\underset{Me}{|}}{Si}}$-$\bigcirc$-O-$\overset{\overset{Me}{|}}{\underset{\underset{Me}{|}}{Si}}$-O-$\bigcirc$-$\overset{\overset{Me}{|}}{\underset{\underset{Me}{|}}{Si}}$-Cl

3. $-\overset{\overset{Me}{|}}{\underset{\underset{Me}{|}}{Si}}$-Cl $\longrightarrow$ $-\overset{\overset{Me}{|}}{\underset{\underset{Me}{|}}{Si}}$-OH $\xrightarrow{R_2SiNMe_2}$ polymer
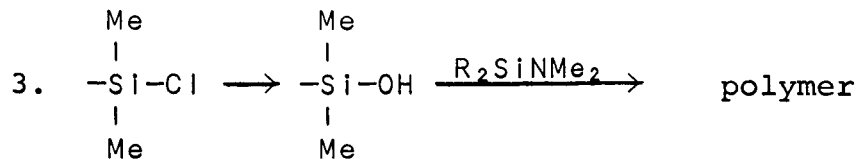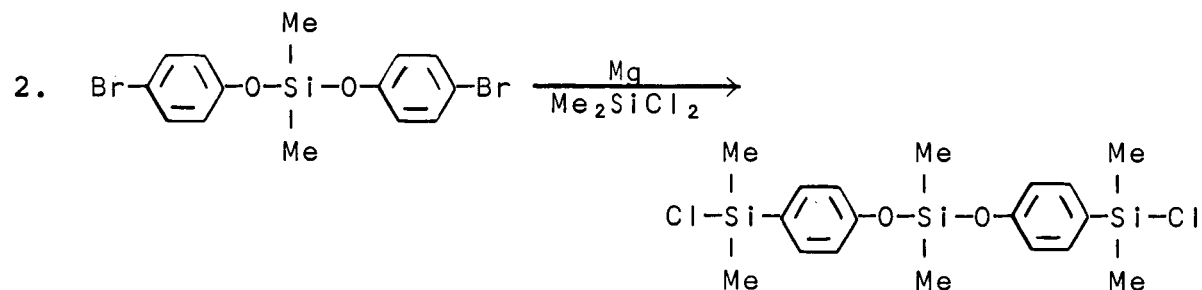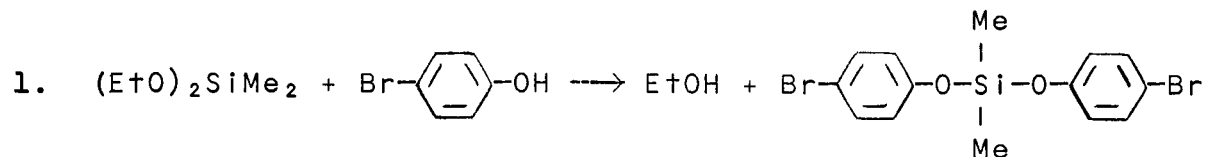
Reaction 1, above, was completed without difficulty, but Reaction 2 was not successfully carried out. Reaction 2 appeared to be comparable to that used for preparing 1,4-bis(dimethylchlorosilyl)benzene, but the magnesium did not react.

B. Experimental Details

1. Preparation of compounds

a.   1,4-Bis(dimethylchlorosilyl)benzene

The method of Sveda[11] was used to prepare 1,4-bis(dimethyl-chlorosilyl)benzene in a 5-liter, 3-neck flask fitted with a stirrer and an extraction device. The extraction device consisted of a still with a partial take-off head which was arranged to return the distilled solvent to the reaction flask through a reservoir of p-dibromobenzene (400 g, 1.69 moles), which also contained 200 ml of ether. In the flask were placed 124.0 g (5.09 moles) of magnesium turnings, 800 ml of dry diethyl ether, and 656 g (5.09 moles) of dimethyldichlorosilane. The system was swept with dry nitrogen, and the reaction was started by gentle heating after adding about 50 ml of the ether solution of p-dibromobenzene. The flask was warmed slightly to reflux the ether which extracted the p-dibromobenzene from the reservoir. As the dibromobenzene returned to the flask, the exothermic reaction kept the ether distilling. After reaction was complete (4 hours), the mixture was refluxed for 30 minutes. The mixture was filtered with a filter stick, the cake was washed with ether, and the ether solutions were combined and distilled. When most of the ether was gone, 400 ml of dry toluene was added and distilled at atmospheric pressure to assure removal of the dichloro-silane. The product remaining in the flask was then distilled at reduced pressure, and the portion that distilled at 110-111°C at 1.5 mm pressure was retained as product. The product weighed 202 g, 46% of theory. It was a white crystalline solid.

b.   1,4-Bis(dimethylhydroxysilyl)benzene

Because of wide variations in yields, 0-81%, hydrolysis of the silphenylene chloride to the diol was tried by a variety of methods. The one adopted is described below in paragraph (4). With that method the yields have varied from 72-84%. Carbon tetrachloride is the preferred solvent for recrystallization. The solubility of the diol is roughly 2% at the boiling point and 0.1% at room temperature. Partly polymerized diol is much more soluble.

(1) Hydrolysis with ammonium hydroxide

A distilled fraction of 1,4-bis(dimethylchlorosilyl)-benzene, b.p. 113-118°C at 0.5 mm, 30.39 g (0.115 mole), was dissolved in 500 ml of dry ether and dropped slowly with rapid stirring into 2500 ml of an aqueous mixture of ice, 115 ml of concentrated ammonium hydroxide (1.7 moles), and 200 ml of ether. After the solution had been stirred for 1 hour, the

layers were separated. The aqueous layer was extracted 4 times
with 200 ml of ether in each washing. The ether layer was
extracted once with 50 ml of water. The ether solutions were
combined, and the ether was allowed to evaporate. The yield
of crude diol from the ether solutions was 21.9 g (0.097 mole).
This crude diol was recrystallized twice from carbon tetra-
chloride to yield 15.12 g (58% yield) of 1,4-bis(dimethyl-
hydroxysilyl)benzene that had a melting point of 135.5-136.5°C.

(2) Hydrolysis with sodium acetate

In a 2-liter Erlenmeyer flask were placed 200 ml of ether
and 1 liter of an aqueous solution containing 197 g (2.4 mole)
of sodium acetate (anhydrous). This mixture was cooled to 0°C,
and 26.7 g (0.010 mole) of 1,4-bis(dimethylchlorosilyl)benzene
(b.p. 119-125°C at 1.0 mm) dissolved in 100 ml of ether was
added slowly to the cold solution with stirring. The two layers
were separated, and the water layer was extracted with two 100-ml
portions of ether. The product from the ether was 19.12 g of
crude diol, m.p. 105-115°C. After two recrystallizations from
carbon tetrachloride, 12.34 g (54% yield), m.p. 136-137.5°C, was
obtained.

(3) Conversion to the silanol acetate followed by hydrolysis

In a 1-liter, 3-neck flask equipped with stirrer, reflux
condenser and Dean-Stark trap for collecting water were placed
300 ml of dry toluene and 14.02 g (0.171 mole) of anhydrous
sodium acetate. The mixture was refluxed for 8 hours, which
was about 2 hours beyond the time when water was no longer
collected by the trap. 1,4-Bis(dimethylchlorosilyl)benzene,
b.p. 113-118°C at 0.5 mm, 21.0 g (0.080 mole), was dissolved in
100 ml of toluene, and the solution was added slowly to the
mixture in the flask. The mixture was refluxed 6 hours, and the
insoluble matter was filtered off and washed with toluene. The
toluene was removed from the filtrate under reduced pressure.
The product, 20.5 g, was a white solid melting at 47-49.5°C.
The infrared spectrum of the product indicated that it contained
the silanol ester group.

About half of the product, 10.0 g, was dissolved in 50 ml
of ether. This solution was added slowly with stirring to 250 ml
of a mixture of ice, 100 ml of water, and 50 ml of ether. The
mixture was stirred for 2 hours, and then 10.5 g (0.1 mole) of
anhydrous sodium carbonate was added, and the two layers were
separated. The water layer was saturated with sodium chloride
and then extracted with two 50-ml portions of ether. The com-
bined ether portions were dried over sodium carbonate and
filtered. After the ether was evaporated, 7.2 g of crude diol

remained. The diol was recrystallized from carbon tetrachloride
to yield 4.74 g (54% yield) of diol melting at 135.5-136°C. The
residue obtained by evaporation of the mother liquor was examined
by pmr spectra and found to contain very little silanol. Evi-
dently the loss in yield was caused by formation of polymer.

(4) Hydrolysis with sodium hydroxide

The most noteworthy feature of the following procedure is
believed to be neutralization after hydrolysis. This operation
must be done carefully to avoid acidification. It greatly
facilitates the ether extraction, which is important because
the entire procedure should be completed as fast as possible.
In many reactions, yields varied from 72-84% on amounts of
chloride ranging from 10-40 g.

1,4-Bis(dimethylchlorosilyl)benzene, 9.89 g (0.0376 mole),
was weighed and dissolved in 150 ml of ether in a nitrogen
atmosphere. The ether solution was then added dropwise to a
solution of 40.0 g (1.0 mole) of sodium hydroxide in about
1500 ml of ice and water mixture that was being stirred rapidly.
The addition required 30 minutes. After the addition was
complete, hydrochloric acid (1:1) was added dropwise with stirring
until the solution was acidic to phenolphthalein and alkaline to
bromthymol blue (pH about 8). The reaction mixture was extracted
four times with 250-ml portions of ether, and the combined ether
extracts were dried with anhydrous sodium sulfate. The ether
was then evaporated with the aid of a stream of nitrogen and
mild heating so the temperature remained below about 20°C. The
crude, white crystals melted at 132.5-135.0°C. One recrystalli-
zation from 750 ml of carbon tetrachloride yielded 6.90 g of
diol (81.1% of theory), m.p. 136-137°C.

c. Bis(methylamino)diphenylsilane

Bis(methylamino)diphenylsilane was prepared by the method
of Larsson and Bjellerup[12] but with some modification to increase
the yield. In a 2-liter, 3-neck flask fitted with a magnetic
stirrer, reflux condenser, thermometer, and dropping funnel was
placed 500 ml of anhydrous ether. The ether was cooled to -15°C.
Methylamine was drawn as a liquid from a cylinder into a 500-ml
Erlenmeyer flask which was filled to a mark at the 325-ml level,
and three pea-size pieces of sodium were added. A small amount
of reaction with the sodium was detected, but it subsided quickly.
The methylamine, estimated 250 g (8.0 moles), was decanted into
the cooled ether. Then diphenyldichlorosilane, 166 ml (202 g,
0.8 mole), was added dropwise with stirring while the reaction
mixture was kept below -15°C. The addition required 2.5 hours.
The mixture was allowed to warm to room temperature, then it was

refluxed for 1 hour. The salts were filtered off and washed with benzene. The benzene and ether solutions were combined, and the solvents were removed by distillation. Distillation of the product through a 30 x 1.2-cm packed column produced 159.3 g of material with a boiling point of 103-104°C at 0.2 mm (82% of theory). The melting point was 20.5-22.0°C.

Considerable difficulty was experienced in obtaining reproducibly high molecular weights until fractions of bis-(methylamino)diphenylsilane were screened to insure that they had high enough melting points. Fractions from distillations were suspended in a controlled-temperature water bath, and the amount of solid in each was estimated visually after the samples had been in the bath for about 4 hours, which was the time required for them to reach equilibrium. Fractions that were at least 50% solid at 21.7°C were combined and used in a polymerization that produced polymers with a molecular weight of 390,000. By contrast, the molecular weight obtained with a fraction that was only 5% solid at 21.7°C was only 100,000.

The stability of bis(methylamino)diphenylsilane is also a matter of concern if polymers of high molecular weight are to be produced. Table IV shows the variations in molecular weights of Polymers 4480-49, -57, -65, and -73, which were prepared successively from the same stock of bis(methylamino)diphenylsilane. The progressively lower molecular weights suggested that degradation of the monomer was occurring during handling and storage. After the monomer was repurified by distillation, the next three polymerizations yielded products with higher molecular weights.

d. Tris(dimethylamino)phenylsilane

Tris(dimethylamino)phenylsilane was prepared in the manner described for bis(methylamino)diphenylsilane but with phenyltrichlorosilane and dimethylamine. In the first distillation, a fraction boiling at 58-59°C at 0.2 mm (71% of theory) was obtained. This was judged to be 94% pure by gas chromatography; redistillation produced a fraction that was judged to be 99% pure(45% yield). Pmr spectra showed the ratio of methyl to phenyl protons to be 18:5 (theory, 18:5).

Anal. Calculated for $C_{12}H_{23}N_3Si$: C 60.71, H 9.76, N 17.70, Si 11.83.

Found: C 61.00, H 9.74, N 17.89.

Mol. wt. Calculated: 237.4.

Found (vapor osmometry): 254.

-19-

e. Bis(dimethylamino)dimethylsilane

In a three-liter, three-neck flask fitted with a thermometer, reflux condenser, stirrer, and gas-inlet tube were placed 194 g (1.5 mole) of dimethyldichlorosilane and 1500 ml of benzene. Liquid dimethylamine, approximately 400 g (8.9 mole), was drawn from a cylinder into a flask containing a few pea-size pieces of sodium and distilled slowly through a rubber tube into the reaction flask over a period of about 5 hours as the chlorosilane and benzene were stirred. The salt formed was filtered off and washed with benzene, and the combined benzene solutions were found to give a positive Beilstein Test for halogens. Consequently, introduction of methylamine was resumed as before with the formation of additional insoluble salt. The reaction mixture was filtered, and the filtrate was distilled through a 15-inch Widmer column to yield 90 g (41% of theory) of bis(dimethylamino)-dimethylsilane, b.p. 121°-121.5°C at 750 mm pressure. Anderson[13] reported 128.4°C at 760 mm.

f. Bis(4-bromophenoxy)dimethylsilane

p-Bromophenol (436 g; 2.52 moles) and diethoxydimethylsilane, 186.7 g (1.26 moles), were placed in a round-bottom flask equipped with a thermometer well, magnetic stirring bar, and a 15-in. Widmer column topped by a fraction-cutting, partial take-off head. The system was stirred and heated to gentle reflux. The ethanol-diethoxydimethylsilane azeotrope (88% ethanol, b.p. 78°C) was removed periodically during a total heating period of 14 hr, at the end of which the temperature in the reaction vessel had reached 230°C.

The residue was then distilled under water-aspirator vacuum, and unchanged p-bromophenol (86.5 g; 19.8%) was recovered. The pressure was reduced and two fractions were distilled:

1. 4-Bromophenoxyethoxydimethylsilane, b.p. 80°-81°C at 0.6 mm; yield 32 g or 4.4% based on p-bromophenol.

2. Bis(4-bromophenoxy)dimethylsilane, b.p. 150°-152°C at 0.20-0.25 mm; yield 357 g or 71% based on p-bromophenol.[14]

Anal. Calculated for $C_{14}H_{14}Br_2O_2Si$: C 41.81, H 3.51, Br 39.74.

Found: C 42.01, H 3.55, Br 39.8.

g. Attempted synthesis of bis[4-(chlorodimethylsilyl)-phenoxy]dimethylsilane

Freshly distilled bis(4-bromophenoxy)dimethylsilane, 400 g (1 mole), in ether solution was added slowly to a refluxing solution-suspension of magnesium turnings, 73 g (3 moles), and dichlorodimethylsilane, 390 g (3 moles), in ether. The dichloro-silane-magnesium-ether system had been activated with a small amount of methyl iodide. There was a moderate exothermic effect during the course of the addition but little or no magnesium was consumed in 5 hours of refluxing. The magnesium and a small quantity of white solid were removed by filtration, and the filtrate was fractionally distilled in vacuo to recover 80-90% of the original bis(4-bromophenoxy)dimethylsilane.

Bis(4-bromophenoxy)dimethylsilane, 400 g (1 mole), dichloro-dimethylsilane, 260 g (2 moles), and magnesium turnings, 48.6 g (2 moles), were heated together at gentle reflux in tetrahydro-furan for 7 hours. No reaction took place even upon addition of methyl iodide followed by a crystal of iodine. Essentially all of the bis(4-bromophenoxy)dimethylsilane was recovered.

An attempt was made to form a normal di-Grignard reagent from bis(4-bromophenoxy)diemthylsilane and magnesium turnings both in anhydrous diethyl ether and in tetrahydrofuran. No reaction took place in either solvent.

2. Polymerization

a. Poly[1,4-bis(oxydimethylsilyl)benzene diphenylsilane]

(1) Preliminary work

Polymerizations did not produce high molecular weights consistently until satisfactory methods of purifying monomers were developed as described above. Then the polymerization method described in Section 2.a.(2), below was adopted for all preparations. Prior to that time a large amount of effort was spent in trying to develop a satisfactory heating schedule and compensate for impurities by adding a slight excess of one reactant. The reaction to form Polymer 3992-151-1 is an example of the entire group, details of which are in Table V. Bis-(methylamino)diphenylsilane, 11.06 g (0.0456 mole), was dissolved in 50 ml of dry toluene in a 300-ml, 3-neck, round-bottom flask fitted with a thermometer, stopper, small reflux condenser, and magnetic stirrer. Then 10.30 g (0.0455 mole) of tetramethyl-p-silphenylene diol was added with 50 ml of toluene. The toluene was refluxed for 2 hours and removed by distillation, finally at reduced pressure. The mixture was heated 2 hours at 200°C

Table V. Preparation of Poly[1,4-bis(oxydimethylsilyl)benzene diphenylsilane] (Reaction of bis(methylamino)diphenylsilane with 1,4-bis(dimethylhydroxysilyl)benzene in toluene)

Reactants	Method — Polymerization conditions				Viscosity, η_{inh}, dl/g [a]	MW estd [b]	Polymer number
	Solution, Reflux time, hr	Melt, Temp, °C	Time, hr	Press, mm			
stoichiometric[c]	2.0	200	2.0	atm	-	-	-
		240	1.5	0.02	0.074	-	-
		240	8.0	0.02	0.071	-	-
		240	8.0[d]	0.02	0.071	-	-
		240	16.0[e]	0.02	0.074	-	3992-151-1
stoichiometric[c]	1.8	240	2.0	0.02	0.26	83,000	
		240	2.0	0.02	0.27	88,000	
		240	8.0	0.02	0.28	90,000	
		240	6.0[f]	0.02	0.28	90,000	4414-3-1
stoichiometric[c]	2.3	240	8.0	0.02	0.14	-	
		240	4.0	0.02	0.14	-	4414-9-1
1% deficiency of diol	11.5	-	-	-	0.072	-	
	6.0	-	-	-	0.081	-	
		350	6.0	0.01	0.095	-	4414-17-1
1% excess diol	6.5	-	-	-	0.046	-	
	14.5	-	-	-	0.057	-	
		400	<0.1	0.02	0.60	250,000	
		350	6.0	0.01	0.44[g]	165,000	4414-17-2
0.5% excess diol	12.0	-	-	-	0.088	-	
		210	0.1	50[h]	0.11	19,000	
		350	2.0	0.005	0.15	32,000	4414-21-1
1.5% excess diol	12.0	-	-	-	0.10	15,000	
		210	0.1	50[h]	0.13	26,000	
		350	2.0	0.005	0.14	30,000	4414-21-2
0.75% excess diol	7.0	-	-	-	0.046	-	
		210	0.1	50[h]	0.055	-	
		310	0.5	0.02	0.059	-	4414-27-1
1.0% excess diol	7.0	-	-	-	0.051	-	
		210	0.1	50[h]	0.044	-	
		320	0.5	0.02	0.059	-	4414-27-2
1.25% excess diol	7.0	-	-	-	0.062	-	
		210	0.1	50[h]	0.15	31,000	
		330	0.5	0.01	0.18	46,000	4414-27-3

a. Inherent viscosity measured in tetrahydrofuran at 30°C at concentrations of 1.00 g per deciliter.

b. Estimated from solution viscosity measurements according to the data of Reference 8.

c. Assuming 100% purity.

d. After addition of 0.3% of stoichiometric amount of diol.

e. After addition of 0.6% of stoichiometric amount of diaminosilane on three successive occasions.

f. After addition of 0.5% of stoichiometric amount of diol.

g. Partly insoluble. The measurement was made on the soluble fraction.

h. Toluene removed at the reduced pressure of a water aspirator.

at atmospheric pressure and then at 240°C for 1 hour at 0.02 mm pressure. The inherent viscosity was 0.07 at 1 g per deciliter in tetrahydrofuran at 30°C. An additional 8 hours of heating at 240°C at 0.02 mm resulted in no change in the inherent viscosity. Consequently, 0.030 g (0.13 millimole) of diol was added in case there had been a deficiency of diol. Six hours of additional heating at 240°C at 0.1 mm pressure did not change the viscosity. Then 0.0602 g (0.24 millimole) of bis(methylamino)diphenylsilane was added on three successive occasions, each followed by several hours of heating at 240°C at 0.1 mm pressure; but the viscosity did not change.

Measurements of solution viscosity were used to estimate molecular weights according to data previously obtained for the relationship between viscosity and molecular weights as determined by light scattering.[8]

(2) Preferred method

Details of a number of reactions to prepare poly[1,4-bis(oxydimethylsilyl)benzene diphenylsilane] are given in Table VI, and one of them, Polymerization 4480-5, is described as an example. A weighed amount of the diol (Table VI) was placed in a 50-ml, round-bottom, 2-neck flask that had been swept with dry nitrogen and fitted with a reflux condenser and magnetic stirrer. Then, while nitrogen was passing slowly through the flask, a stoichiometric amount of bis(methylamino)-diphenylsilane was added from a syringe. Toluene, 2.0 ml, was added, a thermometer was inserted into the vacant neck, and the mixture was heated in an oil bath on a magnetic stirrer hot plate. The apparatus was protected from air by a rubber balloon attached to the condenser. The balloon was emptied whenever it became inflated enough to exert appreciable pressure on the system. The change was made from solution polymerization to melt polymerization by removing the toluene. Since the amount of toluene was only 2.0 ml in 16 g of reactants, the toluene served principally as a scavenger of reactants from the walls of the flask. As the reaction temperature increased, more and more of the toluene was in the vapor above the melt. When the time arrived to remove the toluene, it was drawn off very slowly as a vapor with a long thin tube thrust into the zone of refluxing vapor. The last traces were removed when the pressure was reduced to complete the polymerization.

Table VI. Preparation of Poly[1,4-bis(oxydimethylsilyl)benzene diphenylsilane]
(Reaction of bis(methylamino)diphenylsilane with 1,4-bis(dimethylhydroxysilyl)benzene in toluene)

Polymer	Reactants			Reaction conditions					Product	
	g (millimole)	g (millimole)	Solvent, ml	Solution[a]		Melt[a]			Inherent vis.,[b] dl/g	Estd. M_W
				Time, hr	Temp., °C	Time, hr	Temp., °C	Pressure		
4414-35	2.3520 (9.703)	2.1970 (9.703)	30[d]	0.5 1.5 5.8	27 27-80 110	1.0	310	atm	0.08	6,000
-39	1.9343 (7.980)	1.8068 (7.980)	none	-	-	1.0 1.0 1.0 2.0	80 140 170 260	atm atm atm 0.1 mm	0.50	200,000
-41	1.7896 (7.383)	1.6706 (7.378)	15	2.0	110	0.5	270	0.1 mm	0.64[e]	280,000
-45	2.2472 (9.271)	2.0989 (9.270)	none	-	-	0.5 1.0 0.8	95 220 220	atm atm 0.1 mm	0.28	90,000
-57	3.2906 (13.575)	3.0737 (13.575)	20	1.0 1.5	75 110	0.3 0.8 1.5	130 220 275	30 mm 0.1 mm 0.1 mm	0.33	115,000
-61	3.6114 (14.899)	3.3734 (14.879)	2.0[f]	0.5 1.0 0.3	115 145 190	0.3 0.2 0.7	195 210 265	atm 0.1 mm 0.1 mm	0.32	110,000
-67	3.8298 (15.800)	3.5811 (15.816)	2.0[f]	1.0 1.0 1.0	60 110 150	0.3 0.7 1.0	150 220 260	atm 0.1 mm 0.1 mm	0.32	110,000
-71	3.7959 (15.660)	3.5479 (15.669)	2.0[f]	0.5 1.5 1.0 1.3	80 80-25 25-120 150	0.5 0.5	240 260	0.1 mm 0.1 mm	0.63	275,000
4480-5	8.2187 (33.90)	7.6769 (33.90)	2.0[f]	2.0 2.0	45-90 90-160	1.5	160-240	0.1 mm	0.66	290,000

a. Reactions run first in toluene, then as melt after removal of toluene.

b. Inherent viscosity measured in tetrahydrofuran at 30°C at concentrations of 1.00 g per deciliter.

c. Estimated from solution viscosity measurements according to the data of Reference 8.

d. Methylamine added to facilitate solution of diol at room temperature.

e. A portion of this polymer was insoluble; data given are for soluble portion.

f. At this low concentration of toluene, the reaction temperature could be raised well above the boiling point of toluene. See text for explanation.

(3) Control of molecular weight.

To determine whether stoichiometry could be used to control the molecular weight of the polymers, a 0.7% excess of diol was used in one reaction between bis(methylamino)diphenylsilane and 1,4-bis(dimethylhydroxysilyl)benzene. This was the amount calculated to give a molecular weight of 60,000. The amounts that reacted according to the procedure of the preceding paragraph were bis(methylamino)diphenylsilane, 4.848 g (0.02000 mole), and 1,4-bis(dimethylhydroxysilyl)benzene, 4.559 g (0.02014 mole). The inherent viscosity of the product, Polymer 4480-27, was 0.33 dl/g, which indicated a molecular weight of 115,000.[8] In contrast, a polymerization with stoichiometric equivalents of the same diamine and diol produced Polymer 4480-25 with an inherent viscosity of 0.83 dl/g (estimated molecular weight, 410,000).

b. Poly[1,4-bis(oxydimethylsilyl)benzene dimethylsilane]

The dimethylsilane-silphenylene ether was prepared as follows:

Bis(dimethylamino)dimethylsilane, 9.703 g (0.06623 mole), was added from a hypodermic syringe to 14.996 g (0.06623 mole) of 1,4-bis(dimethylhydroxysilyl)benzene and 3.0 ml of toluene in a 25-ml round-bottom, 2-neck flask fitted with a thermometer, magnetic stirrer, and reflux condenser. Before addition of the diamine, the apparatus and diol had been swept with dry nitrogen for 30 minutes. The reaction flask was heated gently in an oil bath, and evolution of gas became evident at about 40°C. The temperature was increased gradually over 4.0 hours to 140°C, during which time the melt became viscous. The refluxing toluene was drawn off as a vapor with a long thin glass tube. Then the pressure was reduced to 0.1 mm, and the temperature was increased to 205°C over a period of 3.0 hours. When cool, the polymer would barely flow at room temperature. The polymer had an $\overline{M}_w$ of inherent viscosity of 0.63 dl/g (1% in THF at 25°C) and a $\overline{M}_w$ of 160,000 by light scattering.

3. Hydrolysis and end-capping

Polysilphenylene ethers are now routinely hydrolyzed to remove residual amines. Hydrolysis was investigated because of the possibility that amines might interfere with curing by peroxides, and it was found that hydrolyzed polymers were less sticky during milling. Polymer 4480-47, 15.9 g, estimated molecular weight 100,000, was dissolved in 25 ml of benzene and refluxed with 2.0 g of water for 1.5 hours. Then the excess water was removed with a Dean-Stark trap, and the solvent was allowed to evaporate from a thin film of the polymer solution on Teflon. The inherent viscosity before hydrolysis was 0.30 dl/g, and after hydrolysis it was 0.35 dl/g.

Hydrolyzed polymers were capped with trimethylsilyl groups as a possible means of increasing thermal stability. End-capping apparently improved the thermal stability as shown previously in Figure 1 and Table III, and it definitely made milling easier by making the polymers less sticky.

The silylating agent, bis(trimethylsilyl)acetamide, was prepared in 51% yield from acetamide and trimethylchlorosilane in triethylamine solution by the method of Klebe, et al.[15] A sample of previously hydrolyzed polymer (10 g) was dissolved in warm benzene (50 ml) under nitrogen, bis(trimethylsilyl)acetamide (7 ml) was added, and the mixture was refluxed for 30 minutes. After being cooled, the solution was transferred to a separatory funnel and washed with four portions of water. The solvent and water were removed by evaporation from thin films on Teflon. The inherent viscosity of the capped polymer was essentially the same as that of the starting material.

4. Milling and curing

a. Diphenylsilane-silphenylene ether with silica and peroxides

Methods of milling and curing the polysilphenylene ethers are inadequate at their present state of development, as demonstrated by the low tensile strength and solvent susceptibility of the elastomers produced. The methods tried have been mainly those that are used for silicones, namely, reinforcing with silica and crosslinking with peroxides. Press molding of milled polymers containing silica and peroxide at temperatures of 150-190°C definitely increased the elasticity. However, post-curing for 8-24 hours at 300-320°C in air was required to obtain the maximum tensile strengths of about 550 psi. The initial experiments are summarized in Table VII, and later experiments are summarized in Table I. At first, polymers were milled on a Teflon sheet with a Teflon roller. Later, especially after hydrolysis and end-capping were adopted, polymers were milled on a paint mill with stainless steel rolls. It was necessary to keep the rolls cool, 25°C or less, to prevent excessive sticking. Very little experimentation was done with different peroxides, largely because t-butyl perbenzoate is reported to be one of the most effective crosslinking agents available.[16] Furthermore, it is a liquid, which makes it convenient for use with small samples. However, different peroxides will be tried in an effort to find one that is stable enough to permit the use of a higher curing temperature at which the polymer will coalesce more efficiently.

Table VII. Preparation and Properties of Filled Silphenylene Elastomers
(Polymers of Table VI.)

Elastomer	Polymer	Silica,[a] % of total	Peroxide,[b] % of total	Mold	Time	Temp., °C	Appearance	Tens. str., psi	Elongation, %	Hardness (Shore A)
4414-49	4414-39	13.9	2.0	open	24 min	185	tan, tacky, bubbles, sluggishly elastic	-	-	-
					4 hr	250	similar but tougher and non-tacky		500	
-51	41-1	15.5	1.9	open	1 hr	185	tan, tacky, bubbles, sluggishly elastic			
					4 hr	250	similar but tougher and non-tacky	-	600	-
-47	-45	15.0	2.0	open	17 min	185	tan, tacky, bubbles, sluggishly elastic			
					15 hr	185	similar but tougher and non-tacky			
					15 hr	260	no change			
					30 hr	325	tougher	-	-	-
-59	-57	18.5	1.3	press	12 min	190	poor recovery	90	>5000	
					16 hr	280	tan, sluggishly elastic	120	1900	
					24 hr	320	tan, sluggishly elastic	420	240	53
-65	-61	18.8[c]	1.3	press	12 min	190	sticky, semi-solid	-	-	-
					15 hr	280	soft solid, no recovery			
					24 hr	320	no change			
-69	-67	17.2	1.0	press	17 min	190	tan, cheesy, had fissures			
					1 hr	310	tougher, elastic			
					4 hr	310	tougher, more elastic, small fissures healed			
					8 hr	330	tougher	400	120	63
-75	-71	19.3[d]	1.1[d]	press	16 min	190	many small fissures			
					4.8 hr	310	tan, sluggishly elastic			
					24 hr	310	slightly tougher, small fissures remain	-	-	46
4480-11-1	4480-5	14.7	1.1[e]	press	15 min	150	many small fissures	-	-	-
					15.5 hr	300	fewer fissures	345	240	43
					8.0 hr	320	no change	330	140	43
					8.0 hr	330	no change	330	130	43
-11-2	-5	14.7	1.1[e]	press	45 min	150	few small fissures	-	-	-
					15.5 hr	300	v. few fissures	380	170	43
					8.0 hr	320	no change	320	180	43
					8.0 hr	330	no change	270	120	43

a. Cab-O-Sil M-5.

b. tert-Butyl perbenzoate.

c. Hydrous zirconia from TAM Division of National Lead Co.

d. A small amount of final milling on stainless steel.

e. Milled entirely on stainless steel.

The milled polymers were press molded between heated platens in a mold which was a 2-in. square opening in a 4-in. square aluminum plate 0.065 in. thick. The mold was placed between thin ferro-type (chromium plated) sheets. The surfaces of the mold and the sheets were sprayed with a silicone mold-release agent. About 6.5 g of polymer was required to provide a slight excess. After initial curing in the mold, the specimen was post-cured in an oven.

b. Diphenylsilane-silphenylene ether with tris(dimethylamino)phenylsilane

The silanol ends of polysilphenylene ethers are capable of further reaction with silylamines. Hence, it appeared possible to crosslink polysilphenylene ethers, preferably after the hydrolysis treatment described above in Section III.B.3, by treatment with tri- or tetraaminosilanes. The experiment to be described unquestionably resulted in an increase in elasticity and toughness and a reduction in tack, but the resulting sheet contained too many bubbles to permit useful tensile measurements to be made. The experiment and others are summarized in Table I. Polymer 4480-49, which had been hydrolyzed and had a molecular weight of 385,000, was milled with 13% by weight of Cab-O-Sil M5. The polymer was not excessively sticky. Milling was continued with the addition of 0.5% by weight of tris(dimethylamino)phenylsilane, whereupon the polymer became so sticky that completion of milling was difficult. This amount of aminosilane was chosen largely because it was enough to handle with reasonable assurance that most of it would actually be incorporated. However, it was 12 times the amount stoichiometrically needed to react with the silanol groups calculated to be present. After the milled polymer was press molded at 177°C for 45 minutes, it was soft, sluggishly resilient, and only slightly tacky. Post-curing for 16 hours at 320-340°C reduced the elongation and tack slightly and improved the resilience as judged manually, but the sample contained too many bubbles for meaningful measurements to be made.

c. Dimethylsilane-silphenylene ether with peroxide

Attempts were made to cure poly[1,4-bis(oxydimethylsilyl)-benzene dimethylsilane], molecular weight 160,000, in the following manner: The polymer (8.4 g) was dissolved in benzene (33.6 ml), and tert-butylperbenzoate (0.084 g) was added. After 15 minutes of stirring, the benzene was removed in vacuo, and the residual polymer containing catalyst was divided equally into two portions. The first portion was cured in an aluminum dish for 16 hours at 300°C. The polymer did not seem to be fully cured since it was quite tacky. Consequently, it was

transferred to a ferrotype plate and heated for 24 hours at 300°C. The resulting polymer was soft and friable on the surface, but it was tacky on the inside. The second portion of the polymer was heated on a ferrotype plate in air at 180°C and was still quite tacky after 40 hours. The polymer was further cured for 16 hours at 300°C. The final properties of the polymer so treated were quite similar to those of the first sample just described.

5. Polysilphenylene ethers as pressure-sensitive adhesives

A small sheet of glass cloth impregnated with polyimide, Pyre-ML (du Pont), was coated with a sample of poly[1,4-bis(oxy-dimethylsilyl)benzene diphenylsilane] having a molecular weight of 115,000. A 50% solution of the polymer in benzene was doctored onto the polyimide to form approximately a 4-mil layer after the solvent was removed by exposure at room temperature for 16 hours, at 130°C for 2 hours, and at room temperature at 0.1-0.01 mm pressure for 18 hours. The coated surface was quite sticky, and even Teflon adhered to it. The polymer showed essentially no tendency to leave the polyimide and adhere to other materials pressed against it. The polymer was applied the same way to paper, and the coated sides of two pieces were pressed together. The peel-seal strength was 4.8 lb/in. The peel strength of Scotch Magic Tape from itself was 2.7 lb/in.

Tris(dimethylamino)phenylsilane was tried as a crosslinking agent in an attempt to increase the adhesion. A 50% benzene solution of a diphenyl-silphenylene ether polymer, molecular weight 50,000, was mixed with varying amounts of the triamino-silane crosslinking agent. The calculated stoichiometric ratio of polymer to agent was 320:1 (weight ratio). The agent was added in amounts equal to 0, 0.3, 1, 2, 3, 6, and 10 times the stoichiometric ratio. Each mixture was doctored onto 1-inch square areas of two aluminum strips, air-dried for 15 minutes, and then heated 2 hours at 130°C in air. The coated strips were joined over the 1-inch areas and pressed together by hand. The shear strengths under tensile loading, Table II, show that the shear strengths increased as the agent was increased up to 6 times the stoichiometric ratio. After the joint with a shear strength of 60 psi was broken, the adhesive was still tacky. To determine how it performed under more drastic conditions, it was rejoined, clamped, and heated overnight at 180°C. When cool, it had a shear strength of 190 psi. The sheared surfaces were still tacky. This experiment demonstrates the pressure-sensitive character of the adhesive.

6. Measurement of compressibility

Elastomers were heated in air at 350°C, and their hardnesses were measured periodically with a Shore durometer, "A" scale. Measurements were made at room temperature. Gases evolved from the Viton A etched the aluminum on which it rested in the furnace. The findings are summarized in Table III and Figure 1.

7. Measurement of glass-transition temperatures

The glass-transition temperature of Polymer 4480-79, poly[1,4-bis(oxydimethylsilyl)benzene diphenylsilane], was 0°C ±2°C. The glass-transition temperature of Polymer 4480-115, poly[1,4-bis(oxydimethylsilyl)benzene dimethylsilane] was -63°C ±5°C. Glass-transition temperatures were determined with a Perkin Elmer Differential Scanning Calorimeter.* No attempt was made to refine the measurements further than the limits given above for this preliminary comparison.

IV. POLYSILPHENYLENE AMINES

A. Discussion

In previous work,[17] polysilphenylene amines were found to be sources of protective coatings and resilient foams with high thermal stability. The polysilphenylene amines have exceptional thermal stability as coatings when they are pigmented with aluminum. The pigmented coatings undergo pyrolysis to form adherent inorganic residues that have not failed visibly in several hundred hours at 540°C on titanium, stainless steel or mild steel. The silphenylene amines form resilient foams when they are cross-linked with pentaerythritol. Although these foams are resilient after several hours of heating at 350°C, they have not been cured successfully in large pieces, and they have relatively poor strength compared to foams made from silicone rubber.

*Measurements made by Dr. Allan P. Gray, Perkin-Elmer Corporation, Norwalk, Connecticut.

1. Preparation

The first step in the preparation of polysilphenylene amines is amination of 1,4-bis(dimethylchlorosilyl)benzene with methylamine.
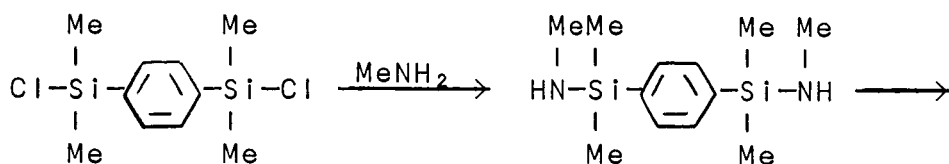
1,4-bis(methylaminodimethylsilyl)-
benzene
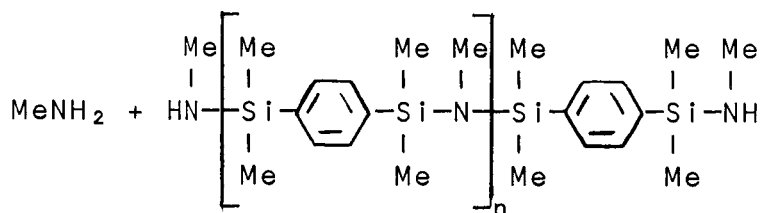
Poly(tetramethyl-p-silphenylene methylamine)

The monomer, 1,4-bis(methylaminodimethylsilyl)benzene polymerizes so readily that it cannot be isolated from the amination reaction unless steps are taken to keep the temperature low. In the product usually obtained, the value of n is less than 100. Polymers of molecular weight about 50,000 (n = 250) are obtained when the silphenylene amine is heated under reduced pressure.

If precautions are taken throughout the preparation to avoid exposure to air, the polymer has essentially the formula shown above; but if air is admitted, part of the =N-Me is replaced by -O-. As an example of the polymer obtained when air is excluded, one polysilphenylene amine had a molecular weight of 52,000 and 92% of the theoretical nitrogen. Such a high nitrogen content is not desirable for making either foams or coatings, but it is of theoretical interest because the polymer is the best example we have made of a silicon-nitrogen polymer with high molecular weight. When first prepared it was elastic, tough, and slightly cloudy. On standing, it crystallized and became white and less elastic. It softened at 51-52°C. An attempt to increase the molecular weight by boiling the polymer in toluene resulted in an increase to 55,000, but at the same time the nitrogen content dropped to 81% of theory. The softening point was still 51-52°C.

When polysilphenylene amines are to be made into foams, the most desirable nitrogen content is 20-40% of the theoretical value, which is 6.32%. It seems to make no difference in the quality of coatings whether the nitrogen content is high or low. In practice, polymerization and partial displacement of the N-Me groups are achieved simultaneously by treating the low-molecular-weight silphenylene amine with 1,4-bis(dimethylhydroxysilyl)-benzene:

+ MeNH$_2$
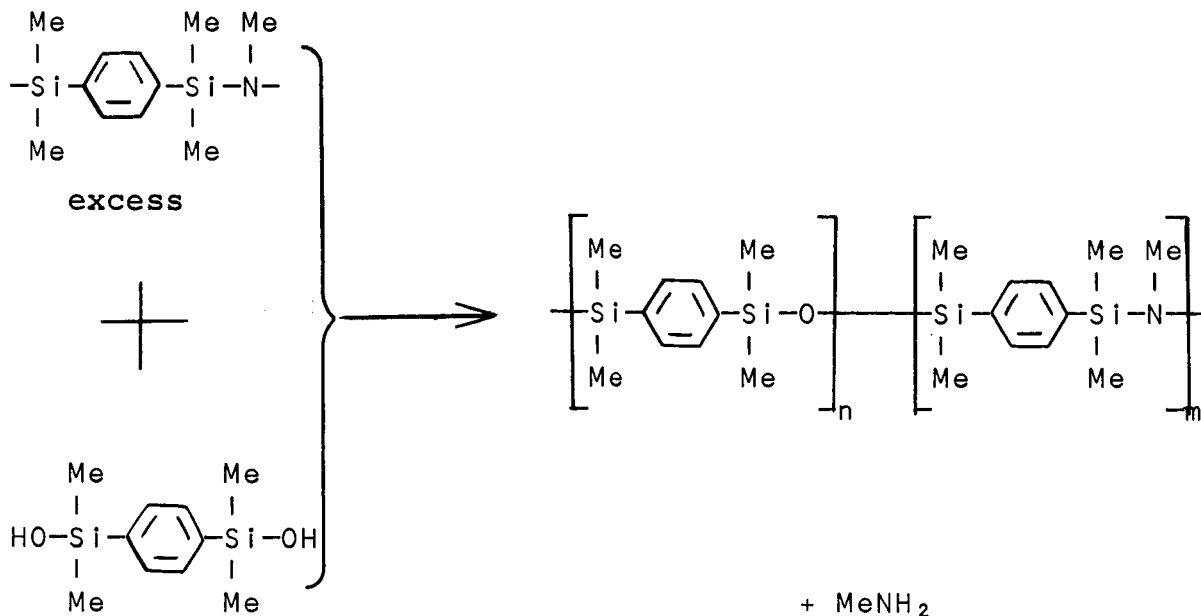
The contract specified that 250 g of polysilphenylene amine be made available for applications studies. The amounts prepared are summarized in Table VIII. Molecular weights were estimated from data previously obtained on the relation of solution viscosity to molecular weight.[18]

It was planned to fractionate a polymeric silphenylene amine by partial reprecipitation to isolate a fraction of exceptionally high molecular weight. A search was made for the required non-reactive non-solvent, but none was found. The polymer dissolves in benzene, tetrahydrofuran, diethyl ether, dioxane, carbon tetrachloride, and hexane. It dissolves partially in dimethylformamide to form a cloudy suspension.

Table VIII. Polymeric Silphenylene Amines

Polymer	N content, %a	Softening point, °C	Inherent viscosity, dl/gb	Est'd MWc	Amount prepared, g	Amount remaining,d g
4369-83	2.52	101-2	0.45	57,000e	75.0	16.0
-145-4	0.74	104-5	0.39	50,000	96.0	57.0
4571-9	2.66	53-4	0.42	54,000	90.1	90.1
-3-3f	6.76	-	0.075	10,000	57.0	57.0
-11-2f	6.52	51-2	0.095	12,500	30.0	30.0
					348.1	250.1

a. Theory for $-Si(CH_3)_2-C_6H_4-Si(CH_3)_2-N(CH_3)-$, $C_{11}H_{19}NSi_2$, 6.32% N.
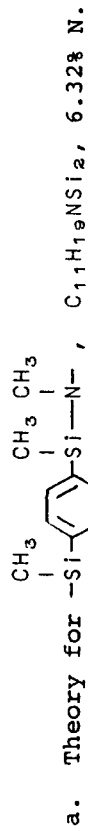
b. Viscosity measurements made in tetrahydrofuran at 30°C at 1.0 g per deciliter.

c. Estimated from solution viscosity, see Reference 18.

d. After experimentation with foams and coatings.

e. 60,000 by light scattering.

f. Not treated with diol to reduce nitrogen content.

2. Coatings

Coatings made from polysilphenylene amines pigmented with aluminum have remained intact on titanium for 675 hours at 540°C (1000°F). The coating had not failed visibly at that time; the exposure was terminated to release the furnace for other use. The coatings, which have the appearance of aluminum paints, were 0.1-0.2 mil thick, and they had lost electrical insulative value. A coating of such a thickness does not afford protection against the embrittling effect of sodium chloride over a period of 1000 hours at 500°F. However, thicker coatings have not been evaluated the same way. It has been found recently that coatings can be applied and cured in thicknesses of 1 mil in one coat without difficulty. It is possible that thicker coatings may provide some protection against sodium chloride. Discussions have been held with manufacturers of jet engines which periodically reach 1200°F in certain areas for which anticorrosive protection is needed. One of the main concerns of these manufacturers is that the available coatings have poor resistance to abrasion, so that, in many applications, they must accept the properties of uncoated titanium. We expect to prepare coated samples for additional evaluations of the coatings.

Experiments with silphenylene amine coatings showed that aluminum has a unique role as a pigment. Coatings made with the polymer alone, polymer pigmented with titanium dioxide, or polymer pigmented with zinc oxide had relatively short life at 400°C. By contrast, coatings made with polymer pigmented with aluminum on titanium, mild steel, and stainless steel remained visibly unaffected after being heated at 540°C for 675, 48, and 90 hours, respectively. In no case did the coating fail visibly; the coatings were intact when the exposures were terminated.

Although protection of titanium is the coating application that is currently of greatest interest, it seems that the performance of the silphenylene coating agent on mild steel is worthy of continued consideration. Coated samples of mild steel retained the appearance of aluminum-painted surfaces for 300 hours at 500°C. Again this was the duration of exposure, not the time of visible failure. Iron oxide flaked from the surface of uncoated areas during the exposure, and, after such exposure, uncoated areas rusted when immersed in water but coated areas remained intact.

Adhesion to copper was relatively poor, but the coating did afford some protection even at red heat as shown by extensive oxidation in the uncoated areas.

Curing of the silphenylene coatings requires heating in air for approximately 3.5 hours at 375°C or 15 minutes at 500°C. The same degree of curing can be accomplished in about 5 minutes by careful heating with a gas burner until smoking ceases. However, none of these methods would be easily adapted to a problem such as repairing a coating that had been damaged. However, curing with a heat gun delivering an air stream at about 500°C would be relatively simple and could be accomplished on an assembled vehicle.

Weight losses on heating were determined for coatings on titanium without pigment and for coatings pigmented with aluminum and titanium dioxide. The unpigmented coating lost about 18% of its weight, the titanium dioxide-pigmented coating lost 10% of the polymer weight, and the aluminum-pigmented coating lost 48% of the polymer weight during curing for 8 hours at temperatures up to 375°C. In 1.5 hours at 450°C, the coatings lost an additional 16%, 11%, and 18% of the initial polymer weights, respectively. At this point the unpigmented and the titanium dioxide-pigmented coatings flaked off the metal. In an additional hour at 540°C, the aluminum-pigmented coating lost another 8% of the initial polymer weight and remained tightly adhered. The weight loss of the aluminum-pigmented coating suggested that the amount remaining was essentially inorganic. The weight losses are shown graphically in Figure 2.

An aluminum-pigmented coating was applied to glass so it could be scraped off and analyzed for organic content. After 3.5 hours at 375°C and 1 hour at 440°C more than half of the original organic matter remained. After an additional 27 hours at 500°C, roughly a quarter remained. The coating remained attached to the glass even after undergoing loss of most of the polymer weight.
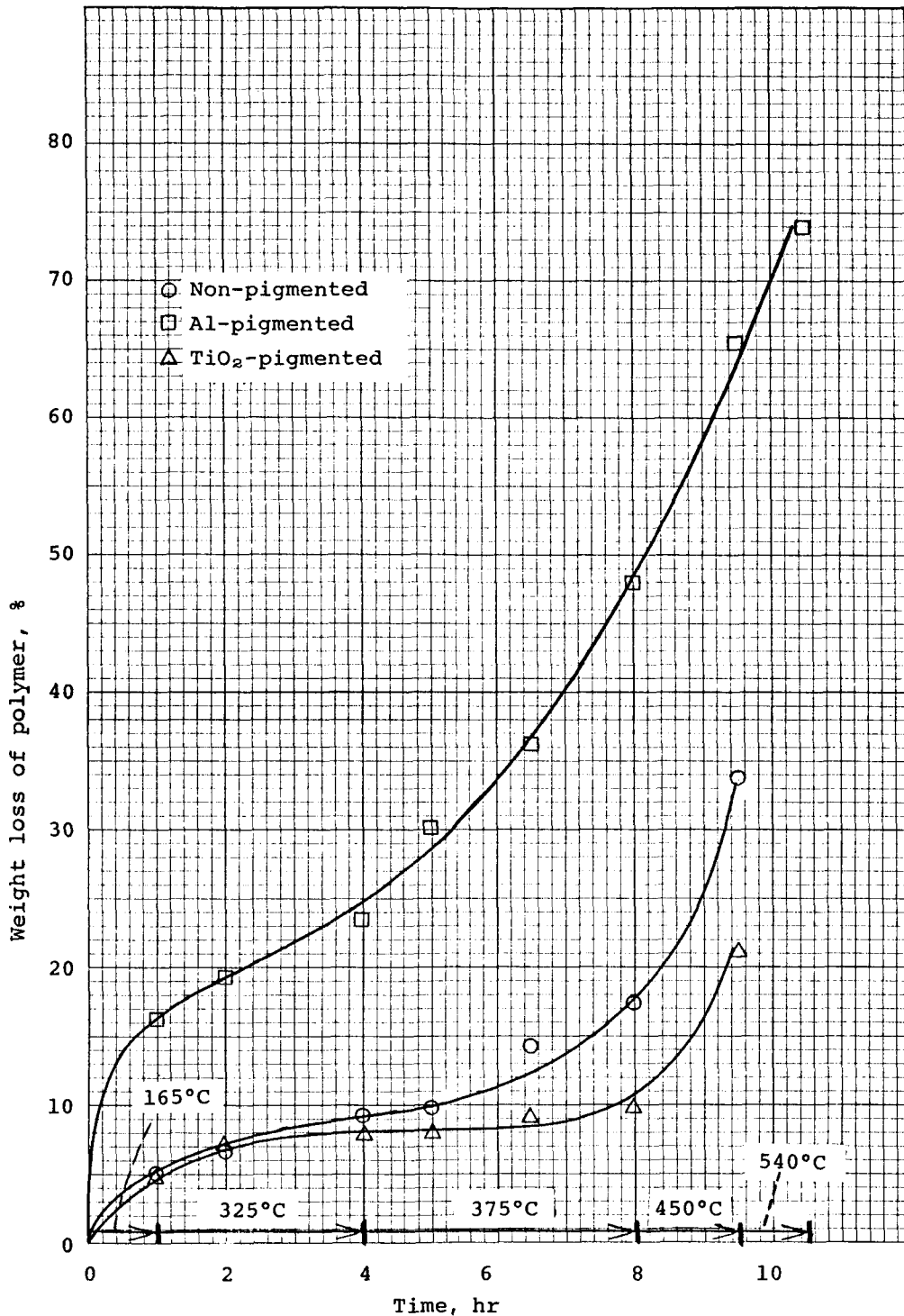
Figure 2. Weight Loss of Silphenylene Amine
Polymers in Coatings

3. Foams

Resilient foams are obtained by crosslinking poly(tetra-methyl-p-silphenylene methylamine) with pentaerythritol:

$$
\begin{array}{c}
\overset{\displaystyle Me}{\underset{\displaystyle Me}{|}} \quad \overset{\displaystyle Me\,Me}{\underset{\displaystyle \;\; Me}{|\;|}} \\
\text{———Si—N—Si———}
\end{array}
$$

+

HOCH$_2$ CH$_2$OH
        C
HOCH$_2$ CH$_2$OH

+

$$
\begin{array}{c}
\overset{\displaystyle Me}{\underset{\displaystyle Me}{|}} \quad \overset{\displaystyle Me\,Me}{\underset{\displaystyle \;\; Me}{|\;|}} \\
\text{———Si—N—Si———}
\end{array}
$$

$\longrightarrow$

MeNH$_2$

+

$$
\begin{array}{c}
-Si-O\diagdown \qquad \diagup O-Si- \\
|\qquad CH_2 \; CH_2 \qquad | \\
\qquad\qquad C \\
|\qquad CH_2 \; CH_2 \qquad | \\
-Si-O\diagup \qquad \diagdown O-Si- \\
|\qquad\qquad\qquad\qquad\quad |
\end{array}
$$

resilient foam
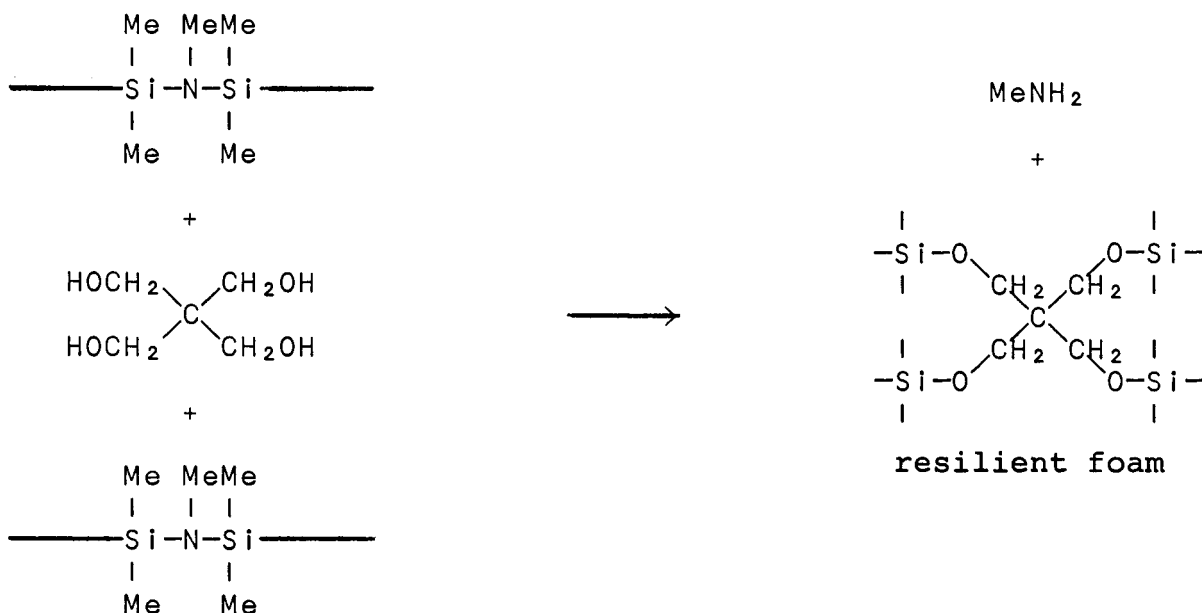
Curing with pentaerythritol is accomplished in 1.0-1.5 hours at 325-350°C. According to the evidence available, it is desirable to have most of the nitrogen replaced by oxygen; but if all of the nitrogen were replaced, the crosslinking reaction would not occur. Foams with good stability were made from polymers having 20%[19] to 40% of the theoretical nitrogen. Foams made from polymers having about 75% changed on standing. However, the stability of a foam made from the polymer with 75% of the theo-retical nitrogen was improved by heating at 350°C in air. Foams cured on aluminum adhere tenaciously, but a Teflon mold-release agent was fairly successful for preventing adhesion.

In preparing foams, it is necessary to choose the right amount of pentaerythritol for the amount of nitrogen in the polymer. The criteria for quality in a foam are softness, thermal stability, lightness of color, and amount of expansion

during foaming. Polymer 4369-83, which contained 2.5% nitrogen (40% of theory for a silphenylene amine), made the best foam when 6 equivalents of polymer were used for 1 equivalent of pentaerythritol. Polymer 4369-145-4 (0.74% N, 12% of theory) made the best foam with a 12:1 ratio of polymer to pentaerythritol. The data are summarized in Table IX.

Sandwich panels of foamed silphenylene amine were made without difficulty by heating silphenylene amine-pentaerythritol mixtures between parallel aluminum sheets held 0.25 in. apart by aluminum spacers. However, considerable difficulty was encountered in making a 1-in. cube of foam in a Teflon mold. Poor heat transmission apparently caused non-uniform foaming.

B. Experimental

1. Preparation of compounds and polymers

    a. 1,4-Bis(dimethylchlorosilyl)benzene

The preparation of 1,4-bis(dimethylchlorosilyl)benzene was described above in Section III.B.1.a.

    b. Poly(tetramethyl-p-silphenylene methylamine)

(1) Initial preparation - low molecular weight

Amination of 1,4-bis(dimethylchlorosilyl)benzene was accomplished by passing methylamine over a stirred solution of chlorosilane. 1,4-Bis(dimethylchlorosilyl)benzene, 85.40 g (0.321 mole), b.p. 117-119°C at 1.0 mm, was dissolved in 1 liter of dry toluene in a 3-liter, 3-neck flask fitted with a thermometer, stirrer, gas inlet tube over the surface of the liquid, and a reflux condenser cooled by dry ice. The toluene solution was cooled to 3°C. Liquid methylamine was run from a cylinder into a flask containing sodium, and then it was allowed to boil off and pass over the stirred solution in the reaction flask. After about 2 hours the methylamine began to reflux. The cold solution was filtered, and most of the toluene was removed from the filtrate by distillation under reduced pressure. The last traces of toluene were removed by heating the liquid for 1.2 hours at temperatures up to 190°C at 1 mm pressure. No evidence of distillation of the monomer was seen. The product, Polymer 4175-143, was viscous at room temperature and became more viscous

Table IX. Preparation of Silphenylene Foams

Foam 4369-	Starting material			Curing conditions			Appearance	
	Polymer	N content, %a	Estd. MW	Eq. ratio pol:penta b	Temp., °C	Time, hr	After curing	After standing
39	4175-143-5D	-	41,000	12:1	225	1.0	sl. tacky, resilient, amber	compressible, non-resilient
41-1	4175-143-1C	4.64	37,000	12:1	225	1.5	sl. tacky, resilient, amber	remained fairly resilient
41-2	4175-143-1C	4.64	37,000	6:1	225	1.0	non-tacky, resilient, amber	remained fairly resilient
59	4175-143-3	-	39,000	6:1	235	2.6	non-tacky, resilient, cream-colored	compressible, non-resilient
					350	1.5	resilient, but weaker	no change
61-1A	4175-143-3	-	39,000	3:1	200	2.0	not foamed	-
					250	1.0	fine-grained foam, sl. resilient	-
					300	1.0	tan, v. resilient while hot	compressible, non-resilient
65-1A	4369-33-2	1.74	40,000	12:1	250	1.0	not examined	compressible, non-resilient
					300	1.0	cream-colored, tacky, sl. resilient	
71-1A	4369-33-2	1.74	40,000	6:1	300	0.5	not examined	no change
					325	0.5	cream-colored, resilient	
99-1	4369-83	2.52	57,000	6:1	350c	1.25c	pale cream-colored, resilientc	no change
99-2	4369-83	2.52	57,000	6:1	325	1.5	pale cream-colored, resilientc	no change
99-3	4369-83	2.52	57,000	6:1	350	1.0	pale cream-colored, resilientc	no change
149-2	4369-145	0.74	50,000	3:1	350	1.0	black, tough solid	no change
149-3	4369-145	0.74	50,000	12:1	350	1.0	pale cream-colored, very resilient	no change
155-4	4369-145	0.74	50,000	6:1	350	1.0	light amber-colored, sl. resilient	no change
157	4369-83	2.52	57,000	6:1	350	1.0	pale, cream-colored, resilient	no change

a. Theoretical nitrogen content of pure silphenylene amine polymer, 6.32%.

b. Ratio of equivalents of polymer (assuming pure polymeric silphenylene amine) to equivalents of pentaerythritol.

c. Portions of this polymer were heated for additional periods to determine thermal stability. Polymers became friable in 30 minutes at 400°C or, 3 hr at 350°C, 8 hr at 325°C.

on standing. The inherent viscosity was 0.18 deciliters per gram, and the molecular weight was estimated to be 22,000. Data previously obtained[18] were used to estimate molecular weights from viscosity measurements in tetrahydrofuran at 30°C at concentrations of about 1.0 g per deciliter.

Anal.   Calculated for $C_{12}H_{24}N_2Si_2$ (monomer):
             C 57.08, H 9.58, N 11.09, Si 22.25.

         Calculated for $C_{11}H_{19}NSi_2$ (polymer repeating unit):
             C 59.66, H 8.65, N 6.32, Si 25.37.

         Calculated for $C_{10}H_{16}OSi_2$ (oxygenated polymer):
             C 57.63, H 7.74, O 7.68, Si 26.95.

         Found: C 58.61, H 8.49, N 4.75, Si 26.52.

A similar amination of 1,4-bis(dimethylchlorosilyl)benzene yielded Polymer 3992-125 with an inherent viscosity of 0.05 dl/g, and an estimated molecular weight of 7,000. Another amination product, Polymer 3992-157-1, had an inherent viscosity of 0.03 deciliters per gram (estimated molecular weight 4,000) and contained 7.57% nitrogen. Since the polymer repeating unit contains only 6.32% of nitrogen, the higher figure is doubtless due to end amine groups.

(2) Increasing the degree of polymerization

The degree of polymerization of poly(tetramethyl-p-silphenylene methylamine) was increased by heating it under reduced pressure. In earlier work[17] there was some evidence that trace amounts of magnesium chloride accelerated polymerization of the silphenylene amines, but in recent work the highest molecular weights were obtained without it. Polymerization experiments are summarized in Table X.

(a) Without solvent

Polymerization 4175-143-5 was typical of the group without solvent. Details are in Table X. Polymer 4175-143, 5.0 g ($\overline{M}_w$, 22,000), and 0.005 g of anhydrous magnesium chloride were stirred and heated at reduced pressure for the periods and at the temperatures listed in Table X. The progress of polymerization was checked periodically by viscosity measurements with

Table X. Preparation of Polymeric Silphenylene Amines,
Poly(tetramethyl-p-silphenylene methylamine)

Polymerization	Starting material	Polymerization conditions					Product		
		Solution, conc, %	Catalyst,[a] %	Time, hr	Temp., °C	Press., mm	Inherent viscosity,[b] dl/g	Est'd. $\bar{M}_w$[c]	Proportion of theoretical[d] nitrogen, %
4175-143	---------------Preparation of silphenylene amine---------------						0.18	22,000	75
4175-143-1A	4175-143	-	0.1	2.0	200	0.02	0.33	42,000	-
-1B				2.0	250	0.01	0.38	48,000	-
-1C				5.5	300	0.02	0.29	37,000	73
4175-143-3A	4175-143	-	-	2.0	200	0.1	0.26	33,000	-
-3B				6.0	200	0.03	0.40	51,000	-
-3C				2.0	250	0.17	0.36	46,000	-
-3D				2.0	250	0.05	0.34	43,000	-
4175-143-5A	4175-143	-	0.1	2.0	200	0.02	0.29	37,000	-
-5B				2.0	200	0.05	0.36	46,000	-
-5C				2.0	250	0.17	0.35	45,000	-
-5D				2.0	250	0.05	0.32	41,000	-
4175-143-2A	4175-143	23.5[e]	-	16.0	reflux		0.27	34,000	-
-2B				12.0			0.17	21,000	-
-2C				7.5	179°C		0.14	17,000	-
4175-143-4A	4175-143	23.5[e]	0.1	16.0	atmospheric		0.13	16,000	-
-4B				11.0			0.23	29,000	-
-4C				7.5	pressure		0.16	20,000	-
4369-27-1	4175-143	-	-	2.0	250	0.25	0.35	45,000	-
-27-2				1.0	250	0.08	0.35	45,000	-
-27-3				1.0	250	0.08	0.35	45,000	-
3992-125	---------------Preparation of silphenylene amine---------------						0.05	7,000	-
3993-125-2	3992-125	-	-	16.0	140-205	0.08	0.12	16,000[f]	-
3992-157-1	---------------Preparation of silphenylene amine---------------						0.03	4,000	120
4369-33-2[g]	3992-157-1	45	-	1.0	250	0.01	0.31	40,000	28
4369-43-3	3992-157-1	-	-	1.5	140	0.30	0.07	9,000	-
				7.0	250	0.10	0.30	39,000	-
				4.0	300	0.02	0.30	39,000	-
4369-77-1	---------------Preparation of silphenylene amine---------------						0.05	6,000	114
4369-81-3	4369-77-1	-	-	7.0	230	0.02	0.26	34,000	83[h]
				5.5	250	0.17	0.35	45,000	91[h]
				6.0	250	0.40	0.41	52,000	92
4571-3-3	---------------Preparation of silphenylene amine---------------						0.08	10,000	107
4571-11-2	4571-3-3	-	-	2.0	225	0.1	0.08	10,000	98[h]
				5.0	240	0.1	0.10	12,500	103

a. Magnesium chloride, % by weight.

b. Viscosity measurements made in tetrahydrofuran at 30°C at a concentration of 1.0 g per deciliter.

c. From data of preceding annual report, see Reference 18, relating viscosity and molecular weight.

d. Based on polymer repeating unit.

e. In o-dichlorobenzene as solvent.

f. Attempts to increase molecular weight by subsequent treatments with catalyst, water, and tetramethyl-p-silphenylene diol were unsuccessful.

g. Starting material mixed in toluene with 50% of its weight of 1,4-bis(dimethylhydroxysilyl)benzene to reduce nitrogen content, refluxed 1 hour, toluene removed, polymerization continued as indicated.

h. Estimated by titration with 0.1 N HCl.

the results shown. The product could be stirred at 250°C; but when cool, it was a cloudy, sticky, elastic solid that recovered slowly when deformed. Polymer 4175-143-1C ($\bar{M}_w$ 37,000) was the only one of the series analyzed. Calculated values for comparison are given in the preceding section [IV.B.1.b.(1)].

Anal. Found: C 58.09, H 8.43, N 4.64, Si 26.61.

Polymer 4369-81-3 was prepared in essentially the same way but without magnesium chloride. Silphenylene amine 4369-77-1, 12.8 g, was polymerized by heating at 230-250°C for 17 hours at 0.01 mm pressure. The inherent viscosity increased gradually and leveled off during the last 5 hours at 0.41 deciliters per gram. The softening point of the polymer was 51-52°C, as indicated by the temperature at which it stuck to the cover glass of a Fisher-Johns melting point apparatus. The solution viscosity of the polymer (4369-81-3) indicated a molecular weight of 52,000, on the basis of previous data correlating solution viscosities with molecular weight determined by light scattering.[18] Actual measurement by light scattering gave the value, 57,000.

Anal. Calculated for the repeating unit, $C_{11}H_{19}NSi_2$:

C 59.66, H 8.65, N 6.32, Si 25.37.

Found: C 57.07, H 8.51, N 5.84, Si 26.33, O 0.93.

Total 98.68%.

Oxygen analysis was done by radioactivation by General Atomics Division of General Dynamics.

Polymer 4369-81-3, 8.0 g, was dissolved in 15 ml of toluene and refluxed for 4 hours. The intention was to dissolve the polymer to improve mobility and increase the likelihood of end-group condensation. Slow evolution of methylamine was detected. After removing the toluene at reduced pressure, the inherent viscosity of the polymer was 0.43 deciliters per gram and the melting point was 51-52°C (Polymer 4369-81-4).

Anal. Found: C 57.55, H 8.32, N 5.12, Si 25.19, O 1.63.

Total 97.81%.

Polymerization 3992-125-2 was one that failed to reach a high molecular weight. The freshly prepared silphenylene amine used in this reaction, Polymer 3992-125, had an estimated molecular weight of 7,000. The polymer, 18.63 g, was heated for a total of 16 hours at temperatures of 140-205°C, which caused an increase of inherent viscosity to only 0.12 (molecular weight, 16,000) - much less than expected, on the basis of earlier results. Addition of 20 mg of magnesium chloride followed by heating for an additional 7 hours at 205°C at 0.1 mm pressure produced no change. When the polymer was at 60°C, 0.18 g (0.01 mole) of water was added and stirred in. Subsequent heating for 16 hours at temperatures up to 250°C at 0.1 mm pressure produced no change in viscosity. Finally, when the mixture was cool, 0.9 g (0.004 mole), 1,4-bis(dimethylhydroxysilyl)benzene was added and stirred in. Subsequent heating at 250°C for 3 hours at 0.04 mm pressure produced no significant change. The final inherent viscosity was 0.13.

Anal. Found: C 58.91, H 8.42, N 5.87, Si 25.92.

Thus, the polymer contained 93% of the theoretical nitrogen.

(b) With solvent

Polymerization 4175-143-4 is typical of two trials with o-dichlorobenzene as solvent. Polymer 4175-143, 5.2 g, magnesium chloride, 0.005 g, and freshly distilled o-dichlorobenzene, 13 ml, were refluxed and sampled periodically as shown in Table X. The molecular weights obtained with solvent were lower than those obtained without. Hence, no merit is seen in the use of solvent.

(3) Reaction with diol to reduce nitrogen content

Since data were needed on the properties of a polymer with most of the nitrogen replaced by oxygen, the nitrogen content was reduced by treating the silphenylene amine with 1,4-bis-(dimethylhydroxysilyl)benzene in toluene. The reactions are summarized in Table XI. Polymer 3992-157-1, a freshly prepared silphenylene amine, 9.48 g, was dissolved in 20 ml of dry toluene in a 100-ml, 3-neck flask. Then 4.50 g of 1,4-bis(dimethylhydroxysilyl)benzene was added with stirring. Gas was evolved as the solution was heated slowly to reflux temperature. After 1 hour of refluxing, the toluene was removed at reduced pressure. The inherent viscosity was 0.29 deciliters per gram. After 1 hour

of heating at 250°C at 0.01 mm pressure, the inherent viscosity was 0.31 deciliters per gram (estimated molecular weight, 40,000). The nitrogen content was 1.74% (theoretical, 6.32%, for the polymer repeating unit.)

Table XI. Reaction Products of Silphenylene Amines with 1,4-Bis(dimethylhydroxysilyl)benzene

Starting material						
Silphenylene amine	Amt, g	Nitrogen, content, %[a]	Diol, g	Polymer	Estd MW[b]	Nitrogen content, %[a]
3992-157-1	9.5	7.6	4.5	4369-33-2	40,000	1.7
4369-77	59.0	7.2	35.1	4369-83	57,000	2.5
4369-143	64.6	8.1	46.0	4369-145-4	50,000	0.7
4369-151-4	81.1	5.1	27.6	4571-9-1	54,000	2.7

a. Theory for repeating unit:

is 6.32% N.
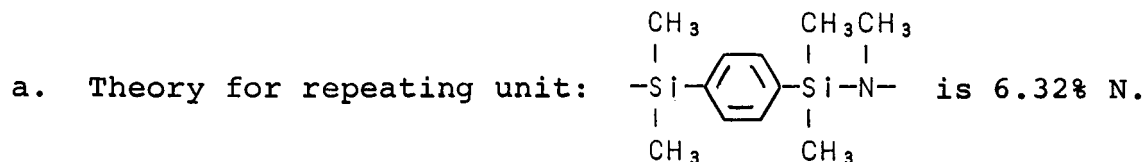
b. Estimated from solution viscosity, see Reference 18.

In another reaction, silphenylene amine 4369-77 (nitrogen content, 7.21%), 59.0 g, was dissolved in 125 ml of toluene and refluxed for 4.5 hours with 35.1 g of 1,4-bis(dimethylhydroxysilyl)-benzene. The toluene was removed at reduced pressure, and the polymer was heated at 205°C for an hour at 0.4 mm pressure. When cool, the polymer, 4369-83, was a tough, elastic, semi-transparent solid. The polymer was subsequently heated to 125°C under nitrogen and transferred to another container. On cooling it changed, apparently because of crystallization, to a tough, white, solid that was only slightly elastic. The softening point was 101-102°C.

The inherent viscosity was 0.45 deciliters per gram. The molecular weight was estimated to be 57,000 by the solution viscosity;[18] and was found to be 60,000 by light scattering.

Anal. Found: C 57.41, H 8.11, N 2.52, Si 27.78, O 5.10.

Total 100.92%.

Analysis of these thermally stable silicon compounds is recognized as being difficult. Nitrogen analysis by the Dumas Method is not satisfactory, because methane is formed and is counted as nitrogen since it traverses the oxidation zone without being completely destroyed. Hence, the Kjeldahl method has been used. Although the carbon and hydrogen analyses are more reliable, they have been a source of trouble in the past. Radioactivation is the only direct oxygen determination that can be used for silicon compounds.

2. Coatings

Silphenylene amine polymers were investigated earlier as coating agents for titanium.[20] In continuing the investigation of the amine polymers in coatings, Polymers 4175-143, 4175-143-3D, 4369-27-3, and 4369-33-2 that ranged in molecular weight from 22,000 to 45,000 were dissolved in benzene and pigmented with aluminum. For example, mixtures of 1.0 g of each polymer with 9.0 g of benzene and 0.33 g of aluminum pigment No. 322 (Aluminum Corporation of America) that had been washed with benzene were shaken with glass beads for 16 hours. Each pigmented mixture was then doctored onto strips of titanium ("Ti, 8 Al, 1 Mo, 1 V"). Curing was satisfactory in 3.5 hours at 375°C or 8-12 hours at 325°C. The coatings could be cured in a vertical position without flowing. No differences were seen in the adhesion of the coatings, all of which remained intact when heated for 100 hours at 540°C (1000°F). The coatings resembled aluminum paint in appearance, but the three made from the polymers with higher molecular weights (4175-143-3D, 4369-27-3, and 4369-33-2) were appreciably lighter and brighter. The uncoated titanium turned dark blue.

Coatings made with Polymer 4369-83 pigmented with aluminum were applied to titanium and heated at 540°C (1000°F) in air. After 28 days (675 hours), the coatings had the appearance of aluminum paint, could not be scratched with a fingernail, and

were not damaged by being dropped into cold water immediately after being removed from the furnace. The uncoated portions of the titanium strips were deep blue, but no blue was apparent in coated areas when the coatings were removed by scraping with a knife.

The silphenylene amine pigmented with aluminum also was applied to mild steel and heated at 500°C for 300 hours. The coated area was visibly undamaged, but the uncoated areas of the steel had a dark brown velvety appearance. Another coating on mild steel was heated 48 hours at 540°C with similar results. A coating applied to Type 304 stainless steel was heated 90 hours at 540°C without visible change.

The same coating applied to copper could be peeled off after 16 hours at 500°C, but there was no evidence of extensive oxidation underneath the coating. The uncoated area of the copper was covered with flakes of copper oxide. Analysis of the coating after heating on the copper showed that it contained only 2.7% carbon and 1.5% hydrogen whereas it would have contained 43% carbon if the organic portion of the polymer had been intact. After a partly coated copper sheet was held over a flame until smoking ceased, the coating was cured and intact while the uncoated copper was covered with powdery oxide. It was obvious that the coating afforded some protection, but comparative data are needed on coating agents already available before the value of the silphenylene amine for coating copper can be evaluated.

The aluminum-pigmented silphenylene amine coatings were cured at several temperatures to determine the relation of curing time to temperature. Coatings were cured in 8-12 hours at 325°C, in 3.5 hours at 375°C, and in 15 minutes at 500°C. A coating can also be cured by holding a specimen just above a gas flame until it smokes gently and holding it there until smoking ceases.

To obtain samples for analysis, aluminum-pigmented coatings were applied to glass. The calculated analysis of the solid material of the coating, (Polymer 4369-83 and aluminum) was:

Anal. Calculated: C 43.1, H 6.1, N 1.9, Si 20.8, Al 25.0, O 3.1.

A similar coating on glass was heated 3.5 hours at 375°C and 1.0 hour at 440°C, then the coating was scraped off and analyzed.

Anal. Found: C 25.1, H 3.7, N 0.15.

Thus, most of the nitrogen had been lost, and most of the carbon and hydrogen remained and in about the original weight ratio to each other (6.8:1 as compared with 7.1:1 originally).

Another coating on glass was heated 27 hours at 500°C.

Anal. Found: C 11.5, H 3.8.

Thus, at least 25% of the initial carbon content remained. Oxidation of the aluminum and possible loss of inorganic matter was not taken into account in these calculations. If the aluminum had been oxidized, the theoretical carbon content of the coating would have been 35.1% instead of the 43.1% reported in the first of the above three experiments.

Three types of coatings were applied to titanium and observed for weight losses during heating. One coating contained no pigment, another was pigmented with aluminum, and the third was pigmented with titanium dioxide. The pigments were mixed with the polymers in the ratio of 1 part of pigment to 3 parts of polymer. Figure 2 shows the weight losses on heating at increasing temperatures up to 540°C. The weight losses are based on the polymer only, with the assumption that the pigments did not change weight. The coating that had no pigment and the one pigmented with titanium dioxide flaked off after 1.5 hours at 450°C, but they lost considerably less weight than the aluminum-pigmented coating which remained intact when the exposure was terminated. The 74% weight loss shown for the aluminum-pigmented polymer is only 56% loss for the whole coating and 49% loss for the amount remaining after 1.0 hour at 165°C.

The titanium used in all of our coating experiments was "Ti-8-1-1 alloy". Specimens measuring 4 x 1/4 x 1/16-inch were coated and cured to apply aluminum-silphenylene coatings 0.1-0.2-mil thick. The two ends were bent to give the strip approximately this shape:

Then two strips were bowed and spot welded together at the ends to form approximately this shape:

```
compression                    compression
  after      →  ⟨====⟩  ←        after
 exposure                      exposure
```

The stressed pair was then placed in contact with sodium chloride and held at 550°F for 1000 hours. At the end of this period, the joined ends were forced together in the direction of the arrows, which resulted in sharper bending. All of the silphenylene-coated specimens cracked, showing that the coating had not been successful in preventing damage by the sodium chloride. This test was designed at Langley Research Center.[21] An unpigmented methylphenyl silazane[22] coating successfully prevented cracking, but it does not endure prolonged exposure to temperatures above 400°C.

When coatings were prepared by brushing the 10% solution of polymer onto the substrates, they were 0.1-0.2 mil thick. After the preceding experiments had been completed, we learned that jet engine manufacturers considered thicker coatings far more desirable to provide additional material for erosion. Thicker coatings were prepared easily by doubling the solids content of the benzene solution and doctoring the solution onto the metal. After the solvent had been allowed to evaporate the coatings were cured as before. If coatings were 0.5-1.0 mil thick, no blistering occurred during curing, but it was necessary to precure coatings 1-2 mils thick for 1.0 hour at 300°C to avoid blistering. After being cured, coatings 1-2 mils thick underwent no visible change during heating at 540°C, but the thick coatings were not observed longer than 120 hours. The performance on titanium and mild steel was the same.

Attempts were made to form thermally stable coatings without pigment and with zinc oxide or titanium dioxide as a pigment, but they were unsuccessful. The coatings peeled away from the substrates when cooled after curing 1-2 hours at 400°C. Aluminum evidently has an important role beyond pigmentation, since the coatings made with the polymeric silphenylene amine exhibited outstanding thermal stability only when pigmented with aluminum.

3. Resilient foams

Earlier work on resilient foams prepared by crosslinking poly(tetramethyl-p-silphenylene methylamine) with pentaerythritol was described in the preceding annual report.[17] Current work is summarized in Table IX. The method is exemplified by the following experiment: Poly(tetramethyl-p-silphenylene methylamine), 4175-143-5D (Table X), 2.0 g (18.1 milliequivalents), was milled by hand with 0.050 g (1.48 milliequivalents) of pentaerythritol with a Teflon roller on a Teflon sheet. This was a 12:1 equivalence ratio of polymer to pentaerythritol. Before it could be milled, the polymer had to be warmed to 60-70°C. Heating was done with a heat gun that produced a stream of hot air. A higher temperature would have caused excessive sticking to the Teflon. The milling required about 10 minutes before the pentaerythritol was worked in sufficiently for the polymer to become uniformly cloudy. It then had the consistency of chewing gum. Portions of the milled polymer foamed when heated to 225°C or higher. Curing was essentially complete in 1 hour at 225°C. The product was a soft, resilient foam. Foams were made also with Polymer 4175-143-1C and pentaerythritol in 12:1 and 6:1 ratios. The foamed products were essentially the same in appearance. They did not harden on standing at room temperature, and they did not disintegrate, but they lost strength, when boiled for 30 minutes in water.

In Table IX, the amounts of pentaerythritol are recorded as the ratio of equivalents of polymeric silphenylene amine (assuming 100% of the theoretical nitrogen) to equivalents of pentaerythritol. The theoretical equivalent weight of the repeating unit of the polymer is 110.73 and of the pentaerythritol is 34.04.

For the preparation of sandwich panels of silphenylene foam between sheets of aluminum, Polymer 4369-83, 23.86 g, was milled with pentaerythritol, 1.22 g, and heated at 350°C for 1 hour between aluminum sheets, (31 mils thick) held 0.25 in. apart by aluminum spacers that had been sprayed with Fluoro-Kem (Bel Arts products). After the aluminum spacers were removed, the sandwiches were resilient. They were designated 4369-157 and submitted to George C. Marshall Space Flight Center for examination. One sample that was retained was resilient after 5.5 hours at 325°C.

Attempts to prepare 1-in. cubes óf the silphenylene foam were not successful. A milled mass of silphenylene amine and pentaerythritol was placed inside a mold of 3/16-in. Teflon sheet, and the assembly was heated in a furnace. Different heating procedures were tried. For example, in one experiment the mold was placed in a furnace at 420°C; and, in another experiment, the mold was preheated for 30 minutes at 125°C before the temperature was increased by steps to 345°C. However, in no case was a uniform foam obtained. In some experiments the milled material failed to fuse properly, and in others inadequate foaming of the interior portions resulted in foams with hard cores.

Several experiments demonstrated the need for choosing the right amount of pentaerythritol for a polymer with a given nitrogen content. In the experiment above, the equivalence ratio of polymer to pentaerythritol was 6:1. This was the preferred ratio in Polymer 4369-83 which contained 2.5% nitrogen. When the equivalence ratio of Polymer 4369-145-4 (0.7% N) to pentaerythritol was 3:1, the mixture first foamed at 325°C, then coalesced and formed a dark liquid. When the ratio was 6:1, the foam was stable during curing for 1.5 hours at 325°C; but, when the foam was cool, it had only fair recovery from compression. When the ratio was 12:1, the foam was amber in color and had excellent recovery and resilience.

Two of the foams were analyzed for nitrogen. Foam 4369-59 contained 0.38% N and Foam 4369-71-1 contained 0.50% N.

V.   SILYLAMINE-CURED EPOXY RESINS

A.   Discussion

Silylamines have been studied as curing agents for epoxy resins because they impart high thermal stability. During the past year, samples were prepared for evaluation as ablative heat barriers; data were obtained on the thermal stability of a silylamine-cured epoxy resin as an adhesive; and attempts were made to find new types of epoxy resins that could be cured with silylamines. The following epoxy resins were included in the study:

Epon 828 (Shell Chemical Company):

$$CH_2\text{--}CHCH_2\text{--}O\text{--}\bigotimes\text{--}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{--}\bigotimes\text{--}OCH_2CH\text{--}CH_2$$
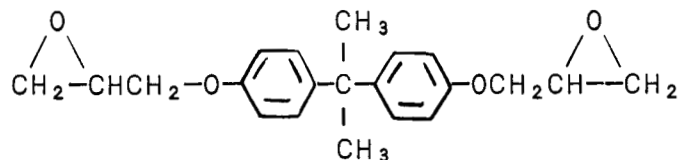
ERL-4221 (Union Carbide Corporation):

$$O\bigcirc\text{--}CH_2\text{--}O\text{--}\overset{\overset{O}{\|}}{C}\text{--}\bigcirc O$$
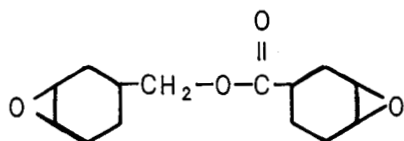
XZ-8-5024 (Dow Corning Corporation):

$$CH_2\text{--}CH\text{--}CH_2\text{--}O\text{--}(CH_2)_3\text{--}\underset{\underset{CH_3}{|}}{\overset{\overset{Me_3Si}{|}\atop\overset{O}{|}}{Si}}\text{--}O\text{--}\underset{\underset{CH_3}{|}}{\overset{\overset{Me_3Si}{|}\atop\overset{O}{|}}{Si}}\text{--}(CH_2)_3\text{--}O\text{--}CH_2\text{--}CH\text{--}CH_2$$
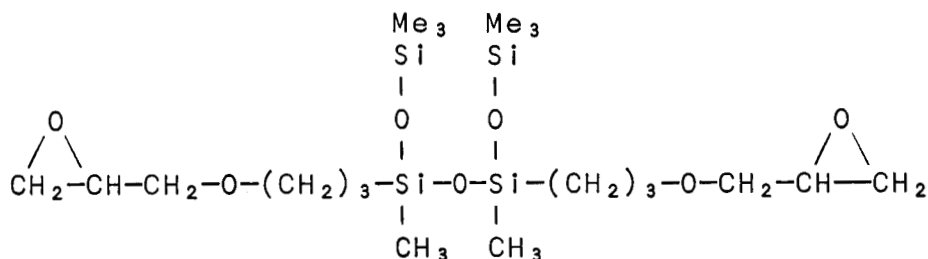
Prior reports[23],[24] have described laminates and experimental heat barriers containing Epon 828 cured with bis(methylamino)-diphenylsilane, and favorable results encouraged extension of the work including attempts to find better epoxy-silylamine combinations.

1. Heat barriers

The initial samples prepared for trial as heat barriers contained Epon 828, bis(methylamino)diphenylsilane, potassium titanate, and glass fiber.[23] The rate of heat transmission was low enough to justify further trials, so additional samples, with some modifications, were prepared during the past year, and these were submitted for evaluation at Marshall Space Flight Center. The results are not yet available.

Two sets of samples contained Epon 828 cured with bis-(methylamino)diphenylsilane. One set contained potassium titanate, glass fiber, and glass microballoons; the other contained only potassium titanate and glass fiber. For comparison a set of samples was prepared with Epon 828 cured with Nadic Methyl Anhydride and filled with potassium titanate and glass fiber.

Some difficulty was experienced with bubbles in both the silylamine-cured and anhydride-cured samples. However, deaeration under reduced pressure and adjustment of the curing schedule eliminated the trouble.

The glass microballoons were incorporated into the resins to reduce the density; the samples without microballoons were about 30% heavier. The samples with microballoons floated on water, their specific gravity being about 0.96.

2. Adhesives

Silylamine-cured epoxies were formerly studied very briefly as adhesives for lap joints of aluminum.[25] Previous data showed that Epon 828 had better thermal stability at 325°C than a commercial resin, ERLA 4221 (now called ERL 4221), cured with anhydrides. It was desirable to obtain a comparison of silyl-amines with commercial curing agents, m-phenylenediamine and Nadic Methyl Anhydride, in the same epoxy resin, Epon 828. Low shear strengths (about 550 psi) were obtained with m-phenylene-diamine even before it was subjected to thermal stress. The anhydride-cured Epon 828 produced a lap joint with a shear strength of 1750 psi. The anhydride-cured specimens lost 17% of their strength in 1 hour at 325°C or 13% in 1 hour at 300°C. Epon 828 cured with bis(methylamino)diphenylsilane had an initial shear strength of 1850 psi, the shear strength increased 19% in 1 hour at 325°C or 35% in 1 hour at 300°C. These exploratory results (summarized in Table XI) suggest that the Epon 828-bis(methylamino)diphenylsilane system is worthy of additional consideration for high-temperature adhesives. A practical evaluation would include comparisons with available materials after thermal exposures approximating those that might be expected in use. Probably, results obtained with longer exposure periods at lower temperatures would be more significant for most purposes than short periods at 325°C and 300°C. Also measurements of shear strength at elevated temperatures would be informative.

Table XI. Adhesive Strengths of Lap Joints of Aluminum

| | Curing conditions | | | Thermal stress, 1 hr | |
	Time, hr	Temp, °C	Shear strength,[a] psi	Temp, °C	Shear strength,[a] psi
Epon 828 + BMADPS,[b] 100:64 ratio					
Group 1, avg 10 samples	2	60			
	2	120	1836 A[c]	300	2492 B[c]
standard deviation			185		391
Group 2, avg 10 samples	2	60			
	2	120	1848 C[c]	325	2200 D[c]
standard deviation			209		252
Epon 828 + m-phenylenediamine, 100:14 ratio					
Group 1, avg 10 samples	1	25	560	300	580
	4	135			
Group 2, avg 10 samples	1	25			
	1	100			
	4	150	540	300	535
Epon 828 + Nadic Methyl Anhydride, 100:95 ratio					
Group 1, avg 10 samples	1	120			
	4	200			
	24	260	1746 E[c]	300	1523 F[c]
standard deviation			184		125
Group 2, avg 10 samples	1	120			
	4	200			
	24	260	1778 G[c]	325	1450 H[c]
standard deviation			234		173

a. Shear strength under tensile loading.

b. BMADPS = bis(methylamino)diphenylsilane.

c. Shear strength values given differ in pairs as follows:
    A and E, C and G, not significantly different;
    A and B, C and D, E and F, G and H, B and F, D and H, all differ at the 99%
    confidence level.

3. Low-temperature curing

Broader applications of silylamine-cured epoxies could
be considered if they cured satisfactorily at room temperature
in 2 days or less. It was found that curing Epon 828 with
bis(methylamino)diphenylsilane required 7 days at 27°C or
22 hours at 40°C. The polymer cured at 27°C was clear and
colorless; that cured at 40°C was clear and pale yellow; both
were hard and tough. The addition of 0.3-0.5% by weight of
stannous octoate or 0.8% dibutyltin diacetate reduced the curing
time at 27°C from 7 days to 4 days; 1.0% stannous octoate destroyed
the clarity. The data are summarized in Table XII.

4. Search for new epoxy-silylamine combinations

Bis(methylamino)diphenylsilane and Epon 828 have been
studied more thoroughly than any other combination of epoxy
resin and silylamine. A small amount of work was done earlier[24]
to cure Epon 828 with hexamethylcyclotrisilazane and hexaphenyl-
cyclotrisilazane, but these two silazanes were ineffective below
200°C. It seemed likely that a better combination of epoxy
resin and silylamine could be found if a more thorough search
were made.

There is information in the patent literature on reactions
somewhat related to our silylamine-epoxy reactions, but the
properties of the polymers produced were not given in the patents.
Schultz and Zike[26] prepared halosilyl derivatives of epoxy
compounds and treated them with amines. Boyer, Molotsky, and
Tarbell[27] prepared resins from polymeric silylamines, epoxy
compounds, and polyhydroxy compounds. Weigel[28] used hexamethyl-
cyclotrisilazane and octamethylcyclotetrasilazane to cure epoxide
resins at temperatures above 100°C. Finestone[29] cured epoxy
resins with compounds having nitrogen and silicon in the same
molecule but having no covalent Si-N bonds.

Although Epon 828 is one of the more widely used epoxy
resins, others are more often mentioned in connection with high-
temperature applications. To obtain recommendations, which are
discussed later, for curing Epon 828 with anhydrides it was
necessary to communicate with Shell Chemical Corporation
directly.[30] Both ERL-4221 and XZ-8-5024 are advertised as
epoxy resins for use when high thermal stability is needed.

Table XII. Tin Compounds as Accelerators for Curing of
Epon 828 and Bis(methylamino)diphenylsilane

Mixture of resin and curing agents				Curing conditions		Appearance of product
Epon 828, %	BMADPS, %	Stannous octoate, %	Dibutyltin diacetate, %	Temp, °C	Time, hr	
60.9	39.1			60	2	clear, pale yellow, tough solid
60.9	39.1			120	1.5	clear, pale yellow, tough solid
60.9	39.1			120	1.0	clear, tan, tough solid
58.9	41.1			180	0.5	clear, pale yellow, tough solid
58.9	41.1			40	22	clear, colorless, tough solid
58.3	40.7	1.0		27	168	milky, brittle solid
58.7	41.0	0.3		27	72	clear, colorless, tough solid
58.6	40.9	0.5		27	96	clear, colorless, tough solid
58.5	40.7		0.8	27	96	clear, colorless, tough solid
58.5	40.7		0.8	60	24	foamed, colorless, tough solid

The recommended curing agents for ERL-4221 are acid anhydrides.[31] XZ-8-5024 is said to improve thermal stability when used as a "diluent" for other types of resins.[32] Neither resin is suggested for use alone with amine curing agents.

We attempted to cure ERL-4221 and XZ-8-5024 with bis(methylamino)diphenylsilane under a variety of conditions, with and without organotin catalysts. In all cases, we obtained either brittle or soft solids. ERL-4221 failed to polymerize with bis(methylamino)diphenylsilane unless the mixtures were held for long periods at high temperatures; then brittle solids were formed. The organotin compounds merely accelerated similar conversions. XZ-8-5024 exhibited the same type of reactivity except that the products were soft solids which changed to brittle solids if heating was prolonged. The data are summarized in Table XIII.

B. Experimental Details

1. Heat barriers

Two types of silylamine-cured resins were prepared for evaluation as heat barriers: one type was filled with glass fiber, potassium titanate, and glass microballoons; the other was filled only with glass fiber and potassium titanate. Ten specimens, each 1 x 1 x 0.5 inch, were required of each type. The compositions and curing schedules are summarized in Table XIV.

All components except the microballoons were blended with a high-speed stirrer. Then the microballoons were stirred in gently by hand. Thereafter, the mixtures were deaerated, cast into slightly oversize 2 x 5 x 0.6-inch blocks, and cured as described in Table XIV. The cured blocks were then sawed and milled to the specified size, 1 x 1 x 0.5 inch. Ten specimens of each type were submitted to Marshall Space Flight Center for evaluation.

The microballoons reduced the density 24%. The ten specimens with microballoons averaged 7.84 g; the corresponding group of ten samples without microballoons, 4480-21, averaged 10.33 g. The samples with microballoons were slightly less dense (specific gravity, 0.96) than water.

Table XIII. Attempts to Cure ERL-4221 and XZ-8-5024, with Bis(methylamino)diphenylsilane

ERL-4221, %	BMADPS, %	XZ-8-5024, %	Stannous octoate, %	Dibutyltin diacetate, %	Curing conditions Temp., °C	Curing conditions Time, hr	Appearance of product
51.8	48.2				70	20	fluid
51.8	48.2				120	20	fluid
51.8	48.2				180	20	fluid, hardened on surface
46.2a	47.2				180	24	fluid
51.4	47.7		0.9		70	30	brittle, tan solid
51.4	47.7		0.9		120	30	brittle, brown solid
51.4	47.7		0.9		180	30	brittle, brown solid
51.6	47.9		0.5		120	28	brittle, brown solid
51.7	48.0		0.3		120	28	brittle, brown solid
51.7	48.0		0.3		180	28	brittle, brown solid
51.7	47.5			0.8	120	40	brittle, brown solid
51.7	47.5			0.8	180	24	brittle, brown solid
	31.1	68.9			70	65	fluid
	31.1	68.9			120	65	fluid
	31.1	68.9	1.0		180	65	rubbery solid
	31.1	68.9	1.0		300	2	rubbery solid
	30.8	68.2	1.0		180	0.75	brittle, brown solid
	30.8	68.2	0.5		120	0.75	brittle, brown solid
	30.8	68.2	0.5		70	6	brittle, tan solid
	31.0	68.5	0.5		180	6	brittle, brown solid
	31.0	68.5	0.2		120	6	brittle, brown solid
	31.0	68.5	0.2		70	8	brittle, tan solid
	30.9	68.9			180	6	rubbery, brown solid
	30.9	68.9			120	6	rubbery, brown solid
	30.7	68.4		0.9	120	40	rubbery, brown solid
	30.7	68.4		0.9	180	40	rubbery, brown solid

a. Contained 6.6% Epon 828.

Table XIV. Epoxy Resins for Evaluation as Ablative Heat Shields

Components	Silylamine-cured 4480-21-1 g	Silylamine-cured 4480-21-1 %	Silylamine-cured 4480-45 g	Silylamine-cured 4480-45 %	Anhydride-cured 4480-23-1 g	Anhydride-cured 4480-23-1 %
Epon 828	45.00	53.64	90.00	51.3	75.00	45.35
Bis(methylamino)-diphenylsilane	29.00	34.56	58.00	33.0	–	–
Nadic Methyl Anhydride	–	–	–	–	71.00	42.93
Tipersul (fibrous potassium titanate)	4.91	5.85	9.80	5.5	9.61	5.81
Refrasil F-100-1/2 (glass fiber)	4.99	5.95	10.00	5.6	9.78	5.91
Eccospheres-Si (glass microballoons)	–	–	8.00	4.6	–	–
Total	83.90		175.80		165.39	

Mixing – Mix Epon 828 and catalyst, stir in Tipersul, then Refrasil, then microballoons; deaerate at less than 1 mm pressure for 1.5 hours.

Curing

2.0 hr at 60°C, 1.5 hr at 120°C	white	1 hr at 120°C, 4 hr at 200°C, 24 hr at 260°C

Appearance after curing: white | white | dark brown on surface, cream underneath

As mentioned previously, recommendations for the formula and curing procedure for the dianhydride-Epon 828 were obtained from Shell Chemical Corporation.[30] The "NADIC Methyl Anhydride" recommended as the curing agent was obtained from Allied Chemical Corporation and has the formula given below. It is a mixture of isomers with the methyl group in various locations.
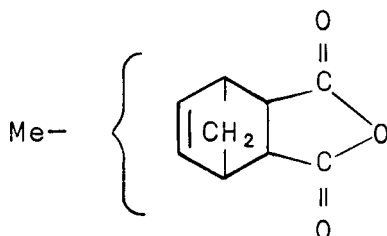
No difficulty was experienced in following the Shell procedure for curing the anhydride-cured epoxy except that bubbles formed in the resin unless it was deaerated for 30 minutes at room temperature at 0.1-1.0 mm before the heating schedule was started. The same trouble was experienced with the silylamine-cured epoxy, and several batches were discarded because of bubble formation. Apparently, large masses of the resin, especially when filled with Refrasil and Tipersul, are likely to foam unless the curing at the low temperatures is prolonged.

Tipersul fibrous potassium titanate was obtained from E. I. du Pont de Nemours and Company, Inc.; Refrasil F-100-1/2 glass fiber was obtained from Special Products, Inc., Gardena, California; Eccospheres-Si glass microballoons were obtained from Emerson and Cuming, Inc., Canton, Massachusetts.

2. Adhesives

The adhesive qualities of epoxy resins before and after exposure to high temperatures were compared by measuring the shear strengths of lap joints of aluminum under tensile loading. Aluminum strips 0.25 in. wide were joined with an overlap of 0.25 in. The uncured resins were spread on marked areas; then the joints were clamped together and cured. The shear strengths were measured with a Scott Tester, Model J-2. The compositions, curing times, and results are given in Table XI. Each of the shear strengths shown is the average of ten measurements.

Epon 828 cured with bis(methylamino)diphenylsilane gained in shear strength in 1 hour at either 300°C or 325°C. By contrast, Epon 828 cured with Nadic Methyl Anhydride according to Shell's recommendations lost strength at the same temperatures. Low shear strengths, about 550 psi, were obtained when Epon 828 was cured with m-phenylenediamine. Since manufacturer's data were not available as a guide, it was decided to discontinue efforts to use this combination as an adhesive. However, Epon 828 and m-phenylenediamine were used previously[33] to prepare laminates containing glass cloth, and the flexural strengths were satisfactory according to Shell.[34]

3. Low-temperature curing of Epon 828 with bis(methylamino) diphenylsilane

Epon 828 was cured satisfactorily with bis(methylamino)-diphenylsilane in 7 days at room temperature or in 22 hours at 40°C. Attempts to accelerate curing at room temperature with additives were only partially successful. The regular blend in a ratio of 100:64 was placed in a test tube at room temperature, about 26°C. In 3 days it became more viscous, and in 7 days it appeared fully cured. It was then clear, colorless, hard, and tough. No evidence was seen of separation of polymer from the glass. A similar sample held at 40°C was fluid and slightly more viscous after 6 hours; and, after 22 hours at 40°C, it was clear, very pale yellow, hard, and tough. Use of dibutyltin diacetate, 0.8% by weight, as catalyst reduced the curing time at 27°C from 7 days to 4 days. Stannous octoate, 0.3% or 0.5%, had the same effect, but 1.0% caused the polymer to be milky.

Stannous octoate was obtained from M & T Chemicals, Inc., and dibutyltin diacetate was obtained from Distillation Products Industries (EKC-P2138).

4. Search for new epoxy-silylamine combinations

Attempts to cure ERL 4221 with bis(methylamino)diphenyl-silane at temperatures up to 180°C were not successful. The two materials were mixed in the stoichiometric ratio, 19.5 g of ERL 4221 to 18.15 g of bis(methylamino)diphenylsilane, as calculated from the published epoxide equivalent of 126-140 for ERL-4221.[31] Then three portions of the mixture were heated for 20 hours separately at 70°C, 120°C, and 180°C.

Only the sample heated at 180°C gave any evidence of polymeri-
zation; it hardened on the surface but was soft underneath. A
blend of 9.8 g of ERL 4221, 1.4 g of Epon 828, and 10.0 g of
bis(methylamino)diphenylsilane turned brown and failed to
solidify in 24 hours at 180°C. A blend of 4.9 g of ERL 4221,
4.55 g of bis(methylamino)diphenylsilane, and 0.09 g of stannous
octoate was divided into three parts for curing at different
temperatures. In 5 hours, the sample at 70°C was still liquid,
and the samples at 120°C and 180°C had become appreciably more
viscous. At the end of 30 hours, all three samples were hard
and brittle. These and other experiments are summarized in
Table XIII.

Attempts to cure XZ-8-5024 gave unsatisfactory results.
XZ-8-5024, 13.25 g, and bis(methylamino)diphenylsilane, 6.0 g,
were blended. These were the amounts calculated from the pub-
lished epoxide equivalent, 250-280.[32] Portions of the blend
failed to solidify in 65 hours at 70°C or 120°C. A portion at
180°C changed to a rubbery solid in 65 hours. A portion at
300°C changed to a rubbery solid in 2 hours. Similar blends
containing 1% stannous octoate became brittle solids in 6 hours
at 70°C or 45 minutes at 120°C. With 0.5% stannous octoate,
the samples solidified somewhat slower, but they were brittle.
The experiments are summarized in Table XIII.

VI. SILYLATION OF POLYVINYL ALCOHOL

A. Discussion

Polyvinyl alcohol was silylated to determine whether a
polymer of such a structure would have useful properties at
either high or low temperatures. Methyl siloxanes have excellent
low-temperature properties, but information was not available on
polymers that have trimethylsiloxy groups as side chains.

$$\left[\begin{array}{c}-CH_2CH-\\ \vert\\ OH\end{array}\right]_n + Me_3SiN=CCH_3 \longrightarrow \left[\begin{array}{c}-CH_2CH-\\ \vert\\ Me_3SiO\end{array}\right]_n + Me_3SiN-CCH_3$$
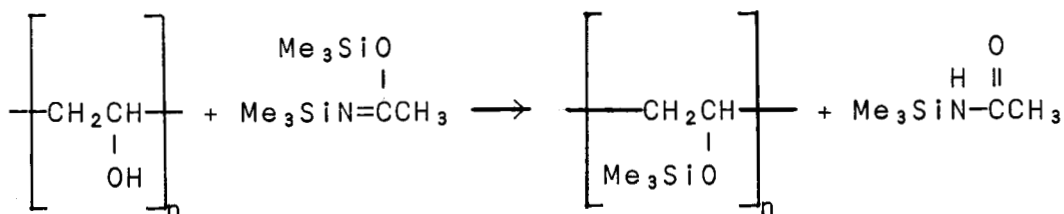
Two commercial polyvinyl alcohols were silylated, and the resulting polymers were similar. One of the original polyvinyl alcohols was 87-89% hydrolyzed, and the other was 99-100% hydrolyzed. Both silylated products were soluble in common organic solvents, and both could be cast into films that were clear, colorless, tacky, and sluggishly elastic. Thick pieces of the polymer were tough at room temperature. However, both polymers became hard at -78°C and quite soft at 70°C. Consequently, they are not promising for applications at either high or low temperatures.

It is interesting, however, to note that the silylated polymers were much more stable thermally than polyvinyl alcohol: they were elastic and light tan after 30 minutes at 300°C in air, while polyvinyl alcohol sintered and turned dark brown in 15 minutes at 300°C. Furthermore, the silylated polyvinyl alcohol lost weight much more slowly at 250°C in air (Table XV).

Table XV. Weight Losses of Polyvinyl Alcohol and Silylated Polyvinyl Alcohol at 250°C in Air

Time, hr	Polyvinyl alcohol, (Elvanol 71-30) weight loss, %	Silylated polyvinyl alcohol, weight loss, %	
		4571-67	4571-77-2
0	0	0	0
1	32	0.8	1.1
3	48	6	4
6	51	18	11

B. Experimental Details

1. Preparation of polymers

Silylation of polyvinyl alcohol was accomplished readily with the reagent described by Klebe,[35] bis(trimethylsilyl)-acetamide, after a satisfactory procedure was developed.

Silylation of polyvinyl alcohol (Elvanol 52-22, E. I. du Pont de Nemours, and Co., Inc., 87-89% hydrolyzed, 21-25 centipoises viscosity) was tried first by stirring for 12 days with an excess of bis(trimethylsilyl)acetamide in pyridine, in diethyl ether, in tetrahydrofuran, and in acetonitrile. Only the trial in pyridine produced a product of interest; other solvents were ineffective. The product with residual reaction byproducts was dissolved in benzene, cast into a film on glass, and heated to 100°C at 0.02 mm to remove the benzene and trimethylsilylacetamide. The product was Polymer 4571-59-2.

Anal. Calculated (for complete silylation of 88% hydrolyzed polyvinyl alcohol): C 52.91, H 10.85, Si 21.26.

Found: C 52.15, H 10.03, Si 21.71.

The silylation procedure preferred presently is the following, which was used to make Polymer 4571-67. Polyvinyl alcohol (Elvanol 71-30, 99-100% hydrolyzed, 28-32 centipoises viscosity), 3.00 g (0.068 mole, repeating unit) was placed in a 50-ml, 3-neck, round-bottom flask equipped with a magnetic stirrer and reflux condenser. To this was added 50 ml of pyridine, and the mixture was refluxed 4 hours to swell the polyvinyl alcohol. The mixture was cooled, and 12.93 g (0.064 mole) of bis(trimethylsilyl)acetamide was added. The mixture was stirred at 85°C for 1.5 hr. The resulting clear solution was cooled, and the pyridine was removed under reduced pressure. The product was dissolved in benzene and cast into a film on glass. After the benzene evaporated, the film was heated at 0.01 mm at 95-100°C to remove the excess reagent and byproduct.

Anal. Calculated for $C_5H_{12}OSi$: C 51.67, H 10.41, Si 24.16.

Found: C 51.44, H 10.22, Si 23.98.

Polymer 4571-77-2 was prepared in the same way as 4571-67, except only 10.05 g (0.050 mole) of bis(trimethylsilyl)acetamide, which is a bifunctional silylating agent, was used. After addition of the silylating agent, the mixture was heated at 95°C for 2.5 hr.

2. Properties of polymers

The fully silylated polymers were soluble in chloroform, ethyl acetate, hexane, benzene, and tetrahydrofuran. Both of the above polymers were elastic and visibly unchanged after immersion in boiling water for 30 minutes. Both polymers were hard and tough when cooled to -78°C with dry ice. Polymer 4571-59-2 had a softening point of 65-66°C and Polymer 4571-67 had a softening point of 47°C, as determined by the temperatures at which polymers stuck to the cover glasses in a Fisher-Johns melting point apparatus. Polymer 4571-59-2 was slightly elastic after being heated 30 minutes at 300°C, but it became rigid in 60 minutes at 300°C.

Polymers 4571-67, 4571-77-2, and Elvanol 71-30 were weighed periodically after being heated in an oven at 250°C in air. The results, which are given in Table XV show that the silylated polymer was appreciably more stable.

VII. CONTROLLED HYDROLYSIS AND CONDENSATION OF SILYLAMINES TO FORM POLYMERS

A. Discussion

The condensation reaction of disilanols with diaminosilanes is a well-known route to polymers.[7] This reaction seemed capable of forming polymers through carefully controlled hydrolysis of di-, tri-, or tetraaminosilanes, because each silanol formed would react with an aminosilane to form a siloxane linkage.

The following equations indicate the possible scope of controlled hydrolysis-polymerization reactions of aminosilanes:

Diaminosilanes can form linear or cyclic polymers:

$$\begin{array}{c} R' \\ H \mid H \\ RN-Si-NR \\ \mid \\ R' \end{array} \xrightarrow{HOH} \begin{array}{c} R' \\ H \mid \\ RN-Si-OH \\ \mid \\ R' \end{array} \longrightarrow \left[\begin{array}{c} R' \\ \mid \\ -Si-O- \\ \mid \\ R' \end{array} \right]_n$$
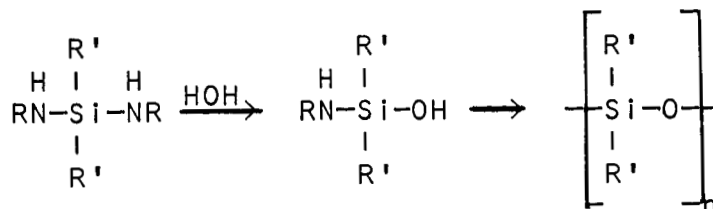
Triaminosilanes can form linear, ladder, or crosslinked polymers:

Linear:

$$\begin{array}{c} R' \\ H \;|\; H \\ RN-Si-NR \\ | \\ HNR \end{array} \xrightarrow[\text{2. condensation}]{\text{1. hydrolysis}} \left[\begin{array}{c} R' \\ | \\ Si-O \\ | \\ HNR \end{array} \right]_n \xrightarrow[\text{2. condensation}]{\text{1. hydrolysis}}$$

$$\begin{array}{ccccccc} R' & & R' & & R' & & R' \\ | & O & | & & | & O & | \\ -Si & < > & Si-O-Si & & < > & Si-O- \\ & O & & & & O & \end{array}$$

Ladder:

$$\begin{array}{ccc} R' & & R' \\ | & O & | & O \\ Si & < > & Si & < \\ O & & O & \\ Si & < > & Si & < \\ | & O & | & O \\ R' & & R' \end{array}$$
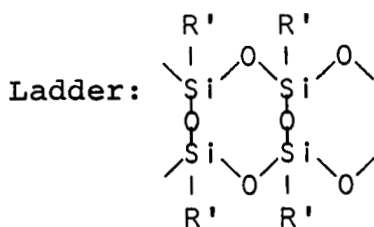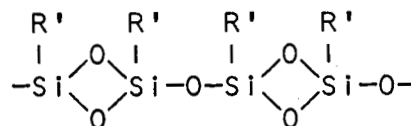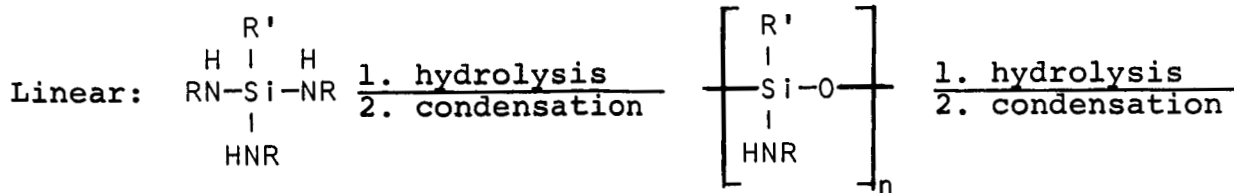
similar to Brown's phenylsilsesquioxane[36,37]

Brown prepared phenylsilsesquioxane by equilibrating phenyl-trichlorosilane hydrolysate in a mixture of alkali, toluene, and water. This two-phase medium facilitated separation of the ladder form.

Tetraaminosilanes can form a variety of structures including:

related to linear $(SiS_2)_n$[38]
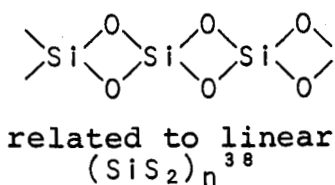
and

The vulnerability of the method lies in the fact that excessive crosslinking will produce intractable gels or infusible and insoluble solids. Brown[37] pointed out a number of cases in which the products were soluble, fusible polymers with desirable properties, particularly high thermal stability.

Since excessive crosslinking would produce intractable gels, we first attempted to favor intramolecular reaction of partially polymerized materials by carrying out the reactions in solvents:

$$(Me_2N)_4Si + H_2O \longrightarrow (Me_2N)_3Si-OH \longrightarrow (Me_2N)_3Si-O-Si(NMe_2)_3$$

$$\downarrow H_2O, \text{ intra-molecular}$$

$$(Me_2N)_2Si \overset{O}{\underset{O}{<>}} Si(NMe_2)_2$$
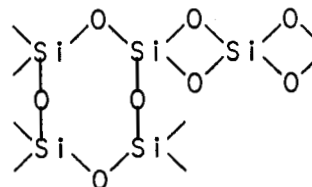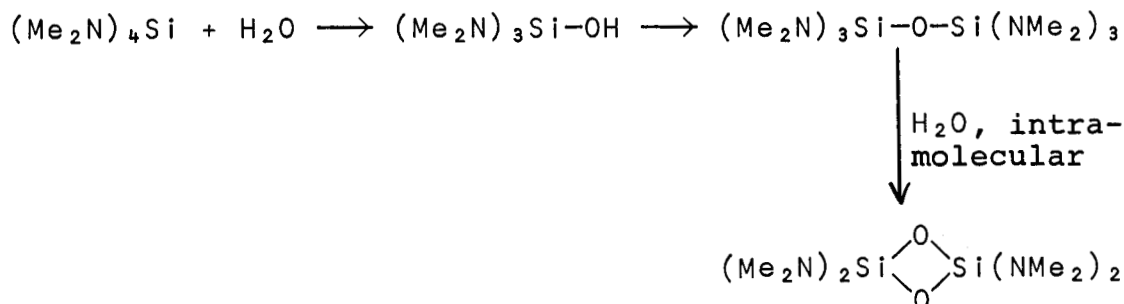
Water was introduced by bubbling moist nitrogen into the aminosilane solution. This method avoided a large concentration of water at any location. Toluene and triethylamine were used as solvents, and the reactions were run at reflux temperatures to avoid excessive reaction times. In only one case, hydrolysis of tetrakis(dimethylamino)silane in triethylamine, was an isolable soluble polymer formed, and its elemental composition showed that it was not an expected product. Later, water vapor entrained in nitrogen was introduced into tetrakis(dimethylamino)-silane over a period of 15.5 hours. The only product that could be isolated was the same type of infusible, insoluble solid. Two reactions of tris(dimethylamino)phenylsilane, one in triethylamine and one in ether, also formed insoluble, infusible solids that ignited when heated strongly on a spatula.

Many factors doubtless determine whether the principal products will be linear, ladder, or crosslinked polymers. If the formation of rings, as required for the ladder or linear forms, were not favored thermodynamically, random polymerization would predominate. Also, the crosslinked form would be favored in the hydrolysis condensation of tri- or tetraaminosilanes if partially hydrolyzed molecules reacted with water more easily than those that had not reacted. For example, if Reaction 2 occurred more readily than Reaction 1 in the equations below, complete hydrolysis

of a few tetraaminosilane molecules followed by random cross-linking would occur before Reaction 3 formed linear polymers. The formation of linear polymers is needed in the early stages of hydrolysis to facilitate formation of double chains.

1. $Si(NR_2)_4 + H_2O \longrightarrow HO-Si(NR_2)_3$

2. $HO-Si(NR_2)_3 + H_2O \longrightarrow (HO)_2Si(NR_2)_2$

3. $(R_2N)_3Si-OH + R_2N-Si(NR_2)_3 \longrightarrow (R_2N)_3Si-O-Si(NR_2)_3$

It appears that the factors favoring crosslinking are strong enough that additional efforts to form soluble, fusible polymers are not justified.

B.   Experimental Details

1.   Preparation of monomers

a.   Tetrakis(dimethylamino)silane

The preparation of tetrakis(dimethylamino)silane was complicated by the difficulty of replacing the fourth chlorine atom of silicon tetrachloride. Silicon tetrachloride, 101 g (0.60 mole), was dissolved in 2 liters of toluene and stirred under an atmosphere of dimethylamine for 6 hours, while the temperature rose to 50°C and then returned to room temperature. The reaction mixture was filtered to remove salts, and the filtrate was refluxed while dimethylamine was introduced under the surface for 3 hours. The mixture was filtered again, and the product was distilled. Since the elemental analysis indicated the product was chlorotris(dimethylamino)silane, it was again dissolved in toluene, 1 liter, and treated with dimethylamine under reflux for 2 hours and at room temperature for 8 hours. Distillation after filtration produced 46.9 g of tetrakis(dimethylamino)-silane, b.p. 74.5°C at 13 mm, m.p. 17-17.5°C (Anderson,[13] -2°C).

Anal. Calculated for $C_8H_{24}N_4Si$:   C 47.01, H 11.84.

Found: C 47.20, H 11.73.

Neutral equivalent. Calculated, 51.1; found 50.5.

b. Tris(dimethylamino)phenylsilane

The preparation of tris(dimethylamino)phenylsilane was described above in Section III.B.1.d.

2. Hydrolysis-condensation polymerizations

(a) Tetrakis(dimethylamino)silane

The first apparatus used for conducting hydrolysis and polymerization simultaneously consisted of a gas train in which nitrogen was bubbled through water and passed into the flask that contained the aminosilane. The reaction flask was fitted with a reflux condenser. The effluent nitrogen passed from the top of the reflux condenser into a flask containing a measured amount of standard acid. Periodically the acid was titrated to determine the amount of dimethylamine reaction product that had been carried from the reaction flask by the nitrogen.

In the first reaction, moist nitrogen was passed into 4.4 g (0.021 mole) of tetrakis(dimethylamino)silane in 25 ml of refluxing toluene. The nitrogen flow rate was 150 ml per minute. Within 2 hours, a small amount of hard, white, granular precipitate formed in the reaction flask. The amount of amine evolved indicated the reaction was about 5% complete. No significant additional change was noted in the next 13 hours except that the amount of insoluble matter increased. The amine evolved indicated 22% of complete reaction. Essentially nothing was dissolved in the toluene except material that evaporated at 55°C at 0.1 mm. The insoluble portion of the product was infusible at red heat. Evidently satisfactory polymerization did not occur.

In the second reaction, moist nitrogen, obtained by passing nitrogen over the surface of water, was admitted under the surface of the tetrakis(dimethylamino)silane at 120°C. Addition of moisture in this manner was continued for 15.5 hours. A yellow deposit formed almost immediately and increased as more moisture was added. The reaction mixture was heated at 55°C under reduced pressure (0.1 mm) to remove any unchanged aminosilane and water. A yellow, granular, insoluble, infusible, and incombustible solid remained.

In the next attempt, 4.57 g (0.022 mole) of tetrakis-(dimethylamino)silane was dissolved in 15 ml of triethylamine, and 0.45 ml (0.025 mole) of water was introduced through a hypodermic syringe under the surface of the solution. The water was introduced in 0.02-0.04-ml increments at 15-minute intervals. After 2 hours, a yellow granular precipitate appeared, and the amount increased as the remainder of the water was added. The product was essentially the same as before except that the solvent, when evaporated, yielded about 0.1 g of an orange, slightly elastic, tacky material that appeared to be polymeric.

<u>Anal.</u> Found: C 49.88, H 7.35, N 0.70, Si 20.04.

C:N ratio, 50:0.7; theoretical, 24:14.

These figures show that the C and N did not occur in the product in the proportions in which they would occur in any of the desired products, because the $(CH_3)_2N-$ groups should be the only source of C and N. Consequently, the product was contaminated or was not related to the desired polymer.

(b)   Tris(dimethylamino)phenylsilane

Water, 0.5 ml (0.028 mole), was added from a hypodermic syringe thrust under the surface of a solution containing 4.44 g (0.019 mole) tris(dimethylamino)phenylsilane in 15 ml of triethylamine. The water was added in small increments (0.02-0.04 ml per hour) over a period of 13 hours while the reaction remained at room temperature. Triethylamine was removed under reduced pressure, and a cream-colored granular solid was recovered. This powder was insoluble in hot hexane, tetrahydrofuran, benzene, dioxane, and ether. It burned when heated in a flame.

A second attempt was made to polymerize tris(dimethylamino-phenylsilane by adding it to an ether-solution of water. Tris(di-methylamino)phenylsilane, 9.35 g (0.0394 moles), was stirred for 4 days in an ether solution containing 0.277 g (0.0153 moles) of water (26% of the theoretical for complete hydrolysis). After 4 days, 8.89 g (95%) of ether-soluble liquid and 0.301 g of white, granular, infusible, combustible powder was recovered. The ether-soluble liquid product, 8.89 g, was heated to 50°C for 5 hours to induce further polymerization in case it contained partially hydrolyzed but uncondensed starting material. The pressure was then reduced to 0.1 mm and the temperature was increased to 80°C to distill off any volatile material. The residue, 0.37 g, was a white, resinous solid that fused partially when heated. Because of the low yield it was not considered important.

VIII. REACTION OF BIS(METHYLAMINO)DIPHENYLSILANE WITH KETONES

A. Discussion

Bis(methylamino)diphenylsilane was found to react exothermally with ketones. A reaction was reported earlier between bis(methylamino)dimethylsilane and acetone,[39] but in that case reaction was slower, and it was detected only by pmr spectra. With bis(methylamino)diphenylsilane and acetone, the reaction was vigorous enough to cause the solution to reflux. The main silicon-containing product was octaphenylcyclotetrasiloxane, which was obtained in 89% yield.

An exothermic reaction occurred, also, between bis(methylamino)diphenylsilane and methyl propyl ketone. Again, octaphenylcyclotetrasiloxane was formed in high yield.

Careful gas-liquid chromatography of the mixture obtained by adding bis(methylamino)diphenylsilane to acetone failed to reveal any products other than octaphenylcyclotetrasiloxane. When the elution temperature of the chromatographic column was raised to the maximum limits of the instrument, 300°C, the only components of the mixture eluted were nitrogen (air), methylamine, acetone, and methyl alcohol. The trace of methyl alcohol (less than 0.1%) was found in the acetone starting material and in the reaction mixture in essentially the same concentration. Accordingly, methanol was not a reaction product. As expected, the octaphenylcyclotetrasiloxane was not eluted at 300°C.

Further attempts to isolate byproducts led to the separation of the 2,4-dinitrophenylhydrazone of isophorone, which was isolated from the mother liquor in 67% yield. Thus, the reaction of bis(methylamino)diphenylsilane with ketones is apparently a base-catalyzed condensation-dehydration of the ketone with the aminosilane supplying the base and removing the water.

It was rather surprising that the reaction produced such a high yield of the cyclotetrasiloxane. In a subsequent experiment, bis(methylamino)diphenylsilane dissolved in dioxane, was treated with a slight excess of water. The solution, which became warm spontaneously, was then refluxed and allowed to stand overnight. Crystals of octaphenylcyclotetrasiloxane were

isolated in 86% yield. This experiment confirmed that the hydrolysis of bis(methylamino)diphenylsilane does proceed with a high degree of specificity to octaphenylcyclotetrasiloxane.

The following reactions are consistent with the available information:

$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \underset{\xleftarrow{\hspace{1cm}}}{\overset{MeNH_2}{\xrightarrow{\hspace{1cm}}}} CH_3-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3 \underset{\xleftarrow{\hspace{1cm}}}{\overset{-H_2O}{\xrightarrow{\hspace{1cm}}}} CH_3-\overset{\overset{O}{\|}}{C}-CH=\overset{}{\underset{\underset{CH_3}{|}}{C}}-CH_3$$

diacetone alcohol   mesityl oxide

$$CH_3-CO-CH_3 \quad \updownarrow$$
$$-H_2O$$

isophorone

$$CH_3-\overset{}{\underset{\underset{CH_3}{|}}{C}}=CH-\overset{\overset{O}{\|}}{C}-CH=\overset{}{\underset{\underset{CH_3}{|}}{C}}-CH_3$$

phorone

$$4 \ HN-\overset{\overset{Me}{|}}{\underset{\underset{Ph}{|}}{Si}}-NH + 4 \ H_2O \longrightarrow \left[\overset{\overset{Ph}{|}}{\underset{\underset{Ph}{|}}{Si}}-O-\right]_4 + 8 \ MeNH_2$$

octaphenylcyclotetrasiloxane
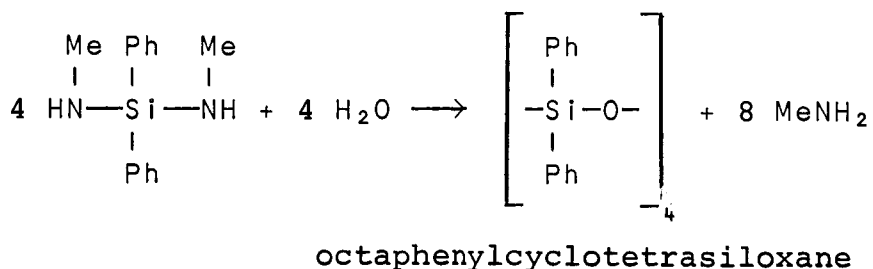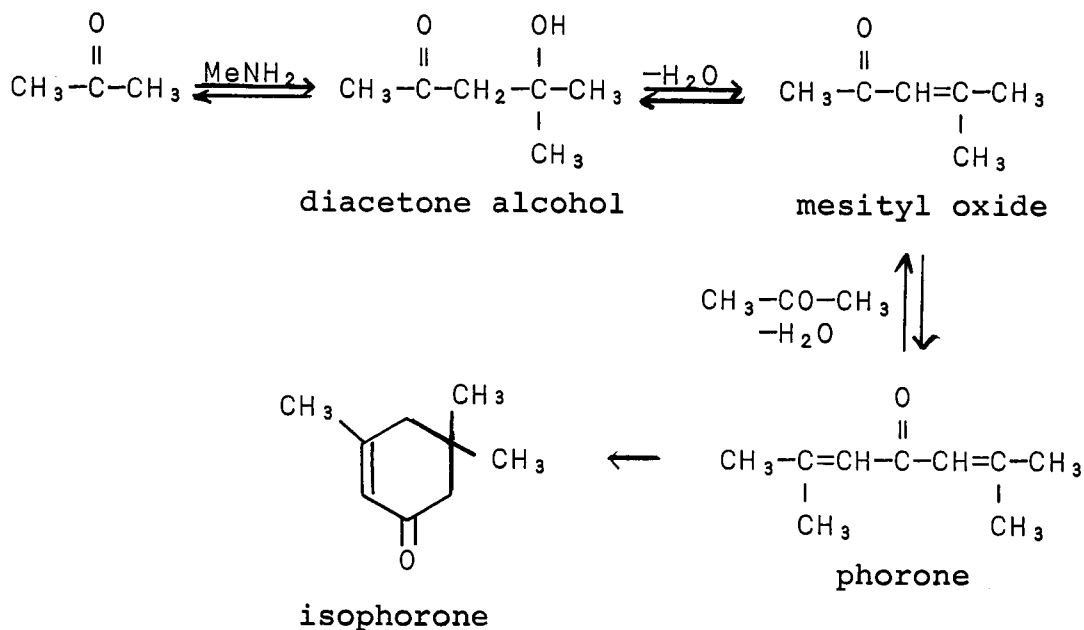
Infrared absorption curves of the reaction mixtures as the reaction proceeded indicated the presence of transient silanols, which can be explained by intermediates such as the following:

```
      Me  Ph       Ph              Ph     Ph
      |   |        |               |      |
     HN—Si —O—Si —OH          HO-Si -0-Si -OH
          |        |               |      |
          Ph       Ph              Ph     Ph


     Me  Ph   Ph   Ph           Ph     Ph    Ph
     |   |    |    |            |      |     |
    HN—Si -O-Si -O-Si -OH    HO-Si —O-Si -O-Si -OH
         |    |    |            |      |     |
         Ph   Ph   Ph           Ph     Ph    Ph
```
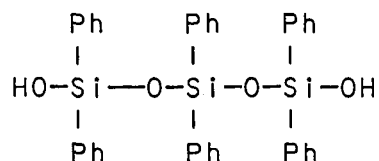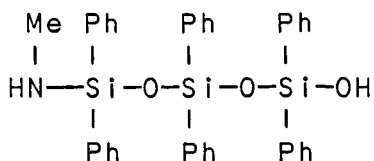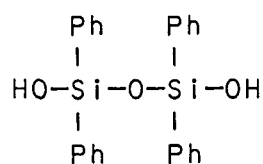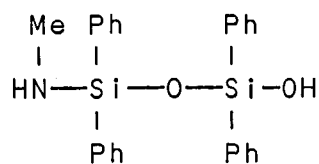
When the reactions reach completion, the octaphenylcyclotetra-siloxane seems to be the exclusive silicon-containing product.

Acetone, in the presence of base, forms the relatively unstable diacetone alcohol, which then condenses to mesityl oxide, phorone, and isophorone. Isophorone is the most stable of these, but all of the reactions can be reversed in the presence of water. It was stated previously that gas chromato-graphy detected no volatile material other than acetone, methyl alcohol, and methylamine. The failure to detect mesityl oxide, phorone, and isophorone can be explained as disappearance of these by reconversion to acetone or further polymerization to materials of lower volatility. No effort was made to isolate the 2,4-dinitrophenylhydrazones of other ketones; others may have been present in small amounts.

B. Experimental Details

1. Reaction of bis(methylamino)diphenylsilane with excess acetone

During an attempt to obtain a pmr spectrum of bis(methyl-amino)diphenylsilane a sample was dissolved in acetone and placed in a sample tube. Within a few minutes the sample boiled out of the tube. The reaction was repeated on a larger scale in a nitrogen atmosphere and with dry acetone that had been purged with nitrogen. Within 4 minutes of the addition of bis(methyl-amino)diphenylsilane, 6.0 g (0.025 moles), to the acetone, 15.9 g (0.273 moles), the reaction became vigorous enough to cause the

solution to reflux for about 1.5 minutes. The acetone had previously been analyzed by gas chromatography and found to contain 0.14% water. Thus, 0.023 g (0.0013 mole) of water was present. The reaction mixture was allowed to stand overnight at 5°C. A product, which appeared in the form of colorless prisms, was collected on a filter, dried and weighed. It amounted to 4.4 g. The "crude" material melted at 185-192°C, and, after recrystallization from acetone, the melting point was 202.5-203°C. The reported melting point[40] for octaphenylcyclotetrasiloxane is 201-202°C.

Anal. Calculated for $C_{48}H_{40}O_4Si_4$:   C 72.68, H 5.08, Si 14.17.

Found: C 72.77, H 5.09, Si 14.10.

Thus, the yield was 89% of theory.

The original filtrate from the reaction was acidified with ethanolic hydrogen chloride and white crystals formed at once. These were collected on a filter, washed with cold ether and dried in vacuo., m.p. 222-224°C. The melting point of methylamine hydrochloride is 226°C.

2.   Reaction of bis(methylamino)diphenylsilane with acetone in a 1:2 molar ratio

Bis(methylamino)diphenylsilane (12.1 g; 0.05 mole) was dissolved in anhydrous n-hexane (50 ml). Acetone (5.80 g; 0.10 mole) was added, and the system was protected from atmospheric moisture while being stirred and heated at gentle reflux for 2 hours. The solution, upon cooling to 5°C, separated cleanly into two liquid layers. Small samples were taken from each layer, and infrared absorption spectra were taken of each. The spectrum of the upper (n-hexane) layer, in addition to the absorption bands expected of n-hexane, contained sharp bands at 1215 cm^{-1}, 1716 cm^{-1}, 3000 cm^{-1} and 3510 cm^{-1}. These strongly indicate the presence of acetone in the mixture. In addition to the bands attributable to n-hexane and acetone, very strong absorption was noted at 1668 cm^{-1}. This is characteristic of the carbonyl stretching frequency in α, β or α', β'; α, β unsaturated ketones such as mesityl oxide, phorone or isophorone. The absorption spectrum of the lower layer was identical with that of octaphenylcyclotetrasiloxane, but, in addition, contained a sharp band at 3600 cm^{-1} and a band of equal intensity

but much broader base at 3350 cm^{-1}. The former band is character-
istic of the OH stretching frequency in primary, disassociated
alcohols while the latter is the frequency of the same type bond
in hydrogen-bonded alcohols.

The reaction mixture (minus the insignificant samples
removed for infrared study) was stirred for 48 hours at room
temperature. At the end of this time there was no second
liquid phase, only a white crystalline solid suspended in a
liquid. The solid was collected on a filter, washed with n-
hexane and dried. The yield was 9.22 g, or 93%, of relatively
pure octaphenylcyclotetrasiloxane (m.p. 190-197°C). The clear
filtrate was treated with an acidic, ethanolic solution of
2,4-dinitrophenylhydrazine, and the orange solid that formed
after 2 hours of stirring was collected on a filter and
recrystallized twice from aqueous ethanol to give 6.84 g of a
phenylhydrazone, which melted at 128-130°C. The reported melting
point of the 2,4-dinitrophenylhydrazone of isophorone is 130°C.
This would indicate a yield of 67% of isophorone from the acetone
initially employed.

3. Reaction of bis(methylamino)diphenylsilane with methyl propyl ketone

Bis(methylamino)diphenylsilane and methyl propyl ketone
(2-pentanone) were combined under conditions that excluded
moisture, and an exothermic reaction ensued. The product, which
crystallized from the reaction mixture, was octaphenylcyclotetra-
siloxane.

4. Reaction of bis(methylamino)diphenylsilane with water

Bis(methylamino)diphenylsilane (6.05 g; 0.025 mole) was
dissolved in anhydrous p-dioxane. Water (1.0 g; 0.055 mole)
was added, and the stirred system became warm at once. The
mixture was heated at gentle reflux for 2 hours and then allowed
to stand overnight at 5°C. The white crystals that formed were
collected on a filter and dried, m.p. 190-195°C.

The product weighed 4.25 g, which represents an 86% yield
of relatively pure octaphenylcyclotetrasiloxane.

IX.   POLYMERIZATION OF ISOCYANATES
WITH SILAZANES

A. Discussion

It was found earlier[41] that aliphatic diisocyanates react with disilazanes to form partially crosslinked polymers. A small amount of additional work has been done to learn more about the scope of the reaction, the character of the polymers, and the requirements for polymerization. The polymers prepared from hexamethylene diisocyanate and heptamethyldisilazane had glass-transition temperatures of 64-108°C, and they crazed slowly at 150°C. The tensile strength (nominal) was 6300 psi, the tensile strength at break (nominal) was 4800 psi, and the elongation at break was 15%. The polymer has not been fully characterized, but it appears that the four- and six-membered-ring structures shown below are both present. The six-membered ring contributes crosslinking while the four-membered ring contributes only linearity.

$$OCN-[-(CH_2)_6-N{<}^{C=O}_{C=O}{>}N-(CH_2)_6-N{<}^{C=O}_{C=O}{>}N-]-(CH_2)_6NCO$$
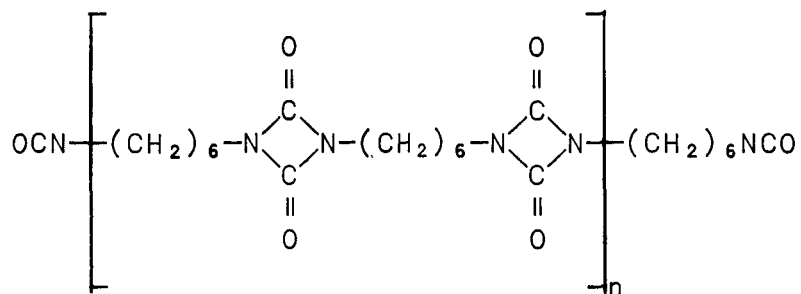
linear polymer
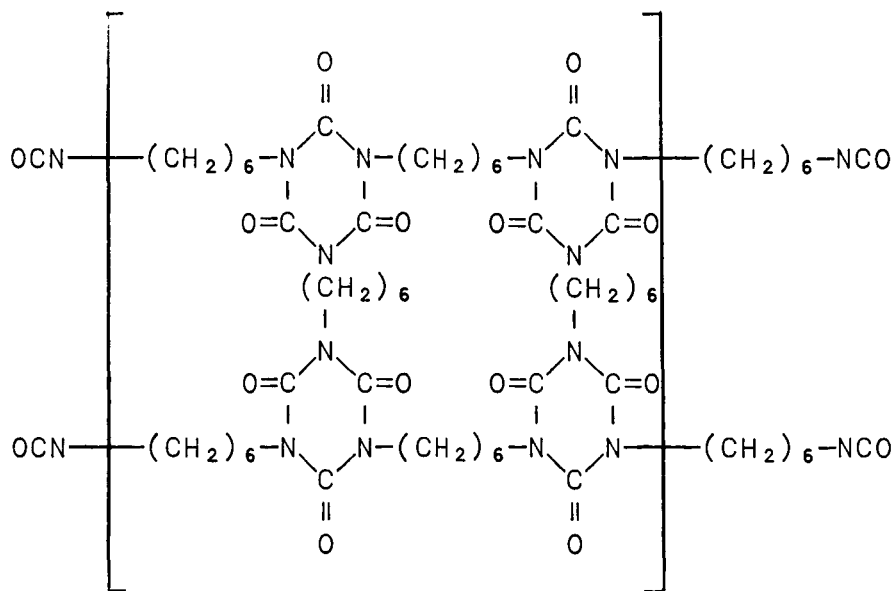
crosslinked polymer

The relationship between shear modulus and temperature[41] indicated that the amount of crosslinking was too high for all of the isocyanate groups to have formed four-membered rings and too low for all to have formed six-membered rings.

Polymers made from hexamethylene diisocyanate and heptamethyldisilazane were clear and almost colorless when freshly purified reactants were used.

Although no reports of prior work on the use of silazanes to polymerize diisocyanates have been found, other catalysts or initiators have been used. Jones and Savill[42] made triaryl isocyanurate compounds and polymers by adding a trace of pyridine to solutions of aromatic isocyanates in compounds containing oxirane rings. Herbstman[43] trimerized aryl isocyanates with trialkylarsenic and -antimony oxides. Hexamethylene diisocyanate was polymerized in solution in dimethylsulfoxide to yield an insoluble powder. Sandler[44] prepared polyisocyanurate adhesives from aromatic isocyanates with organometallic catalysts, for example, calcium naphthenate. Butler and Webster[45] prepared isocyanurate polymers of hexamethylene diisocyanate and DDI Diisocyanate with triethylenediamine and styrene oxide as co-catalysts.

The preceding report[41] also described polymers made from DDI Diisocyanate, a product of General Mills, Inc. DDI Diisocyanate is derived from "a dimeric fatty acid", and probably has this structure:

$$OCN-(CH_2)_8-\text{[ring]}-(CH_2)_8NCO$$

with substituents $(CH_2)_5CH_3$ and $(CH_2)_7CH_3$
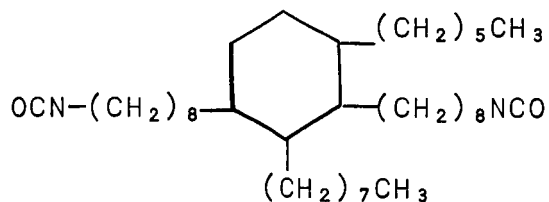
The DDI polymer was a clear, yellow, flexible, elastic polymer that had a glass-transition temperature of -11°C, but tensile properties were not measured.

Recent work with the isocyanate-silazane polymers has shown that they change in ways that suggest they are undergoing rearrangement in the solid state. The observations are summarized in Table XVI. In Experiments 4571-125-3, -149-1, and 149-5, polymers that were initially flexible stiffened on standing. These polymers had been cured at less than the usual 130°C, except for -125-3 which contained some butyl isocyanate. In Experiment 4571-149-5, most of the polymer initially was only slightly flexible as in 4571-101-1. However, the upper corners of the product were flexible when it came out of a thin, square, vertical mold. After standing a month, it was entirely stiff and the corners were brittle. As another example of instability, the polymers formed in Experiments 4571-89 and 4571-111-1 crazed badly when they were heated subsequently at 180°C. Both of these types of change indicate unstable structures, but there was no evidence of depolymerization such as softening or liquefaction. Consequently, the change must have been rearrangement. No evidence of instability at 180°C was observed in the polymers from Experiments 4571-101-1 or 4571-111-2; in both of these polymers, the amount of silazane was relatively low. Apparently, if the curing temperature is 130°C or above and the molar ratio of hexamethylene diisocyanate to heptamethyldisilazane is 1:17 or 1:30, the polymer is strong, tough, and

Table XVI. Curing and Thermal Stability of Silazane-Diisocyanate Polymers

Expt. 4571-	Diisocyanate	Silazane	Molar ratio, silaz:diiso	Heating conditions Time, hr[a]	Temp., °C	Appearance of product
89	hexamethylene diisocyanate	heptamethyl-disilazane	1:6	18 18.8	130 180	hard, sl. flexible badly crazed
107-3	hexamethylene diisocyanate	heptamethyl-disilazane	1:6	70 99	72 72	fluid fluid
101-1	hexamethylene diisocyanate	heptamethyl-disilazane	1:30	11 19 20	130 130 180	hard, sl. flexible hard, sl. flexible no change
101-2	hexamethylene diisocyanate	heptamethyl-disilazane	1:38	11 14 28	130 130 130	soft easily torn easily torn
111-1	hexamethylene diisocyanate	heptamethyl-disilazane	1:10	18.5 19.3	130 180	hard, sl. flexible crazed
111-2	hexamethylene diisocyanate	heptamethyl-disilazane	1:17	18 18.8	130 180	hard, sl. flexible sl. darker, no craze
101-3	hexamethylene diisocyanate	hexamethyl-disilazane	1:23	21 26 40	130 130 130	viscous soft hard, brittle
101-4	hexamethylene diisocyanate	hexamethyl-disilazane	1:11	10 19	130 130	sl. flexible hard, sl. flexible
111-3	DDI[b]	heptamethyl-disilazane	1:6	18 24	130 130	viscous sl. tacky sheet, resilient
91-1	DDI[b]	heptamethyl-disilazane	1:10	138	130	viscous
91-2	DDI[b]	heptamethyl-disilazane	1:29	23	130	tacky, rubbery
103-1	DDI[b]	hexamethyl-disilazane	1:3	7 18 24	130 130 130	resilient, easily torn resilient, easily torn resilient, easily torn
105-1	DDI[b]	hexamethyl-disilazane	1:4	8 18	130 130	resilient, easily torn resilient, easily orn
107-4	DDI[b]	hexamethyl-disilazane	1:6	70 99	72 72	viscous viscous
105-2	DDI[b]	hexamethyl-disilazane	1:8.5	11 35 43	 130 	viscous tacky, rubbery tacky, rubbery
107-1	DDI[b]	hexamethyl-disilazane	1:13	31 39	130 130	viscous viscous
107-2	DDI[b]	hexamethyl-disilazane	1:19	31 38.5	130 130	viscous viscous
115-1	DDI[b]	heptamethyl-disilazane	1:5.6	28	130	flexible
119-1	DDI[b]	heptamethyl-disilazane	1:6.3	28	130	flexible, sl. tacky, easily torn
125-3	hexamethylene diisocyanate + butyl isocyanate[c]	heptamethyl-disilazane	1:2.2:23	17	130	flexible, stiffened on standing[d]
131-1	hexamethylene diisocyanate	heptamethyl-disilazane	1:23	72	65	viscous
149-1	hexamethylene diisocyanate	heptamethyl-disilazane	1:23	17	125	flexible, stiffened on standing
149-3	hexamethylene diisocyanate	heptamethyl-disilazane	1:25	16	110	sl. flexible
149-5	hexamethylene diisocyanate	heptamethyl-disilazane	1:23	16	110	part rigid, part flexible;[e] stiffened on standing
157-1	Adiprene L-100	heptamethyl-disilazane	1:7	9	110	flexible, easily torn
157-2	Adiprene L-100	heptamethyl-disilazane	1:18	8	110	flexible, easily torn

a. Each figure is accumulated time.

b. DDI Diisocyanate, General Mills, Inc.

c. Butyl isocyanate added to modify crosslinking.

d. Lost weight on standing equal to initial butyl isocyanate content.

e. Upper corners of sheet flexible; see text.

only slightly flexible when formed. Furthermore, it undergoes
no visible change in 20 hours at 180°C. When the ratio was 1:38,
polymerization did not occur satisfactorily, since the product
was soft and easily torn.

Heptamethyldisilazane is preferred as a catalyst over
hexamethyldisilazane. The latter, which contains an N-H group,
was tried in an effort to reduce the curing time; but it did not
accelerate curing; and it was less effective than heptamethyl-
disilazane for producing tough polymers.

Adiprene L-100 was polymerized by heptamethyldisilazane
to a resilient, flexible sheet that could be torn fairly easily
once a break was made in the surface. Adiprene L-100 is an
isocyanate-terminated prepolymer derived from poly(tetramethylene
glycol) and an aromatic diisocyanate. It can be cured in the
conventional manner with a diamine to a tough, elastic polymer.
Adiprene L-100 cured with the silazane was similar but not as
tough.

An effort to modify the character of the isocyanate-
silazane polymers by adding butyl isocyanate was based on the
structural formulas shown above. The addition of butyl isocyanate,
which is monofunctional, should reduce the amount of crosslinking
and increase the flexibility. It proved to be difficult to retain
the butyl isocyanate in the polymer while it was being cured at
130°C. In one experiment, 4571-125-3, an initially flexible
polymer containing about 10% of butyl isocyanate was obtained.
However, it stiffened on long standing and lost weight in an
amount equal to the butyl isocyanate present.

To elucidate the structure of the polymers, aliphatic and
aromatic monoisocyanates were heated in sealed tubes with
heptamethyldisilazane. At 60°C, methyl isocyanate reacted to
form the cyclic trimer, methyl isocyanurate in 70% yield. At
130°C, the yield was 87%.

Trimethyl isocyanurate
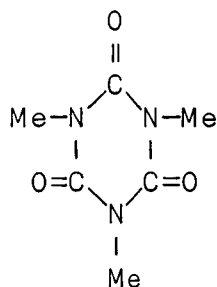
Phenyl isocyanate formed the cyclic trimer in 14% yield
at 60°C and in 7% yield at 130°C. The remainder of the product,
which was not the starting material, was not identified. Butyl
isocyanate, heated at 60°C with heptamethyldisilazane, reacted
to form a viscous material that contained less than 2% volatile
material at 100°C and 0.01 mm pressure. Again, the product was
not identified. It is evident that heptamethyldisilazane catalyzes
cyclization of both aliphatic and aromatic isocyanates, but addi-
tional work would be required to determine the conditions affecting
the relative amounts of the various products.

B. Experimental Details

1. Materials

Heptamethyldisilazane was prepared from methylamine and
trimethylchlorosilane according to the method described by
Osthoff and Kantor.[46] Hexamethyldisilazane was obtained from
Peninsular Chemresearch, Inc. Hexamethylene diisocyanate was
obtained from Aldrich Chemical Co., Inc. DDI Diisocyanate was
obtained from General Mills, Inc. Adiprene L-100 was obtained
from E. I. du Pont de Nemours, Inc.

2. Polymerization

Polymerizations were carried out by mixing weighed quantities
of the reactants and heating for the periods and at the temperatures
shown in Table XVI. Some samples were cast in a mold that was
made of two ferrotype plates held 1/8 inch apart by rubber gaskets,
the whole being held together by clamps. Use of this mold resulted
in smooth sheets of uniform thickness, but frequent inspections
could not be made conveniently. Consequently, some samples were
cured in aluminum dishes. The samples cured more rapidly at their
upper surfaces. The observations reported in Table XVI are for
the main mass of material, disregarding the surface.

The equivalent values of reactants were calculated from
their formulas. The equivalent value of Adiprene L-100 was 1000,
according to du Pont.

3. Trimerization of monoisocyanates

a. Methyl isocyanate

Methyl isocyanate and heptamethyldisilazane were mixed in a 5:1 equivalence ratio and heated in a sealed Pyrex tube at 65°C for 17 hours. The product was partially crystalline. From it, trimethyl isocyanurate was isolated in 70% yield. A similar reaction with a 6.5:1 ratio of reactants at 130°C resulted in an 87% yield of trimethyl isocyanurate.

b. Phenyl isocyanate

Phenyl isocyanate and heptamethyldisilazane mixed in a 4.3:1 equivalence ratio and heated 45 hours at 65°C gave a 14% yield of triphenyl isocyanurate. A similar reaction at 130°C for 17 hours produced triphenyl isocyanurate in 7% yield.

c. Butyl isocyanate

The product of a reaction between butyl isocyanate and heptamethyldisilazane in a 5:1 ratio for 41 hours at 65°C, 72 hours at 85°C, and 144 hours at 110°C was not identified. It was more viscous than the starting material. Only about 2% of it could be distilled off at 100°C and 0.01 mm pressure. About 10% of it was insoluble in an ethanol-water mixture at room temperature, and this material melted at about 0°C. However, it did not have the correct elemental analysis for tributyl isocyanurate.

X. LITERATURE SURVEY

The literature on silicon-nitrogen compounds has been surveyed continuously, and the articles that have appeared in the past year are summarized briefly below.

A. Reports Involving Polymers

B. J. Aylett and G. M. Burnett[47] were granted a patent on polymers having the repeating unit, $-SiF_2NR-$, where R is preferably methyl. The polymers are prepared by the reaction of SiF_4 with primary amines in the presence of Lewis bases. The polymers are stable and inert. They do not melt below 500°C. Neither molecular weights nor physical properties were given.

Arylenesiloxane polymers related to the silphenylene ethers were described by Omietanski and Reid.[48] They prepared 1,4-bis(dimethylhydroxysilyl)-2,5-dichlorobenzene and co-polymerized it with octamethylcyclotetrasiloxane to form a "tough polysiloxane gum" that could be converted to an elastomer by conventional methods. The new polymers described were probably random block copolymers.

Andrianov, Kononov, and Makarova[49] polymerized silazanes in the presence of alkalies at temperatures above 300°C to form linear and spirocyclolinear polysilazanes. Molecular weights and properties were not given.

Baney and Haberland[50] synthesized polymers containing $-Me_2SiCH_2CH_2SiMe_2NH-$ units. A study of broadline nuclear magnetic resonance spectra, in comparison with siloxane analogs, revealed no extensive stiffening of chains caused by SiNSi units. The silylamine polymer had a molecular weight of about 2300.

Weibrecht and Rochow[51] prepared sym-dimethoxytetramethyl-disilazane and attempted to polymerize it with sodium methoxide and potassium t-butoxide. They obtained linear Si-N polymers of low molecular weight and other more complicated Si-N compounds.

Goossens[52] prepared organosilyl tris(carbamates), such as $RSi(O_2CNR'R'')_3$, by treating silylamines with carbon dioxide. These carbamates vulcanize silanol-chain-stopped silicone rubbers in the cold.

Silylamine-terminated polysiloxanes, which cured spon-taneously at room temperature to elastomers, were patented by the General Electric Company.[53]

Fink[54,55] reported that catalytic amounts of alkali metals or alkali metal hydrides cause interaction of Si-H and N-H groups to split out hydrogen. The reaction is versatile and will pro-duce mono- or disilylated amines and cyclic silazanes. Cyclo-disilazane polymers are formed from dihydrosilanes and diamines.

Silbiger and Fuchs[56] prepared silazanes of the structure $R''(SiR_2'NR')_nSiR_2''R'''$ for use as coating agents. Performance data were not given.

Polyoxymethylene was stabilized by treatment with silyl-amines, silylamides, or silazanes.[57]

Maijs and Rumba[58] converted oligomeric dimethylcyclo-silazanes into polycyclic polymers by heating in the presence of KOH. Molecular weights were not given.

Rochow[59] was granted a patent on a linear polymer having the formula:

$$\left[\begin{array}{c} C_6H_{11} \\ | \\ Si-NHCH_2CH_2NH \\ | \\ C_6H_{11} \end{array}\right]_n$$
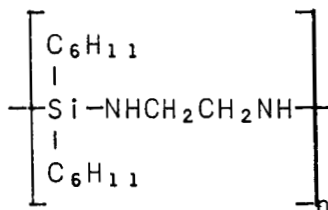
The polymer was said to be useful as a coating agent and as a primer for silicone coatings.

Rochow[60] synthesized polymethylsilazanes, both linear and with crosslinking through silicon, through nitrogen, and through vinyl groups, or by oxidative coupling.

Rochow and Redl[61] prepared poly(methylsilazanes) by the ammonolysis of mixtures of Me_2SiCl_2 and Me_3SiCl. The viscosity of the polymer was varied by changing the ratio of the silyl chlorides.

Redl[62] was able to suppress crosslinking which occurs during the Kruger condensation of dimethylsilazane by conducting the reaction under a moderate pressure of NH_3.

Parker[63] obtained a patent for coatings from oil-modified alkyd resins and silylamine polymers. The silylamines poly-merized to give liquid, linear silylamines with Si-N-Si linkages. A coating made from a 50% xylene solution of equal parts of a silylamine and Renzyl 873-1 was light in color, flexible over a 0.25 in. mandrel, and passed a 30 in.-lb impact test.

Weibrecht and Rochow[64] prepared sym-dimethoxytetramethyl-disilazane and the corresponding tri- and tetrasilazanes by treating dimethyldichlorosilane with MeOH, followed by treatment with anhydrous NH_3. Prolonged heating of sym-dimethoxytetramethyl-disilazane in the presence of NaOMe, $Al(OMe)_3$, $Al(OCHMe_2)_3$, and tert-BuOK led to the formation of low-molecular-weight linear Si-N polymers.

Wannagat[65] published a review of methods of preparation of cyclic silicon-nitrogen compounds including polysilazanes.

B. Fundamental Chemistry of Silicon-Nitrogen Compounds

Randall and Zuckermann[66] pointed out some unique features of $(p \rightarrow d)\pi$ interaction in Si-N bonds and stated that the existing theory is inadequate to predict the steric character of Si-N compounds.

Wells and Collins[67] found that both dehydrohalogenation and silicon-nitrogen bond cleavage occur when hexamethyldi-silazane is allowed to react with triethylamine-boron tri-chloride adduct.

Kawai and Tamura[68] found dimethylsulfoxide to be a good solvent for trimethylsilylation of catecholamines.

Itoh, Sakai, and Ishii[69] studied addition reactions of trimethylsilylamines with β-propiolactone.

Höfler, Bürger, and Wannagat[70] described reactions of SiF_4-amine-adducts with disilazanes and cyclotrisilazane and the cleavage of cyclotrisilazane with HF. They also described the reaction of SiF_4 with metalated amines, which yield fluoro-substituted SiN-compounds.

Gevaert-Agfa N.V.[71] obtained a patent on utilization of the thermolytic decomposition of silylamine compounds to provide the alkalinity to develop a silver or azo dye image in a silver halide emulsion used in copying methods.

Bayer and Santiago[72] obtained a patent for an olefin-polymerization catalyst prepared by substituting an organosilazane for all or part of the metal alkyl in a Ziegler catalyst.

Toyo Rayon Co., Ltd.,[73] received a patent for the use of tetrakis(dimethylamino)silane as a catalyst for α-olefin poly-merization of C_3H_6 to polypropylene. Another patent[74] was granted for aminosilanes or silazanes other than tetrakis-(dimethylamino)silane.

Zhuzhgov, Bubnov, and Voevodskii[75] used electron para-magnetic resonance spectra at 77°C and mass spectra to study the reaction products resulting from the ultraviolet irradiation of hexamethyldisilazanes, methylsilazanes, and dimethylcyclosilazanes. Results confirmed that scission of Si-C occurred in all compounds and of Si-H as well as C-H in the methylsilazanes.

Beezer and Mortimer[76] used heats of hydrolysis to calculate energies of Si-Cl and Si-N bonds which were respectively -92 and -124 kcal per mole.

Aylett and Hakim[77] studied base-catalyzed disproportionation reactions of N-methyl and N-phenyl disilazanes, $H_3Si-NR-SiH_3$, to yield silane, SiH_4. A complex formed by bonding between the silicon and the nitrogen through its unshared electrons was postulated as an intermediate.

Wells and Schaeffer[78] studied the base-catalyzed elimination of silane from trisilylamine, $N(SiH_3)_3$. Under certain conditions N,N',N''-trisilylcyclotrisilazane was obtained.

Ashby[79] studied silicon-containing derivatives of pyrrole and found that N-trimethylsilylpyrrole was stable at 650°C in the vapor phase in argon. N-trimethylsilylmethylenepyrrole, by contrast, decomposed slowly at 550°C. Earlier Fessenden and Crowe[80] had found that N-trimethylsilylpyrrole decomposed at 225°C in a sealed tube.

Wannagat, Höfler, and Bürger[81] studied isomeric bis-(trimethylsilyl)hydrazines and described their physical properties.

Wannagat and Schreiner[82] prepared and studied the properties of compounds having the form R_2NSiMe_2Cl and $RNHSiMe_2Cl$. They are very hygroscopic and those containing NH tended to self-decomposition. The nature of the self-decomposition was studied also.[83] In a third paper they studied amination reactions of the aminochlorosilanes with sodium amide.[84]

Aylett and Hakim[85] prepared and studied some of the properties of disilylamine, $(SiH_3)_2NH$.

Rühlmann, Simon, and Becker[86] used hexamethyldisilazane to silylate dipeptides and make them volatile.

Geymayer and Rochow[87] prepared silylaminoboranes of the type $R_2NBClN(SiMe_3)_2$. When R was ethyl or higher, the compounds underwent no self-condensation in 24 hours at 240°C, but the methyl compounds condensed at 140°C. They condensed, however, in the presence of sodium N,N-bis(trimethylsilyl)amide to form cyclodisilazanes.

Cragg and Lappert[88] studied aminosilylation and amino-phosphination of carbon dioxide, carbon disulfide, phenyl isocyanate, and phenylisothiocyanate with $Me_2Si(NEt_2)_2$, $Me_2Si(NHEt)_2$, $PhP(NMe_2)_2$ and $PhP(NMe_2)Cl$. Structures were proposed for the compounds obtained, but stability character-istics were not discussed.

Randall, Ellner, and Zuckerman[89] used nuclear magnetic resonance to study interaction in the SiN bond of N-trimethyl-silylaniline. Observations suggested that the degree of inter-action of the $(p{\rightarrow}d)\pi$ type was low.

Bürger[90] studied vibrational spectra and force constants of trimethylsilylazide, $(CH_3)_3SiNNN$. He concluded that the SiNNN group was nearly linear and that the SiN bond order was not increased by $(p{\rightarrow}d)\pi$ bonding.

Fink[91] published a review of cyclosilazanes including structure, properties, and methods of preparation.

Zhinkin and his coworkers[92] studied reactions of silylamines with alkylaluminum compounds, for example:

$$Et_3Al+2(Me_3Si)_2NH \rightarrow (Me_3Si)_2N-\overset{\overset{\displaystyle Et}{|}}{Al}-N(SiMe_3)_2$$
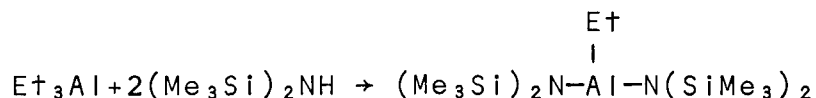
The replacement of 2 alkyl groups on the aluminum proceeded readily, but the third could not be replaced.

Ebsworth[93] considered that $(p{\rightarrow}d)\pi$ bonding was, at least partly, responsible for planarity in silylamines such as tri-silylamine.

Klebe, Finkbeiner, and White[35] used bis(trimethylsilyl) acetamide to silylate amides, ureas, amino acids, phenols, carboxylic acids, and enols. The authors found the silylamide to react faster than better known silylating agents.

Allan, Aylett, and Ellis[94] found that fluorine-containing silylamines are weaker Lewis bases and stronger Lewis acids than their unfluorinated analogs. BF_3 does not react with $(SiF_3)_2NMe$ below 100°C; at 100°C it forms SiF_4 and $(MeNBF)_3$. HCl cleaves the SiN bond rapidly at room temperature to form SiF_3Cl. Fluorodisilazanes form adducts and undergo disproportionation with amines. At 1°C, $(SiF_3)_2NH$ decomposes to form SiF_4 and $(SiF_2NH)_n$.

Russ and McDiarmid[95] studied the relative reactivities of Si-N, Si-P, and Si-As bonds and found that they reacted in a similar manner, but that, in some cases, Si-As bonds were less reactive. All were more reactive than the analogous carbon compounds.

Klebe and Bush[96] studied tautomerism in silylated anilides. Interconversion of the O-Si and N-Si forms occurred at a measurable rate at about 10°C.

Zhinkin, Morgunova, and Andrianov[97] studied the reaction of hexamethyldisilazane with phenyl isocyanate and phenyl isothiocyanate at 120°C, which gives different products from reactions previously reported at 30°C. At 120°C, disproportionation occurs to yield trimethylsilyl isocyanate (or isothiocyanate) and N-trimethylsilylaniline.

Metras and his coworkers[98] studied reactions of $(Me_3SiN=)_2$ with methyl benzoate and γ-butyro- and γ-valerolactones.

Andrianov and his coworkers[99] studied reactions of hexamethyldisilazane with phenyl isocyanate. Several disporportionation products were obtained.

Anders and Malz[100] found that silanyl isothiocyanates exchange readily with acyl halides to form acyl isothiocyanates and chlorosilanes. Thus, $OC(NCS)_2$ was prepared from phosgene and Me_3SiNCS. Silanyl isothiocyanates were made from chlorosilanes with alkali isothiocyanates.

Wannagat and Höfler[101] described the hypergolic behaviour of over 20 organosilyl substituted hydrazines, in contact with concentrated HNO_3, with gaseous F_2, with liquid O_2, with liquid O_3, and with gaseous O_3 (diluted with O_2).

Itoh, Sakai, and Ishii[102] reported opening the ring of
β-propiolactone with trimethylsilyldiethylamine to produce
$Et_2NCH_2CH_2CO_2SiMe_3$ or $Et_2NCOCH_2CH_2OSiMe_3$.

West, Ishikawa, and Bailey[103] made isomeric structural
assignments for eight new bis(organosilyl)hydrazines based on
a new method involving the splitting between the infrared N-H
stretching modes, which is greater for 1,1- than for 1,2-
hydrazines. New structural assignments were made for the
known bis(trimethylsilyl)hydrazines.

Goubeau[104] reported metal complexes with Zn, Cd, Co, and
Ni of silicon-nitrogen compounds of the following type:

$$H_2C\!-\!\!-\!\!-\!Si(CH_3)_2$$

$$CH_3\!-\!N \qquad N\!-\!CH_3$$

$$M$$

$$X \quad X$$
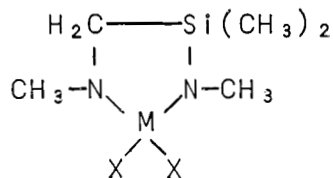
When M is Zn or Cd, the complex molecule has a tetrahedral
arrangement, when M is Co or Ni, the molecule has a planar
arrangement.

Andrianov and Kotrelev[105] prepared new dialkylpoly-
cyclosilazanes and alkylsilsesquiazanes by reaction of ammonia
with dialkyldichlorosilanes and alkyltrichlorosilanes. Infra-
red spectra and reactivity toward nucleophilic reagents indicated
the compounds possessed a type of aromaticity.

C. Preparation of New Compounds

Wannagat and Höfler[106] prepared some organosilyl-substituted
dimethylhydrazines.

Amonoo-Neizer, Shaw, Skovlin, and Smith[107] produced lithium
bis(trimethylsilyl)amide by the reaction of butyllithium with
hexamethyldisilazane and then allowed it to react with trimethyl-
chlorosilane to give tris(trimethylsilyl)amine.

Elliott and Breed[108] prepared a series of allyl- and vinyl-substituted silazanes and found the vinyl derivates were more reactive.
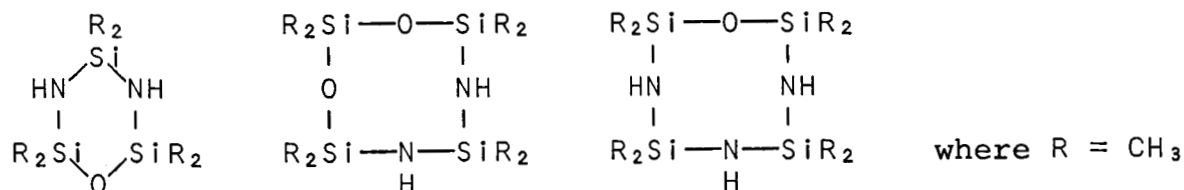
Duffaut and Dupin[109] described the reaction of silazanes and silylamines with some carbonyl compounds, such as ketones and benzaldehyde, to give imines.

Ebsworth, Rocktaschel, and Thompson[110] reported that trisilylamine and N-methyldisilylamine do not react with CO_2, CS_2, or carbon oxysulfide at temperatures up to 100°C and pressures up to 30 atmospheres. N,N-Dimethylsilylamine combines with CO_2 and CS_2. With carbon oxysulfide a compound is produced whose nmr spectrum indicates that rotation about the Me_2N-C bond is restricted.

Krueger and Niederpruem[111] reported the production of sodium bis(trimethylsilyl)amide (I) from hexamethyldisilazane and sodium amide and the subsequent production of tris(trimethylsilyl)amine by reaction of I with trimethyl chlorosilane.

Wiberg and Neruda[112] prepares silyl azides, $R_nSi(N_3)_4-n$, in high yields from the reaction of silyl halides, at room temperature with sodium azide in pyridine or lithium azide in tetrahydrofuran.

Haiduc[113] reported the synthesis of three new cyclosilazoxanes.

$$
\begin{array}{ccc}
\begin{array}{c}
R_2 \\
\diagup Si \diagdown \\
HN \quad\quad NH \\
| \quad\quad\quad | \\
R_2Si \quad SiR_2 \\
\diagdown O \diagup
\end{array}
&
\begin{array}{c}
R_2Si{-}O{-}SiR_2 \\
| \quad\quad\quad\quad | \\
O \quad\quad\quad NH \\
| \quad\quad\quad\quad | \\
R_2Si{-}N{-}SiR_2 \\
\quad\quad H
\end{array}
&
\begin{array}{c}
R_2Si{-}O{-}SiR_2 \\
| \quad\quad\quad\quad | \\
HN \quad\quad\quad NH \\
| \quad\quad\quad\quad | \\
R_2Si{-}N{-}SiR_2 \\
\quad\quad H
\end{array}
\end{array}
$$

where R = CH_3

Nmr and infrared data are given for nine cyclosilazoxanes.

MacDiarmid, et. al.,[114] converted N,N'-bis(trimethylsilyl)carbodiimides in a one-step reaction to N-trifluorosilylcarbodiimides.

Pike and Moynahan[115] prepared several symmetrical diisocyanatotetraorganodisilanes.

Lasev[116] synthesized several new silylamines by disproportionation of tetramethylenediamine and dimethylchloromethylethoxysilane.

Wannagat, Bogusch, and Höfler[117] reported the reaction of 1,5-dichlorooctamethyltrisilazane with dilithiomethylhydrazine to form a seven-membered Si-N ring system, cyclotrisilatetrazane.

$$
\begin{array}{c}
R_2 \\
Si \\
RN \qquad NR \\
| \qquad\qquad | \\
R_2Si \qquad SiR_2 \\
N{=}N
\end{array}
$$
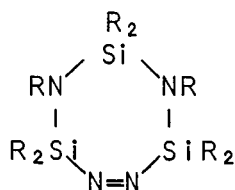
Scherer and Hornig[118] prepared Si-N heterocycles containing C=N bonds by treating the addition product of benzonitrile and lithium methylamide with dimethyldichlorosilane in the presence of triethylamine.

$$
\begin{array}{c}
R \\
| \\
C{=}N \\
CH_3N \qquad Si(CH_3)_2 \\
| \qquad\qquad | \\
(CH_3)_2Si \qquad NCH_3 \\
N{=}C \\
R
\end{array}
$$
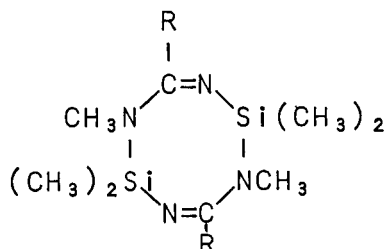
Cook and Lyons[119] found that trimethylsilane adds to pyridine and the picolines in the presence of palladium and other catalysts to yield a variety of 1,2- and 1,4-silyldihydropyridines. Confirmation of structure was obtained from ultraviolet, infrared, and Raman spectra.

A Netherlands patent[120] was granted for methods of preparing cyclic disilazanes.

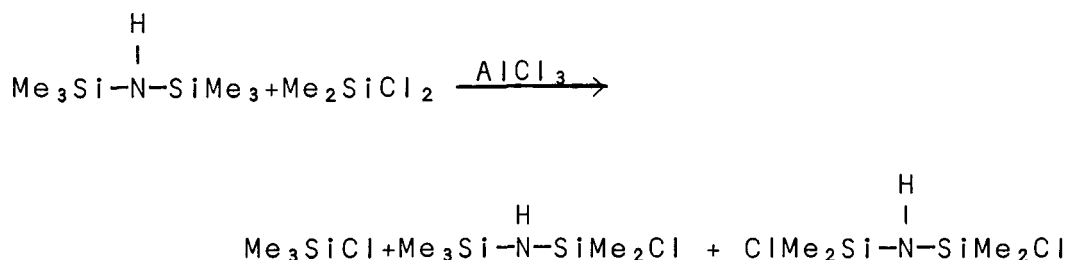Wannagat, Schreiner, Bradstätter, and Peach[121] prepared several new dimethylsilyl derivatives of hydrazine.

Hils, Hagen, Ludwig, and Ruehlmann[122] prepared N,N-bis-(trimethylsilyl)amines by amine exchange between Me_3SiNEt_2 and various amines, alkylenediamines, and amino acids. The products, except those made from amino acids, were resistant to hydrolysis.

Mattogno and Monaci[123] used lithium and potassium to assist with the silylation of all hydrogens attached to nitrogens in triphenylsilylamine and N,N'-dimethylethylenediamine.

Zhinkin and his coworkers[124] used the reaction of amino-silanes and disilazanes to prepare compounds containing Si-N-Al groups. For example, hexaethyldisilazane and triethylaluminum reacted to liberate ethane and attach the diethylaluminum group to the nitrogen of the disilazane. The reaction evidently required heating to 115°C in the later stages, and the yield was 88%.

Schreiner, Pohl, and Wannagat[125] prepared compounds with phenoxy and amino groups attached to the same silicon atom.

Silbiger and Fuchs[126] prepared chlorodisilazanes in an exchange reaction between hexamethyldisilazane and dimethyl-dichlorosilane catalyzed by aluminum chloride.

$$Me_3Si-\overset{\overset{\displaystyle H}{|}}{N}-SiMe_3 + Me_2SiCl_2 \xrightarrow{AlCl_3}$$

$$Me_3SiCl + Me_3Si-\overset{\overset{\displaystyle H}{|}}{N}-SiMe_2Cl + ClMe_2Si-\overset{\overset{\displaystyle H}{|}}{N}-SiMe_2Cl$$

The chlorodisilazanes were treated with sodium methylate to yield a methoxysilazane and with zinc oxide to yield a 1,5-diaza-3,7-dioxa-2,4,6,8-tetrasilacyclooctane ring.
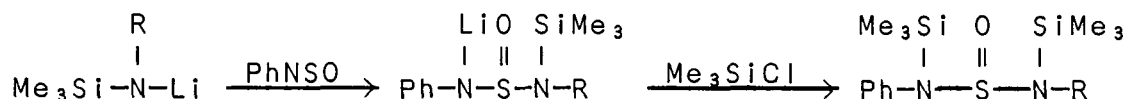
Nametkin and his coworkers[127] studied the synthesis and properties of silazane derivatives of silacyclobutane: for example, a cyclotrisilazane in which each silicon was part of a silacyclobutane ring.

Hundeck and Volkamer[128] prepared organosilylimines by the reaction of Me_3SiNEt_2 and Me_3SiI with acetonitrile. The product, $(Me_3Si)_2C=C=NSiMe_3$, essentially resulted from substitution of trimethylsilyl groups for the hydrogens of a tautomeric form of acetonitrile.

Geymayer and Rochow[129,130] prepared silicon-nitrogen-boron compounds by the reaction of aminochloroboranes and sodium derivatives of silylamines.

Scherer, Hornig, and Schmidt[131] prepared several compounds with Si-N-As, Si-N-Sb, or Si-N-Bi groups by treating alkyl metal halides with lithium trimethylsilylamide.

Scherer and Hornig[132] described the addition of lithium N-alkyltrimethylsilylamides to N-sulfinylaniline:

$$
\begin{array}{ccc}
\underset{Me_3Si-N-Li}{\overset{\overset{\displaystyle R}{|}}{\vphantom{|}}} & \xrightarrow{PhNSO} & \underset{Ph-N-S-N-R}{\overset{\overset{\displaystyle LiO\ \ S\ iMe_3}{|\ \ ||\ \ |}}{\vphantom{|}}} \xrightarrow{Me_3SiCl} \underset{Ph-N\!-\!\!-\!S\!-\!\!-\!N-R}{\overset{\overset{\displaystyle Me_3Si\ \ O\ \ SiMe_3}{|\ \ ||\ \ |}}{\vphantom{|}}}
\end{array}
$$

Wannagat and Bogusch[133] prepared tris(dimethylchlorosilyl)-amine and several similar compounds.

Scherer and Schmidt[134] studied reactions of sodium and lithium derivatives of trimethylsilylmethylamide. They reacted with chlorosilanes in the usual way.

Scherer and Schmidt[135] studied reactions of dimethyl-dichlorosilane with amines such as N,N'-dimethylethylenediamine. No polymers were mentioned.

Pitt and Skillern[136] prepared Si-N heterocyclic compounds from hydrazine and 1,2-bis(dimethylchlorosilyl)ethane.

Fink[137] prepared variously substituted silylamines by treating halosilanes with a salt of a disilazane such as $(Me_3Si)_2NLi$.

Calas, Duffaut, and Favre[138] prepared $(Me_3Si)_2NBr$ by reaction of $(Me_3Si)_2NMgBr$ with bromine in ether.

Bekiaroglu[139] prepared $Ph_3SiNHCl$ and Ph_3SiNCl_2 from Ph_3SiNH_2 and tert-butyl hypochlorite.

Wannagat[140] reported several new silyl derivatives of hydrazine including cyclic compounds having Si-N-N-Si units.

Birkofer and Wegner[141] reported that the 1,3-dipolar cyclo addition of trimethylsilylazide to acetylenic compounds, $RC\vdots CR$, yielded the corresponding 1,2,3,-triazoles.

$$R\diagdown \diagup N\diagdown$$
$$NSiMe_3$$
$$R'\diagup \diagdown N\diagup$$
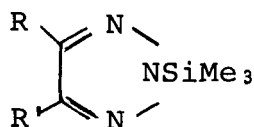
Scherer, Biller, and Schmidt[142] described the reaction of lithium N-methyltrimethylsilylamide with dichlorodimethylsilane to give a product, $Me_3SiNMeSiMe_2Cl$. Amino derivatives of the product were prepared. N,N-Dimethylhydrazine reacted with dichlorodimethylsilane to give $Me_2NNHSiMe_2Cl$. Nmr data were given for the new compounds.

Ruehlmann, Liebsch, and Michael,[143] in their study of the Si-N bond, prepared silyl derivatives of the ethyl esters of a number of amino acids by treating the esters with trimethyl-silyl-n-butylamine or trimethylsilyldiethylamine.

Henning and Haack[144] silylated amino derivatives of N-containing heterocyclic compounds with Me_3SiNEt_2 and then treated the product with phosphinic acid chlorides to produce phosphinic acid amides.

Klebe[145] was granted a patent for silylated ureides, which are said to be useful as lubricants and hydraulic fluids, and sometimes as hypnotics, anticonvulsants, insecticides, and pesticides.

Klebe[146] was also granted a patent for poly(silylbiurets), with a unit of the general formula [-R'N(SiR₃)CONR"CON(SiR₃)-], prepared by treating organic diisocyanates with a bis(triorgano-silyl)amine.

Wannagat and Brandstätter[147] prepared and characterized the six-membered ring system of cyclo-1,2,4,5,-tetrasil-3,6-diazane and the five-membered ring system of cyclo-1,2,4-trisil-3,5-diazane from 1,2-dichlorotetramethyldisilane

Nikitenkov[148] condensed bis(dimethylhydroxysilyl)benzene in an acidic ethereal solution to phenylenesiloxanes containing seven and eight structural units.

Breed, Budde, and Elliott[149] prepared and studied the functional derivatives of the four-membered ring compound, N,N'-bis(chlorodimethylsilyl)tetramethylcyclodisilazane.

D. Spectroscopic Data

Gerry, Thompson, and Sugden[150] reported the microwave spectrum of silyl isocyanate.

Buerger and Höfler[151] reported and assigned the infrared and Raman spectra of some silyl-substituted dimethylhydrazines.

Buerger[152] reported and assigned the infrared and Raman spectra of some halogen-containing di- and trisilylamines.

Levy and Grizzle[153] studied the wide-line nmr and powder X-ray spectra of tetramethyl-N,N-bis(trimethylsilyl)cyclodisilazane (Me₃SiNSiMe₂)₂ over the temperature range 77-300°K.

Schmidbaur and Wolfsberger[154] prepared and described nmr spectra of

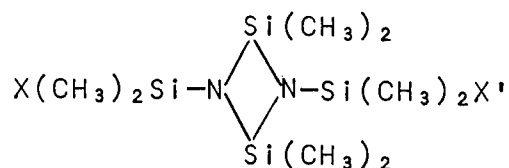$$\begin{array}{c} \text{SiMe}_3 \\ | \\ \text{N} \\ Me_3P \diagup \quad \diagdown MMe_3 \end{array}$$
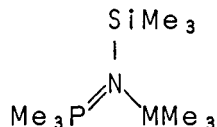
in which M was aluminum, gallium, or indium.

Bailey and West[155] studied infrared and nmr spectra of N-halogenated hexamethyldisilazane. They also studied the reactivity of the N-halogen silylamines and found that hydrolysis proceeded in a basic medium through breaking of the N-X bond and in acid through breaking of the Si-N bond.

Wiberg and Schmid[156] studied structure, thermal decomposition, and infrared spectra of trimethylsilylammonium compounds represented by $(Me_3Si)_2NH \to MCl_3$ where M was aluminum or gallium.

Buerger, Bogusch, and Geymayer[157] reported and assigned the infrared and Raman spectra of the disilylcyclodisilazanes

$$X(CH_3)_2Si-N \overset{\overset{\displaystyle Si(CH_3)_2}{\diagup\diagdown}}{\underset{\underset{\displaystyle Si(CH_3)_2}{\diagdown\diagup}}{}} N-Si(CH_3)_2X'$$

with $X = X' = CH_3$, H, Cl, Br, I, OCH_3, $NHCH_3$, $N(CH_3)_2$, C_4H_9, and $X = Cl$, $X' = NHSi(CH_3)_2Cl$. The Si_4N_2 skeleton exhibits characteristic infrared and Raman frequencies.

Höfler and Wannagat[158] synthesized 2-trimethylsilyl-1,1,2-trimethylhydrazine and reported the infrared, raman, and nmr spectra of it and a number of other trimethylsilyl-substituted hydrazines.

REFERENCES

1. Annual Summary Report, Contract No. DA-01-009-506-ORD-829, U. S. Army Ballistic Missile Agency, February 20, 1961.

2. Annual Summary Report, Contract NAS 8-1510, George C. Marshall Space Flight Center, February 28, 1962.

3. Ibid, April 29, 1963.

4. Ibid, May 28, 1964.

5. Ibid, May 18, 1965.

6. Ibid, Contract NAS 8-20190, May 12, 1966.

7. James E. Curry and James D. Byrd, J. Appl. Polymer Sci. 9, 295-311 (1965).

8. Annual Summary Report, Contract NAS 8-20190, George C. Marshall Space Flight Center, May 12, 1966, pages 29-31.

9. Ibid, Section III, Table V, page 25.

10. Ibid, page 14.

11. M. Sveda, U. S. Patent 2,561,469 (assigned to E. I. du Pont de Nemours and Company, Inc.), July 24, 1951.

12. E. Larsson and L. Bjellerup, J. Am. Chem. Soc., 75, 995-997 (1953).

13. H. H. Anderson, ibid, 74, 1421 (1952).

14. J. L. Speier, ibid, 1003 (1952).

15. J. F. Klebe, H. Finkbeiner and D. M. White, ibid, 88, 3390, (1966).

16. J. R. Harper, A. D. Chipman, and G. M. Konkle, Rubber World, 137, 711-716, 758 (1958).

17. Annual Summary Report, Contract NAS 8-20190, George C. Marshall Space Flight Center, May 12, 1966, Section IV.

18. Annual Summary Report, Contract NAS 8-20190, George C. Marshall Space Flight Center, May 12, 1966, p. 43-45.

19. Ibid, pages 32-35, 40-42.

20. Ibid, Section V.

21. D. N. Braski and G. J. Heimerl, NASA Technical Note D-2011, Langley Research Center, Hampton, Virginia, 1963.

22. Annual Summary Report, Contract NAS 8-1510, George C. Marshall Space Flight Center, May 18, 1965, page 44.

23. Ibid, Contract NAS 8-20190, May 12, 1966, Section VI.

24. Ibid, Contract NAS 8-1510, May 18, 1965, Section VIII.

25. Ibid, page 86.

26. J. H. Schultz and Clarence G. Zike, U. S. Patent 2,970,969 (to the Richardson Company), February 7, 1961.

27. W. M. Boyer, H. M. Molosky, and H. E. Tarbell, Jr., U. S. Patent 3,038,875 (to the Richardson Co.), June 12, 1962.

28. Fritz Weigel, German Patent 1,035,897 (to Siemens-Schuckertwerke Akt-Ges.), August 7, 1958.

29. A. B. Finestone, U. S. Patent 2,953,545 (to Westinghouse Electric Corporation), September 20, 1960.

30. Shell Chemical Corp., Chemical Sales Div. Atlanta, Georgia, private communication.

31. Union Carbide Corporation Technical Bulletin ERL-4221, May, 1965.

32. Dow Corning Corporation Technical Bulletin XZ-8-5024, February 28, 1966.

33. Annual Summary Report, Contract NAS 8-1510, George C. Marshall Space Flight Center, May 18, 1965, page 85.

34. Shell Chemical Company Technical Sales Bulletins, SC: 56-18 and SC: 62-60.

35. J. F. Klebe, H. Finkbeiner, and D. M. White, J. Amer. Chem. Soc. 88, 3390(1966).

36. J. F. Brown, Jr., et al, J. Am. Chem. Soc. 82, 6194-6195 (1960).

37. J. F. Brown, Jr., J. Polymer Sci., Pt. C, 1 83-97 (1963).

38. E. Zintl and K. Loosen, Z. physik Chem. A174, 301-11 (1935).

39. Annual Summary Report, Contract NAS 8-20190, George C. Marshall Space Flight Center, May 12, 1966, page 109.

40. C. A. Burkhard, B. F. Decker and D. Harker, J. Amer. Chem. Soc., 67, 2174 (1945).

41. Annual Summary Report, Contract NAS 8-20190, George C. Marshall Space Flight Center, May 12, 1966, pages 55-70.

42. J. I. Jones and N. G. Savill, J. Chem. Soc., 4392 (1957).

43. S. Herbstman, J. Org. Chem. 30, 1259 (1965).

44. S. R. Sandler, J. Appl. Poly. Sci. 11, 811-815 (1967) under National Aeronautics and Space Administration Contract NAS 8-11518.

45. J. M. Butler and J. A. Webster, Second Quarterly Report, National Aeronautics and Space Administration, Contract NAS 8-20402, January 15, 1967.

46. R. C. Osthoff and S. W. Kantor, Inorganic Syntheses 5, 58-59 (1957).

47. B. J. Aylett and G. M. Burnett, U. S. Patent 3,234,148, Feb. 8, 1966; C.A. 64, 16012a (1966).

48. G. M. Omietanski and W. G. Reid, U. S. Patent 3,200,137 (to Union Carbide Corp.), Aug. 10, 1965.

49. K. A. Andrianov, A. M. Kononov, and N. N. Makarova, U.S.S.R. Patent 178,108, Jan. 8, 1966; C.A. 65, 830a (1966).

50. R. H. Baney and G. G. Haberland, J. Organometal. Chem. 5(4), 320-5 (1966).

51. W. E. Weibrecht and E. G. Rochow, J. Organometal Chem. 5 (6), 520-5 (1966).

52. John C. Goossens, French Patent 1,426,346 (to Compagnie Francaise Thomson-Houston) Jan. 28, 1966; C.A. 65, 13795h (1966).

53. General Electric Co., British Patent 1,030,625, May 25, 1966.

54. W. Fink, Helv. Chim. Acta., 49(4), 1408-15 (1966).

55. W. Fink, Chem. Ber. 99(7), 2267-74 (1966).

56. J. Silbiger and J. Fuchs, Belgian Patent 672, 101 (to Yissum Research and Development Co.), March 1, 1966; C.A. 65, 13758e (1966).

57. Farbenfabriken Bayer A.G. Netherlands patent application 6,512,705, March 31, 1966; C.A. 65, 9117d (1966).

58. L. Maijs and G. Rumba, Latvijas PSR Zinatnu Akad. Vestis, Kim. Ser. 1966 (2), 164-6; C.A. 65, 10677b (1966).

59. E. G. Rochow, U. S. Patent 3,159,668 (to General Electric Company), Dec. 1, 1964.

60. E. G. Rochow, Pure Appl. Chem. 13 (1-2), 247-62 (1966).

61. Eugene G. Rochow and George Redl, Amer. Chem. Soc. Org. Coatings Plastics Chem., Preprints 25 (2), 316-18 (1965); C.A. 66, 29212u (1967).

62. George Redl, U.S. Dept. Comm. AD 627640, 50 pp (1965); C.A. 66, 95466f (1967).

63. Konrad Parker, U.S.Patent 3,284,384 (to Dow Corning Corp.), Aug 2, 1963; C.A. 66, 20002t (1967).

64. Walter E. Weibrecht and Eugene G. Rochow, U.S.Dept. Comm. AD 627639, (1965); C.A. 66, 95467g (1967).

65. U. Wannagat, Pure Appl. Chem. 13(2), 263-79 (1966).

66. E. W. Randall and J. J. Zuckerman, Chem. Commun. 1966 (20), 732-3; C.A. 66, 41900z (1967).

67. Richard L. Wells and Alva L. Collins, Inorg. Chem. 5 (8), 1327-8 (1966).

68. Satoshi Kawai and Zenzo Tamura, J. Chromatog 25, 471-2 (1966).

69. Kenji Itoh, Shizuyoshi Sakai, and Yoshio Ishii, Chem. Commun. 1967 (1), 936-7; C.A. 66, 85218n (1967).

70. F. Höfler, H. Bürger, and U. Wannagat, Intern. Symp. Organosilicon Chem., Sci, Commun., Prague 1965, 335-9; C.A. 66, 28827m (1967).

71. Gevaert - Agfa N.V., Netherlands Patent application, 6,612,556, Nov. 25, 1966; C.A. 66, 70875a (1967).

72. John W. Bayer and Edgardo Santiago, U.S. Patent 3,300,465 (to Owens-Illinois Glass Co.), Jan. 24, 1967; C.A. 66, 66003X (1967).

73. Yuji Atarashi and Osamu Fukumoto, Japanese Patent 19,992 ('66) (to Toyo Rayon Co.), Nov. 19, 1967; C.A. 66, 86114n (1967).

74. Ibid, 19,991 ('66) (to Toyo Rayon Co.), Nov. 19, 1967; C.A. 66, 86114n (1967).

75. E. L. Zhuzhgov, N. N. Bubnov, and V. V. Voevodskii, Radiats. Khim. Polim., Mater. Simp., Moscow 1964, 224-7 (1966); C.A. 66, 95537e (1967).

76. A. E. Beezer and C. T. Mortimer, J. Chem. Soc., A, Inorg., Phys., Theoret. 1966(5), 514-16.

77. B. J. Aylett and M. J. Hakim., Chem. and Ind. 1965(5), 1626.

78. R. L. Wells and R. Schaeffer, J. Am. Chem. Soc. 88 (1), 37-42, (1966).

79. B. A. Ashby, J. Organometal. Chem. 5, 405-12 (1966).

80. R. Fessenden and D. F. Crowe, J. Org. Chem. 25, 598 (1960).

81. U. Wannagat, F. Höfler, and H. Bürger, Monatsh. Chem. 96(6), 2038-45 (1966).

82. U. Wannagat and G. Schreiner, _ibid_, 1889-1894.

83. U. Wannagat and G. Schreiner, _ibid_, 1895-1901.

84. U. Wannagat and G. Schreiner, _ibid_, 1916-24.

85. B. J. Aylett and M. J. Hakim, _Inorg. Chem._ _5_(1), 167 (1966).

86. K. Rühlmann, H. Simon, and M. Becker, _Chem. Ber._ _99_, 780-1 (1966).

87. P. Geymayer and E. G. Rochow, _Monatsh. Chem._ _97_, 437-43 (1966).

88. R. H. Cragg and M. H. Lappert, _J. Chem. Soc. (A)_, _1966_ 82-5.

89. E. W. Randall, J. J. Ellner, and J. J. Zuckerman, _J. Am. Chem. Soc._ _88_ (3), 622 (1966).

90. H. Bürger, _Monatsh. Chem._ _96_(6), 1710-15 (1966).

91. W. Fink, _Angew. Chem. Intern. Ed._ _5_(9), 760-776 (1966).

92. D. Ya. Zhinkin, G. K. Korneeva, N. N. Korneev, and M. V. Sobolevskii, _Intern. Symp. Organosilicon Chem., Sci. Commun., Prague_, _1965_ 311-14; _C.A._ _65_, 8943c (1966).

93. E.A.V. Ebsworth, _Chem. Commun._ _1966_ (15), 530-1; _C.A._ _65_, 12867a (1966).

94. M. Allan, B. J. Aylett, and I. A. Ellis, _Chem. Ind. (London)_ _1966_ (33), 1417; _C.A._ _65_, 13197f (1966).

95. C. R. Russ and A. G. McDiarmid, Univ. Microfilms (Ann Arbor, Mich.), Order No. 66-294, 182 pages; _Dissertation Abstracts_ _26_(9), 5027 (1966).

96. J. F. Klebe and J. B. Bush, Jr. _Intern. Symp Organosilicon Chem., Sci. Commun., Prague_, _1965_, 328-34.

97. D. Ya. Zhinkin, M. M. Morgunova, K. A. Andrianov, _Doklady Akad. Nauk_, _SSR_ _165_ (1-6), (Translation by Consultants Bureau, N.Y.) pages 1072-74 (1965).

98. F. Metras, J. Plazanet, M. Lecoq, and J. Valade, *Intern. Symp. Organosilicon Chem., Sci. Commun., Prague, 1965,* 10-12; *C.A.* 65, 12224h (1966).

99. M. M. Morgunova, D. Ya. Zhinkin, K. K. Popkov, and K. A. Andrianov, *ibid,* 317-19; *C.A.* 65, 8943b (1966).

100. B. Anders and H. Malz, German Patent 1,215,144 (to Farbenfabriken Bayer A. G.), April 28, 1966; *C.A.* 65, 3908c (1966).

101. U. Wannagat and F. Höfler, *Monatsh. Chem.* 97(4), 1157-62 (1966) (Ger).

102. Kenji Itoh, Shizuyoshi Sakai, and Yoshio Ishii, *Tetrahedron Letters* 1966 (41), 4941-5 (Eng); *C.A.* 66; 11015u (1967).

103. Robert West. Mitsuo Ishikawa, and Robert E. Bailey, *J. Am. Chem. Soc.* 88(20), 4648-52 (1966) (Eng); *C.A.* 65, 18606 f (1966).

104. Von J. Goubeau, *Pure Appl. Chem.* 13(1-2), 81-91 (1966).

105. K. A. Andrianov and G. V. Kotrelev, *J. Organometal Chem.* 7(2), 217-25(1967); *C.A.* 66, 65567x (1967).

106. Ulrich Wannagat and F. Höfler, *Monatsh. Chem.* 97(3), 976-83 (1966); *C.A.* 66, 38001b(1967).

107. E. H. Amonoo-Neizer, R. A. Shaw, D. O. Skovlin, and B. C. Smith, *Inorg. Sym.* 8, 19-22(1966); *C.A.* 66, 37999w (1967).

108. R. L. Elliott and L. W. Breed, *J. Chem. Eng. Data* 11(4), 604-5(1966); *C.A.* 66, 76081k (1967).

109. Norbert Duffaut and Jean Pierre Dupin, *Bull. Soc. Chim. Fr.* 1966(10), 3205-10; *C.A.* 66, 37479b.

110. E.A.V.Ebsworth, G. Rocktaschel, and J. C. Thompson, *J. Chem. Soc.* A 1967(3), 362-5; *C.A.* 66, 85815e (1967).

111. Carl R. Krueger and Hans Niederpruem, *Inorg. Syn.* 9, 15-19 (1966); *C.A.* 66, 28834m (1967).

112. N. Wiberg and B. Neruda, _Intern. Symp. Organosilicon Chem._
     Sci. Commun., _Prague_ 1965, 232-5; _C.A._ 66, 37996t (1967).

113. Ionel Haiduc, _ibid_, 301-305.

114. A. G. MacDiarmid, J. J. Moscony, C. R. Russ, and T. Yoshioka,
     ibid, 100-103.

115. Ronald M. Pike and Edward B. Moynahan, _Inorg. Chem._ 6(1),
     168-9 (1967); _C.A._ 66, 38000a (1967).

116. V. B. Lasev, _Zh. Obshch. Khim._ 37(1), 253-4 (1967); _C.A._ 66,
     95115v (1967).

117. Ulrich Wannagat, Erich Bogusch, and Friedrich Höfler,
     J. Organometal. Chem. 7(2), 203-10 (1967); _C.A._ 66,
     95117t (1967).

118. O. J. Scherer and P. Hornig, _Angew. Chem._ IEE 6(1),
     89(1967).

119. Newell C. Cook and James E. Lyons, _J. Am. Chem. Soc._ 88,
     3396-3403 (1966).

120. Monsanto Co., Netherlands Patent 6,507,996, Dec. 23, 1965;
     _C.A._ 64, 19677d (1966).

121. U. Wannagat, G. Schreiner, O. Brandstätter, and M. Peach,
     Monatsh. Ch. 96, 1902-8 (1965).

122. J. Hils, V. Hagen, H. Ludwig, and K. Ruehlmann, _Chem. Ber._
     99 (3), 776-779 (1966); _C.A._ 64, 15911f (1966).

123. G. Mattogno and A. Monaci, _Ric. Sci., Rend., Sec._ A 8 (3),
     482-3 (1965).

124. D.Ya.Zhinkin, G. K. Korneeva, N. N. Korneev, and M. V.
     Sobolevskii. _Zh. Obshch. Khim._ 36(2), 350-2 (1966).

125. G. Schreiner, J. Pohl, and U. Wannagat, _Monatsh. Chem._
     96(6), 1909-15 (1966).

126. J. Silbiger and J. Fuchs, _Inorganic Chemistry_ 4(9), 1371-2
     (1965).

127. N. S. Nametkin, V. M. Vdovin, and E. D. Babich, Intern. Symp. Organosilicon Chem., Sci. Commun., Prague, 1965, 296-300; C.A. 65, 12226f (1966).

128. J. Hundeck and Kl. Volkamer, ibid 320-2; C.A. 65, 10606e (1966).

129. P. Geymayer and E. G. Rochow, Monatsh. Chem. 97(2), 437-43 (1966); C.A. 65, 5478b (1966).

130. P. Geymayer and E. G. Rochow, Intern. Symp. Organosilicon Chem., Sci. Commun., Prague, 1965, 306-310; C.A. 65 10605h (1966).

131. O. J. Scherer, P. Hornig, M. Schmidt, J. Organometal. Chem., 6, 259-64 (1966).

132. O. J. Scherer and P. Hornig, Angew. Chem. Inter. Ed. 5, 729-30 (1966).

133. U. Wannagat and E. Bogusch, Inorg. Nucl. Chem. Letters 2(4), 97-9 (1966); C.A. 65, 8946h (1966).

134. O. Scherer and M. Schmidt, Intern. Symp. Organosilicon Chem. Sci. Commun., Prague, 1965, 315-16; C.A. 65, 10606h (1966).

135. O. Sherer and M. Schmidt, Inorg. Nucl. Chem. Letters 2(4), 101-2 (1966); C.A. 65, 8945h (1966).

136. Colin G. Pitt and K. R. Skillern, ibid, 2(8), 237-41 (1966); C.A. 65, 13746d (1966).

137. W. Fink, U. S. Patent 3,253,008 (to Monsanto Co.), May 24, 1966; C.A. 65, 5487g (1966).

138. R. Calas, N. Duffaut, and A. Favre, Intern. Symp. Organosilicon Chem., Sci. Commun., Prague, 1965, 340-1; C.A. 65, 12225h (1966).

139. P. Bekiaroglu, Z. anorg. allgem. chem. 345 (5-6), 290-3 (1966).

140. U. Wannagat, Angew Chem. Intern. Ed. 5(6), 614 (1966).

141. Leonhard Birkofer and Peter Wegner, Chem. Ber 99(8), 2512-17 (1966) (Ger); C.A. 65, 15414d (1966).

142. Otto J. Scherer, Dietmar Biller, and Max Schmidt, Inorg. Nucl. Chem. Letters 2(4), 103-5 (1966) (Ger); C.A. 65, 16992g (1966).

143. K. Ruehlmann, K. Liebsch, and Ch. Michael, J. Prakt. Chem. 32(5-6), 225-9 (1966) (Ger); C.A. 65, 15494d (1966).

144. H. G. Henning and G. Haack, Z. Chem. 6(7), 261-2 (1966) (Ger); C.A. 65, 15416e (1966).

145. Johann F. Klebe, French Patent 1,434,770 (to Compagnie Francaise Thomson-Houston), April 8, 1966; C.A. 65, 20163f (1966).

146. Johann F. Klebe, French Patent 1,434,769, (to Compagnie Francaise Thomson - Houston), April 8, 1966; C.A. 66, 3003r (1967).

147. U. Wannagat and O. Brandstätter, Monatsh. Chem. 97(5), 1352-6 (1966).

148. V. E. Nikitenkov. J. Gen. Chem. USSR 35(9), (Translation by Consultants Bureau, N.Y.) pages 1667-9 (1965).

149. L. W. Breed, W. L. Budde, and R. L. Elliott, J. Organometal. Chem. 6, 676-7 (1966).

150. M. C. L. Gerry, J. C. Thompson, and I. M. Sugden, Nature 211(5051), 846-7 (1966) (Eng); C.A. 65, 19489a (1966).

151. H. Bürger and F. Höfler, Monatsh. Chem. 97(3), 984-9 (1966).

152. H. Bürger, ibid, 869-78 (1966) (Ger).

153. Hiram Levy, II. and William E. Grizzle, J. Chem. Phys. 145(6), 1954-60 (1966) (Eng); C.A. 65, 14677a (1966).

154. H. Schmidbaur and W. Wolfsberger, Angew. Chem. Intern. Ed. 5(3), 312 (1966).
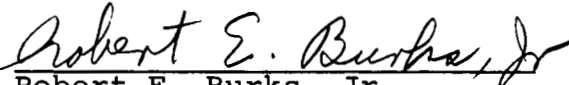
155. Robert Earl Bailey and Robert C. West, Jr. Univ. Microfilms (Ann Arbor, Mich.), Order No. 65-11, 144, 143 pages; Dissertation Abstracts 26(7), 3620-21 (1966).

156. N. Wiberg and K. H. Schmid, Z. Anorg. Allgem. Chem. 345, 93-105 (1966).

157. Von Hans Buerger, Eric Bogusch, and Peter Geymayer, ibid, 349(3-4), 124-130 (1967).

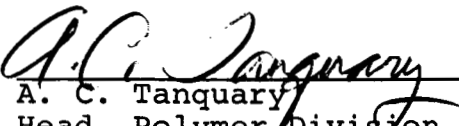158. F. Höfler and U. Wannagat, Monatsh. Chem. 97(6), 1598-1610 (1966).

ACKNOWLEDGMENTS

Mr. Thomas W. Ray, Assistant Chemist; Miss Clara A. Cox, Assistant Chemist; Mr. William L. Mayfield, Research Technician; Miss M. Virginia Jackson, Associate Chemist; Mr. Robert E. Lacey, Head, Membrane Processes Section; and Dr. E. R. Covington, Senior Chemist, assisted with the work discussed in this report.

Submitted by:

Joseph L. Greene, Jr.
Senior Chemist

Robert E. Burks, Jr.
Head, Organic Section

Approved by:

A. C. Tanquary
Head, Polymer Division

REPORT DISTRIBUTION

National Aeronautics and Space Administration   20
George C. Marshall Space Flight Center
Purchasing Office
Huntsville, Alabama 35812
Attention: PR-EC

Mr. Warren Johnson, MANE   1
Aeronautical Systems Division
U.S. Air Force Materials Laboratory
Wright-Patterson Air Force Base, Ohio 45433

North American Aviation   1
Space and Information Division
Department 462-144
Downey, California
Attention: Mr. Irving Katz

Midwest Research Institute   1
425 Volker Boulevard
Kansas City 10, Missouri
Attention: Mr. L. W. Breed

Commanding Officer   1
Rock Island Arsenal
Rock Island, Illinois
Attention: 9320

Lockheed Aircraft Corporation   1
Missiles and Space Division
Technical Information Center
3251 Hanover Street
Palo Alto, California

Mr. H. S. Schwartz (MANC)   1
Air Force Materials Laboratory
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio 45433

Liquid Propellant Information Agency   3
The Johns Hopkins Applied Physics Laboratory
Silver Springs, Maryland

RRMA 5   1
Bureau of Naval Weapons
U. S. Department of the Navy
Washington, D. C. 20546

REPORT DISTRIBUTION
(continued)

Mrs. Dorothy T. Crabtree   1
Technical Library
Monsanto Research Corporation
Dayton Laboratory
Dayton 7, Ohio

Dr. R. N. Minne   1
Science Department
Culver Military Academy
Culver, Indiana

Dr. P. B. Stickney   1
Batelle Memorial Institute
505 King Avenue
Columbus, Ohio 43201

Dr. Lewis W. Butz   1
Head, Chemistry Branch
Department of the Navy
Office of Naval Research
Washington, D. C. 20546

Mr. C. A. Cassola, Superintendent   1
High Polymer Division, AML
Naval Air Engineering Center
Aeronautical Materials Laboratory
Philadelphia 12, Pennsylvania
Attention: MP-1-WWH:rbt
            10320/5 (1293)

U. S. Naval Applied Science Laboratory   1
Technical Library
Building 291, Code 9832
Naval Base
Brooklyn, New York 11251
Attention: Mr. Murray Rogofsky
            Head, Technical Library Branch

Commander (Code 753)   1
U. S. Naval Ordnance Test Station
China Lake, California 93557
Attention: Technical Library

REPORT DISTRIBUTION
(continued)

Dr. Lindsey Hobbs, R-P&VE-MNP Materials Division Propulsion and Vehicle Engineering Laboratory National Aeronautics and Space Administration George C. Marshall Space Flight Center Huntsville, Alabama 35812	1
Mr. Glen Goodwin Chief, Thermo- and -Gas Dynamics Division Ames Research Center Moffett Field, California 94035	1
Total	39