# A STUDY OF POLYMERS CONTAINING SILICON-NITROGEN BONDS

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Annual Summary Report for the Period
February 4, 1962 to April 3, 1963

To

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

SOUTHERN RESEARCH INSTITUTE
2000 9th Avenue S. Birmingham 5, Alabama

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Project 1259, Report 26

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# FOREWORD

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## ABSTRACT

Compounds and polymers with silicon-nitrogen bonds were studied in a search for new materials that are needed to withstand the extreme temperature conditions encountered in space technology. It was found that both thermal and hydrolytic stability are drastically affected by the character of the groups attached to the silicon and nitrogen atoms, and that a high degree of stability to heat and to water can be obtained by selection of the groups. Silicon-nitrogen compounds can be produced with several valuable characteristics such as affinity for metals and ceramics, good thermal and chemical stability, and the ability to undergo endothermic polymerization at high temperatures. These properties have led to encouraging preliminary results with silicon-nitrogen compounds in protective coatings for metals and as components of heat-barrier formulations.

The outstanding difficulty in making silicon-nitrogen polymers that can be formed into useful shapes is the tendency of the reactants to cyclize or cross-link rather than form linear polymers. Attempts were made to find polymerizing conditions and starting materials that would favor the formation of linear polymers. So far, these have been only moderately successful, but other methods remain to be tried.

Silylamines differ widely from organic amines in reactivity, and the best means of attaching substituent groups to nitrogen atoms is through the N-alkali derivatives. The reaction was investigated in detail. It was found that potassium offers appreciable advantages in the substitution reaction, and it opens additional pathways to synthesis of specific compounds and polymers.

# A STUDY OF POLYMERS CONTAINING SILICON-NITROGEN BONDS

## I. INTRODUCTION

The demands of space technology require new liquid and plastic materials that are capable of performing under conditions of temperature, pressure, and radiation exposure that cause conventional materials to fail. New materials are needed for sealants, lubricants, coatings, heat-barriers, hydraulic fluids, elastomers, potting compounds, and structural plastics, that can be used at extremes of temperature, low pressures, or in intense radiation fields. Polymers containing silicon-nitrogen bonds offered possibilities of having properties which would make them useful for applications such as these. This study was undertaken to investigate the potentials of compounds and polymers containing silicon-nitrogen bonds for meeting the many varied requirements for new materials for launch vehicles. This report summarizes the results of the third year of work on the project which has been carried out under Contracts DA-01-009-506-ORD-829 and NAS 8-1510. The results of earlier studies are summarized in previous reports.[1,2]

Polymers and compounds containing silicon-nitrogen bonds have been investigated to determine whether they may be useful in launch vehicles. The work has shown that silicon-nitrogen compounds compare well with other potentially useful polymer systems in terms of thermal stability, structural versatility, and ability to adhere to metals and ceramics. A variety of silicon-nitrogen compounds has been studied to determine which types have the most promising properties.

## II. DISCUSSION OF RESULTS

Desirable qualities possessed by selected silicon-nitrogen compounds that have been prepared are: high thermal and chemical stability, good adhesion to inorganic materials, wide variability in structure, and fluidity and plasticity over wide temperature ranges. Many simple silicon-nitrogen compounds can be polymerized at high temperatures by a condensation reaction that promises to be a source of useful materials. As polymerization progresses, chemical and thermal stability increase and eventually become quite high. The finding at the George C. Marshall Space Flight Center that the high-temperature polymerization of the silicon-nitrogen compounds is endothermic suggests their utility in heat-barrier coatings.

The tendency of silicon-nitrogen compounds to cyclize rather than polymerize is a major problem that has been an obstacle to the preparation of polymers with desirable strength. The resonance of the cyclic silazanes, which have alternating silicon and nitrogen atoms in rings, probably accounts for their high thermal stability; but it is probably the cause of their tendency to cyclize rather than polymerize. Although many attempts to form useful silicon-nitrogen polymers have failed, apparently for this reason, the use of metallosilylamine derivatives as intermediates[3] offers opportunities for controlling functionality and for polymerization by formation of chains of cyclic silazanes, thereby enhancing stability and circumventing the tendency to defeat polymerization by formation of small rings.

A disadvantage of some silicon-nitrogen compounds is their moisture sensitivity, but it has been determined that the proper selection of substituent groups can reduce moisture sensitivity greatly.

It is of interest to compare silicon-nitrogen and silicon-oxygen compounds as high-temperature polymers, not only because of chemical similarity, but because the silicon-oxygen compounds are already useful in so many high-temperature applications. The silicon-nitrogen compounds appear to have some advantages. Greater variations in structure are possible because of the trivalence of the nitrogen atoms. Silicon-nitrogen compounds apparently have greater affinity for inorganic surfaces than the silicon-oxygen compounds, and this property suggests utility of the silicon-nitrogen compounds in lubricants, adhesives, coatings, and paint vehicles.

During the period covered by this report, we have studied factors affecting the hydrolytic and thermal stability of silazane polymers, the effectiveness of silazane polymers as coatings and in heat barriers, and methods of preparing several new silicon-nitrogen polymers.

Hexaphenylcyclotrisilazane was incorporated into polymeric materials to enhance the action of the polymers as heat barriers. Hexaphenylcyclotrisilazane was not satisfactory alone because of its low melting point and poor strength, but it helped to reduce the rates of heat transfer.

Studies of hydrolysis rates have shown that silylamines vary widely in hydrolytic stability. Hexaphenylcyclotrisilazane is only 0.5% hydrolyzed when it is dissolved in benzene and shaken with water for 5 hours. By contrast bis(methylamino)dimethylsilane is 80% hydrolyzed in 1 minute under the same conditions. The phenyl-silicon-nitrogen polymer made by heating hexaphenylcyclotrisilazane at 450-560°C is essentially inert to water. Stability was not enhanced by halogen substitution on phenyl rings attached to silicon or by acetylation of nitrogen atoms.

Protective coatings for aluminum were made from several mixtures of silazanes. The best mixture produced a coating that was flexible and protective after 18 hours at 370°C. It was made from a mixture of ethylenediamine silazane and the by-product obtained in the preparation of hexaphenylcyclotrisilazane.

The condensation polymerization of hexaphenylcyclotrisilazane was studied in detail and it was found that the volatile by-product was at least 97% benzene. The mechanism is believed to be intermolecular condensation of Si-phenyl and N-hydrogen groups to release benzene and form new Si-N bonds.

The lithium, sodium, and potassium derivatives of silazanes were studied as intermediates for making N-substituted silazanes. The potassium derivatives performed better, and the N-trimethylsilyl derivatives were found to have improved hydrolytic stability. This method of synthesis is potentially valuable as a means of producing silazanes with specific structures.

Silicon-nitrogen polymers were made by treating mixtures of di-, tri-, and tetrafunctional chlorosilanes with methylamine and heating the product. Clear, colorless, resinous solids were obtained in some experiments, but no polymers were produced that had softening points above 175°C.

Silicon-nitrogen polymers were produced by exchange and rearrangement reactions with a number of different silazanes. Ammonium chloride and ammonium sulfate were used as catalysts. The polymers were too low in molecular weight to have much strength.

Attempts to produce silicon-nitrogen polymers by treating amines and ammonia with silicon isocyanates, isothiocyanates, and isonitriles resulted largely in the production of materials with low molecular weights. However, reactions occurred that might be useful in the future in specific synthesis problems.

Silylhydrazine polymers were prepared, but they also had low molecular weights and were not outstanding in their physical properties.

A soft, solid polymer that contained aromatic bridges between the silicon-nitrogen groups had moderate thermal stability. However, it apparently polymerized more readily than other silicon-nitrogen systems, and so continued study of it is recommended.

## III. SILAZANES IN HEAT-BARRIER MATERIALS

### A. Discussion of Results

Several silazanes were found to be potentially valuable for use in heat-barrier coatings, because they polymerized endothermically in the range of 450-560°C. Hexaphenylcyclotrisilazane is an outstanding example of a silazane that undergoes endothermic polymerization, but essentially all of the silazanes studied that could be heated to 450-500°C without boiling could also be converted to foamed infusible solids of high thermal stability. The endothermic character of this conversion was revealed by a differential thermal analysis performed at the George C. Marshall Space Flight Center.

It was desirable to make heat-barrier coatings of undiluted silazanes, but those that were available had low melting points or they were brittle. Although the silazanes could be polymerized by heating to form infusible solids, they simultaneously lost the property of further endothermic condensation, and they did not lose their brittleness.

At first, the investigation of heat-barriers emphasized attempts to blend or partially polymerize silazanes to produce satisfactory physical properties while retaining the endothermic properties. Attempts were also made to plasticize partially polymerized silazanes with organic compounds that had flame-retardant properties. The polymers that melted at low temperatures were incorporated into glass fibers or ceramic matrices, and they were also blended with commercial products that were known to have desirable thermal properties.

The experimental samples were spread on aluminum panels and compared by measuring the temperature rise at the back of the panel as it was exposed to a radiant heat-source that provided 40 Btu of energy per square foot per second. A sheet of phenolic resin that contained asbestos was used as a standard. The thicknesses of the samples were comparable. This resin-impregnated asbestos was obtained as a sample of material that has been used as a heat barrier. Several silazane-containing barriers exhibited slower heat transfer than the standard phenolic-asbestos sheet under the conditions used. However, other important factors, such as strength, were not evaluated systematically in these preliminary trials.

In the first series of trials, a thermocouple mounted at the back of the standard phenolic-asbestos sheet indicated 118°C after exposure to the heat source for 15 seconds. By comparison, aluminum panels coated with the following blends showed lower temperatures as indicated:

| | |
|---|---|
| 50% Silastic 140 Adhesive<br>50% Hexaphenyl prepolymer | 82°C |
| 50% Viton B rubber<br>50% Hexaphenylcyclotrisilazane | 100°C |
| 49% Hexaphenyl prepolymer<br>49% Silastic 140 Adhesive<br>2% $NH_4Cl$ | 101°C |
| 50% Hexaphenylcyclotrisilazane<br>50% Pyroshield 21 | 101°C |
| Ceramic fiber pad impregnated with hexaphenylcyclotrisilazane | 108°C |
| 32% Hexaphenyl prepolymer<br>68% Silastic 140 Adhesive<br>Hypalon 20 overcoat | 116°C |

Additional data are listed in Table I for these and other blends that were less effective. All of the above coatings except the one containing Pyroshield 21 flamed when exposed to the heat source in air. Flaming may be objectionable in some applications but not in all, because in some cases insufficient oxygen is available for combustion.

A second series of trials that emphasized blends of hexaphenylcyclotrisilazane with silicone rubbers is summarized in Table II. The thermocouple was more firmly attached to the back of the panels in this series than in the previous series; so the data for each series, Table I and Table II, should be compared with that for the standard panel in the same series. Each of the four panels of the second series (Table II) transferred heat more slowly than the standard panel, but all flamed except the standard and one panel containing Pyroshield 21.

Table I. Evaluation of Heat-Barrier Coatings

| Sample number | Composition | Coating thickness, mils | Temperature on back of panel, °C, after exposure 5 sec | 10 sec | 15 sec | Time to appearance of flame, sec | Amount flowed | Condition of residue |
|---|---|---|---|---|---|---|---|---|
| Standard | Phenolic resin-asbestos | 100-125 | 38 | 71 | 118 | none | none | black, firm |
| 2627-95-4 | 50 Silastic 140 Adhesive<br>50 Hexaphenylcyclotrisilazane prepolymer | 80 | 40 | 63 | 82 | 10 | few drops | brown and white, rubbery, strongly adhered |
| 2802-3-1 | 50 Hexaphenylcyclotrisilazane<br>50 Pyroshield 21 | 90 | 44 | 81 | 101 | none | none | black, very hard, strongly adhered |
| 2627-97-1 | 49 Silastic 140 Adhesive<br>49 Hexaphenylcyclotrisilazane prepolymer<br>2 $NH_4Cl$ | 100-125 | 40 | 71 | 101 | 13 | few drops | brown and white, rubbery, strongly adhered |
| 2802-3-2 | 49.75 Viton B<br>49.75 Hexaphenylcyclotrisilazane<br>0.5 Diethylenetriamine | 60 | 56 | 86 | 100 | 10 | none | black, crazed, poorly adhered |
| 2802-3-3 | Fiberfrax<br>Hexaphenylcyclotrisilazane | 100 | 36 | 67 | 108 | 12 | none | black, well adhered |
| 2627-97-2 | 62 Silastic 140 Adhesive<br>38 Hexaphenylcyclotrisilazane prepolymer<br>Hypalon overcoat | 100-125 | 43 | 85 | 116 | 10 | few drops | black, rubbery, strongly adhered |
| 2802-3-4 | 38.5 Viton B<br>30.6 Hexaphenylcyclotrisilazane<br>30.5 Pyroshield 21<br>0.4 Diethylenetriamine | 60 | 47 | 89 | 139 | 12 | none | black, slightly flexible, poorly adhered |
| 2627-97-3 | 34 Hypalon 20<br>66 Hexaphenylcyclotrisilazane prepolymer | 100-125 | 88 | 193 | 282 | 5 | 50% | black, hard |
| 2627-95-3 | 50 Methyl hydrogen silazane<br>50 Hexaphenylcyclotrisilazane prepolymer cured at 110°C | 100-125 | 63 | 151 | 257 | 5 | 50% | white ash |
| 2802-3-5 | Methyl hydrogen silazane cured at 300°C | - | 81 | 169 | 292 | 5 | few drops | white ash |
| 2627-97-4 | Ethylenediamine silazane cured at 110°C | - | 127 | 257 | 366 | 8 | few drops | white ash |
| 2627-95-1 | Glass cloth<br>Hexaphenylcyclotrisilazane prepolymer | 100-125 | 88 | 143 | 171 | 8 | 25% | loose, curled glass cloth |
| 2802-3-6 | Methyl hydrogen silazane cured at 200°C | - | 89 | 203 | 333 | 5 | few drops | white ash |
| 2802-3-7 | Ethylenediamine silazane cured at 200°C | - | 106 | 225 | 353 | 10 | few drops | white ash |
| 2627-95-2 | 20 Aroclor 1248<br>80 Hexaphenylcyclotrisilazane prepolymer | 100-125 | 85 | 238 | 366 | none | most | shiny, transparent |



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Table II. Effectiveness of Experimental Heat-Barrier Coatings

| Sample | Composition | Temperature on back of panel, °C: During exposure, °C: 5 sec | 10 sec | 15 sec | Maximum: °C | Sec[a] | Flame |
|---|---|---|---|---|---|---|---|
| 2802-7-1 | 46% Silastic 140<br>27% Hexaphenylcyclotrisilazane<br>27% Pyroshield 21 | 80 | 86 | 99 | 203 | 65 | no |
| 2802-7-5 | 50% Silastic 52U<br>50% Hexaphenylcyclotrisilazane (kneaded, not cured) | 85 | 95 | 106 | 243 | 80 | yes |
| 2802-7-2 | 50% Silastic 52U<br>50% Hexaphenylcyclotrisilazane (milled and cured) | 85 | 91 | 110 | 270 | 65 | yes |
| 2802-7-3 | 50% Silastic 140<br>50% Hexaphenylcyclotrisilazane | 80 | 95 | 110 | - | - | yes |
| Standard | Phenolic resin containing asbestos | 87 | 98 | 125 | 356 | 70 | no |

[a] Time to reach maximum temperature after start of exposure to heat source.



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After these preliminary trials, flexible barriers were prepared by milling hexaphenylcyclotrisilazane into uncured silicone rubber in amounts ranging from 0 to 25%. Then sheets of the mixture measuring 4 x 6 x $\frac{3}{8}$ inch were molded and cured under pressure. The cured sheets, with and without the silazane, closely resembled each other with respect to feel and appearance. They were sent to the George C. Marshall Space Flight Center for evaluation. The samples were exposed to a radiant heat source that delivered 24 Btu per square foot per second while the sample was being shaken violently. The observations showed that the incorporation of hexaphenylcyclotrisilazane reduced the back-face temperature rise and the thickness loss without causing an appreciable change in fragmentation loss and the time when smoking began. The samples that contained 10% or more hexaphenylcyclotrisilazane flamed slightly sooner than the samples with 4% or less. The inclusion of Pyroshield 21 was not beneficial in that it reduced the mechanical strength and did not retard ignition or combustion.

## B. Experimental Details

### 1. Plasticizers for the hexaphenylcyclotrisilazane prepolymer

The initial experiments to prepare heat-barrier coatings were directed mainly to attempts to plasticize the prepolymer that was made by heating hexaphenylcyclotrisilazane at 450-500°C until polymerization proceeded far enough to prevent crystallization on cooling. The prepolymer adhered well to aluminum in thick coatings, but it was too brittle to survive rough handling. Hydrocarbons, such as benzene, plasticized the prepolymer; but they were too volatile, and they added to the inflammability. Hence, Aroclor 1248 (a chlorinated polyaromatic hydrocarbon made by Monsanto Chemical Company) and Hypalon 20 (a chlorinated polyethylene made by E. I. du Pont de Nemours and Company), which are less volatile and less flammable, were tried. The brittleness of the hexaphenyl prepolymer was satisfactorily reduced in mixtures containing 40% Aroclor 1248 or 50% Hypalon 20. The Aroclor 1248 was blended with the prepolymer by melting them together, and the melt was then poured onto the panel to be coated. Hypalon 20 was blended with the prepolymer in benzene, a mutual solvent. The solution of Hypalon 20 and prepolymer was applied to the aluminum panel in layers, and each layer was allowed to dry approximately 2 hours before applying the next.

The materials listed below were tried unsuccessfully as plasticizers for the hexaphenyl prepolymer. They failed to reduce the brittleness of the prepolymer when they were melted and mixed with the prepolymer in the amounts shown.

| | |
|---|---|
| Mixed methylphenyl silazanes[4] | 10% |
| Mixed methylphenyl silazanes[4] | 30% |
| Silylhydrazine polymer[5] | 10% |
| Amine-exchange product (octamethylcyclotetrasilazane with ethylenediamine in pyridine)[6] | 10% |
| Aroclor 1262 | 10% |
| Aroclor 1262 | 50% |
| Aroclor 1248 | 10% |
| Ethylenediamine silazane[7] | 10% |
| Ethylenediamine silazane[7] | 30% |
| Methylhydrogen silazane[8] | 10% |
| Amine-exchange product (octamethylcyclotetrasilazane with ethylenediamine, no solvent)[9] | 10% |

The last four materials listed were incompatible with the prepolymer, and the films formed were not homogeneous.

## 2. Preparation of coatings for heat-barrier trials and their evaluation

A variety of materials was tried to prevent the flow of experimental coatings when they were heated. The coatings, 100-125 mils thick (except as noted), were prepared on 2 x 3-inch aluminum panels, which were approximately 30 mils thick. The phenolic-asbestos panel that was used as a standard was 155 mils thick.

The "hexaphenyl prepolymer" was prepared by heating hexaphenylcyclotrisilazane at 430°C for 6 hours. At this temperature, some polymerization had occurred, but not enough to produce infusibility. Thus some of the endothermic properties were retained, and the prepolymer could be blended with other materials either by mixing as a melt or in a mutual solvent.

The coatings were evaluated for general appearance, flexibility, and adhesion to the aluminum panels. Then they were subjected for 15 seconds to a thermal energy input of 40 Btu per square foot per second from 5 General Electric quartz infra-red 2000T-3/CL lamps mounted in a gold-coated AV-212 reflector unit. (This unit is made by Research, Incorporated.) This heat flux was sufficient to raise the temperature of the coating surface at an initial rate of approximately 200°F per second to a maximum of 2000-2500°F. The coatings were observed while they were being heated, and the temperature on the unexposed surface of the panel was plotted automatically against time. Each coating is described separately in the following paragraphs. The observations are summarized in Tables I and II.

Details of the individual preparations follow:

2627-95-4: Silastic 140 Adhesive (50%) and the hexaphenyl prepolymer (50%) were blended with a spatula. The resulting paste was spread on a panel and cured in air at room temperature for 2 days. The coating was approximately 80 mils thick; it was flexible and well bonded to the aluminum panel. Upon being exposed to the high energy heat source, the coating smoked heavily and burst into flame after about 10 seconds. The flame went out when exterior heat was removed. A few drops of molten hexaphenylcyclotrisilazane prepolymer flowed off the panel. After cooling, the coating was mottled brown and white; and there were large bubbles just under the outer surface of the coating. The coating remained pliable. The temperature on the back surface of the panel rose to 40°C in 5 seconds, 63°C in 10 seconds, and 82°C in 15 seconds (Table I).

2802-3-1: A mixture of Pyroshield 21 (Columbia Technical Corporation), which contained 80% solids and 20% water, and hexaphenylcyclotrisilazane (50:50 on a solids basis) was spread on an aluminum panel with a spatula. The coating thickness was approximately 90 mils. The coating was white, smooth, relatively hard, and brittle, and it was fairly well bonded to the aluminum. The coating did not burn when exposed to high heat, but it smoked slightly. The coating was frothed, black, hard, and well adhered to the metal after heating. The temperature on the back of the panel reached 44°C after 5 seconds, 81°C after 10 seconds, and 101°C after 15 seconds. (Table I)

2627-97-1: Silastic 140 Adhesive and the hexaphenyl prepolymer were blended as for 2627-95-4 except that 2% ammonium chloride was added. The mixture was spread on a panel and cured in air at room temperature for 2 days. Ammonium chloride sublimes at 540°C, and thus it was expected to serve as a flame retarder, a heat sink, and a foaming aid. The performance of the coating was the same as that of coating 2627-95-4 with the following exceptions: The coating did not burst into flame until near the end of the 15-second heating period, and the temperature rose to 40°C in 5 seconds; 71°C in 10 seconds; and 101°C in 15 seconds. (Table I)

2802-3-2: A 30% solution of Viton B (E. I. du Pont de Nemours and Company, Inc.) in methyl ethyl ketone was prepared. One part of diethylenetriamine per hundred of Viton B was added, then finely ground hexaphenylcyclotrisilazane was added so that a film cast from the mixture was composed of 49.75% Viton B, 49.75% hexaphenylcyclotrisilazane, and 0.5% diethylenetriamine. Films were cast on glass, dried overnight, then cured at 250°F for 10 minutes. The cured films were attached to aluminum panels with Silastic 140 Adhesive (Dow Corning Corporation). The coating was approximately 60 mils thick. It was tan, flexible, and smooth. Upon being exposed to the heat source, the coating burst into flame after 10 seconds and emitted a black smoke. The residue was crazed and black, and it adhered poorly to the aluminum. Temperatures on the back side of the panel were 56°C after 5 seconds, 86°C after 10 seconds, and 100°C after 15 seconds. (Table I).

2802-3-3: A ceramic fiber pad, Fiberfrax (Carborundum Company), was attached to aluminum with Silastic 140 Adhesive. The pad weighing 1 gram (apparent density 0.1 g/cc) was then impregnated with 7 grams of hexaphenylcyclotrisilazane. The coating thickness was approximately 100 mils. It was smooth, white, and hard. When exposed to heat, the coating surface burst into flame after about 12 seconds. The flames were easily extinguished after heat was removed. The residue had a black surface, but other than this the coating underwent no apparent change. The temperatures recorded on the back of the panel were 36°C after 5 seconds, 67°C after 10 seconds, and 108°C after 15 seconds. (Table I).

2627-97-2: The hexaphenyl prepolymer (38%) and Silastic 140 Adhesive (62%) were blended, coated on a panel, and cured the same as 2627-95-4. Then a film of Hypalon 20 was applied as a protective cover with a paint brush. The performance on heating was essentially the same as that of coatings 2627-95-4 and 2627-97-1. However, in this case the coating burst into flame in about 10 seconds, and the coating surface became black. This was probably due to decomposition of the Hypalon 20 overcoating. The temperature on the back of the panel rose more rapidly than with 2627-95-4 or 2627-97-1—in 5 seconds the temperature was 43°C, in 10 seconds it was 85°C, and in 15 seconds, it was 116°C. (Table I)

2802-3-4: A coating similar to 2802-3-2 was prepared with the exception that Pyroshield 21 was included. The final composition was 38.5% Viton B, 30.6% hexaphenylcyclotrisilazane, 30.5% Pyroshield 21, and 0.4% ethylenediamine. A coating was prepared in the same way as in 2802-3-2. Coating thickness was approximately 60 mils. It was tan, smooth, flexible, and it was attached to the aluminum substrate by Silastic 140 Adhesive. In general, the same comments apply to this coating as the 2802-3-2. Temperatures on the back of the aluminum panel were 47°C after 5 seconds, 89°C after 10 seconds, and 139°C after 15 seconds. (Table I)

2627-97-3: The hexaphenyl prepolymer (66%) and Hypalon 20 (34%) were dissolved in benzene and applied to a panel in several successive layers, allowing approximately 2 hours for the benzene to evaporate from each layer. The coating was smooth, flexible, and white, and it adhered well to the aluminum substrate. The coating began to smoke and flame vigorously about 5 seconds after being exposed to the heat source. It is possible that some of the benzene was still present. Some flaming material dripped off the panel; and a black, hard residue remained. The temperature on the back of the panel rose to 88°C in 5 seconds, 193°C in 10 seconds, and 282°C in 15 seconds. (Table I)

2627-95-3: The hexaphenyl prepolymer (50%) and the methylhydrogen silazane polymer (50%)[8] were blended in a melt. The mixture was poured on a panel and heated for 4 hours at 110°C. The coating was approximately 80 mils thick. Heating was expected to effect a partial cure of the methylhydrogen silazane and reduce its fluidity. The coating was white, flexible, smooth, and well bonded to the aluminum. The coating burst into flame 4 to 6 seconds after application of heat. This sample burned more vigorously than any other sample that was evaluated. Only ash remained on the panel at the end of the heating cycle. A considerable portion of the coating flowed from the panel during heating. The temperature on the back surface of the panel rose to 63°C in 5 seconds, 151°C in 10 seconds, and 257°C in 15 seconds. (Table I)

2802-3-5: Methylhydrogen silazane was applied to aluminum panels in several thin layers with a 2-hour cure at 300°C following each application. The final coating was very uneven, relatively brittle, and dark brown in color. Adhesion to the aluminum was fair; however, the coating was easily abraded from the surface. After heating for 8 seconds, the coating burst into vigorous flame. After heating was completed, only a white ash remained on the panel. A small amount of flaming material ran off the panel surface while heat was being applied. The temperature on the back of the panel rose to 81°C in 5 seconds, 169°C in 10 seconds, and 292°C in 15 seconds. (Table I)

2627-97-4: Ethylenediamine silazane was applied to a panel in several successive layers. Each layer was cured at 110°C for about 2 hours before the next layer was added. The sample stood 5 days before being exposed to the heat. The coating was the same as 2802-3-7 (below) except it was cured at 110°C, and its color was light brown. The performance was similar. The temperature on the back of the panel was 127°C after 5 seconds, 257°C after 10 seconds, and 366°C after 15 seconds. (Table I)

2627-95-1: Glass cloth was impregnated with the hexaphenyl prepolymer and four layers were bonded to each other by fusion of the prepolymer. The resulting laminate was attached to an aluminum panel with Silastic 140 Adhesive (Dow Corning Corporation). It was very brittle and light tan in color. The outer surface was relatively smooth. The prepolymer began to flow off the glass cloth almost immediately when heat was applied, and the prepolymer that remained began to flame after 8 seconds of heating. The glass cloth began to curl and come loose from the panel by the end of the heating period. The temperature of the unexposed panel face rose to 88°C in 5 seconds, 143°C in 10 seconds, and 171°C in 15 seconds. (Table I)

2802-3-6: A coating similar to 2802-3-5 was prepared from methyl hydrogen silazane except the cure temperature was 200°C. The coating was very rough, but it had some flexibility. It was white, and it adhered well to the aluminum substrate. On exposure to heat, the coating burst into vigorous flame in approximately 5 seconds, and the flame was difficult to extinguish even after external heat was removed. Some drops of flaming material flowed from the panel. A loose white ash remained as a residue. The temperature on the back side of the panel rose to 89°C in 5 seconds, 203°C in 10 seconds, and 333°C in 15 seconds. (Table I)

2802-3-7: Ethylenediamine silazane was coated on panels in several thin layers with a 2-hour cure at 200°C following each application. The final coatings were very uneven and had the appearance of "ruffles." The coating was rubbery in character and very easily abraded. On exposure to heat, flame appeared in 8 seconds, a few drops of material melted and ran off, and a white ash remained. The temperature on the back of the panel was 106°C after 5 seconds, 225°C after 10 seconds, and 353°C after 15 seconds. (Table I)

3. Preparation of flexible heat barriers

To prepare experimental flexible heat barriers hexaphenylcyclotrisilazane was milled into silicone rubber, and the blends were molded into sheets to form flexible heat barriers. The silicone rubber was commercially available as Silastic Rubber 651-U (Dow Corning Corporation). The hexaphenylcyclotrisilazane was the pure compound, not polymerized. Pyroshield 21, a commercial intumescent-paint component sold by Columbia Technical Corporation, was added to one sample. Six different blends were prepared.

The samples were blended on a laboratory two-roll rubber mill. The Silastic 651-U was banded on the mill; and the peroxide catalyst, followed by the hexaphenylcyclotrisilazane, was added over a period of 5-15 minutes. To make the blend that contained Pyroshield 21, the Pyroshield and the hexaphenylcyclotrisilazane were first mixed; and the mixture was added to the rubber on the mill. After the additions were completed, milling was continued for 30 to 35 minutes to insure uniformity. The milled blends were then cured at 260°F for 5 minutes in a 4 x 6 x $\frac{3}{8}$-inch mold under slight pressure to insure flow of the rubber into all sections of the mold. One sample was cured only 2 minutes, because an incompletely cured material was desired for one trial. Fluorocarbon Mold Release Agent S-122 (Miller-Stephenson Chemical Company, Inc.) was used to prevent sticking to the mold. Six samples were submitted to the George C. Marshall Space Flight Center for evaluation. There they were cemented to 4 x 6 x 0.080-inch aluminum plates with Silastic 140 adhesive, and then they were exposed, in a vertical position, to a radiant heat source that delivered 24 Btu per square foot per second. The samples were shaken violently by moving them closer to and farther away from the source at a rate of 30 cycles per second over a distance of 0.25 inch. The resulting acceleration was equivalent to 11 times gravity. All of the samples that contained hexaphenylcyclotrisilazane transmitted heat more slowly and underwent less thickness loss than the control without causing appreciable changes in mechanical loss by vibration. The details of the performance and composition of the six samples are presented in Table III.

Table III. Composition and Performance of Flexible Heat Barrier Samples

| Sample number 2802- | 9-1 | 9-2 | 9-3A | 9-3 B | 9-4 | 9-5 |
|---|---|---|---|---|---|---|
| A. Composition | | | | | | |
| Silastic 651-U | | | | | | |
| Weight, g | 250 | 240 | 450 | 450 | 200 | 187.5 |
| Weight, % | 100 | 96 | 90 | 90 | 80 | 75 |
| Hexaphenylcyclotrisilazane | | | | | | |
| Weight, g | 0 | 10 | 50 | 50 | 25 | 62.5 |
| Weight, % | 0 | 4 | 10 | 10 | 10 | 25 |
| Pyroshield 21 | | | | | | |
| Weight, g | 0 | 0 | 0 | 0 | 25 | 0 |
| Weight, % | 0 | 0 | 0 | 0 | 10 | 0 |
| Benzoyl peroxide | | | | | | |
| Weight, g | 1.0 | 1.0 | 1.8 | 1.8 | 0.8 | 0.8 |
| Weight, % | 0.4 | 0.4 | 0.36 | 0.36 | 0.32 | 0.32 |
| Curing time, 260°F, min | 5 | 5 | 2 | 5 | 5 | 5 |
| Thickness of sample, mils | 373 | 405 | 395 | 395 | 390 | 393 |
| B. Performance - Exposure to radiant lamp at 24 Btu per square foot per second for 120 seconds; vibrated at 30 cycles per second with displacement of 0.25 inch; acceleration of 11 times gravity. | | | | | | |
| Back-face temperature rise at cut-off, °F | 194 | 145 | 170 | 159 | 183 | 144 |
| Smoking began at, sec | 4 | 4 | 4 | 5 | 3 | 4 |
| Flaming began at, sec | 10 | 12 | 7 | 8 | 6 | 6 |
| Char fell off at, sec | - | - | - | - | 60, 90 | - |
| Thickness loss, mils | 98 | 55 | 60 | 53 | all | 68 |
| Additional remarks | a | b | b | b | c | d |

[a] Started flaking off at 60 sec; material under crust gummy.

[b] Crust "mud-cracked" did not fall off; material under crust slightly gummy while hot, hard when cool.

[c] Entire sample fell off at cut-off.

[d] Surface cracked into very small areas; material under crust slightly gummy while hot, hard when cool.

# IV. FACTORS AFFECTING HYDROLYTIC STABILITY

## A. Discussion

### 1. Results

Silicon-nitrogen compounds of widely different structures were prepared and studied to determine what factors influence their hydrolytic stability. Rates of hydrolysis were compared by dissolving each compound in benzene or carbon tetrachloride and shaking it with water or dilute acid. The rate of appearance of the amine hydrolysis product was considered to be a measure of the compound's sensitivity to moisture. The condensation polymer made by heating hexaphenylcyclotrisilazane at 450-550°C could not be studied by this method, because it was not only insoluble but essentially inert to water.

The most easily hydrolyzed silylamine was bis(methylamino)-dimethylsilane, which was 80% hydrolyzed by water in 1 minute. By contrast, the silylamine most stable to moisture was N-trimethylsilyl-hexaphenylcyclotrisilazane, which was not detectably hydrolyzed by water in several hours and was less than 10% hydrolyzed in dilute acid in 20 minutes. The following factors favored hydrolytic stability:

- attachment of phenyl groups to silicon or nitrogen atoms
- replacement of hydrogen atoms on nitrogen atoms with phenyl, methyl, or isopropyl groups
- cyclization or elimination of amine end groups
- silylation of nitrogen atoms in cyclic silazanes

Attachment of the trimethylsilyl group to hexaphenylcyclotrisilazane and hexamethylcyclotrisilazane evidently increased the hydrolytic stability of the entire rings. The extent of the increase was greater than expected, since only one of the three NH groups was involved. In the case of hexamethylcyclotrisilazane, the amount hydrolyzed in the first 20 minutes was reduced from 23% to 4% by silylation of one NH group. It was also interesting to note the drastic improvement in stability that resulted from N-methylation. Nonamethylcyclotrisilazane hydrolyzed at a rate of approximately 1 to 2% per minute, while hexamethylcyclotrisilazane hydrolyzed at a rate of about 38% per minute.

Attachment of chlorine atoms to the phenyl rings in a silazane did not improve the hydrolytic stability. A pure crystalline chlorophenyl silazane was not isolated and identified positively; but analytical data indicated strongly that the material in question was a chlorophenyl silazane, and its hydrolytic stability was not outstanding. It is interesting to note, however, that while the chlorophenyl compound was considerably less stable to moisture than pure hexaphenylcyclotrisilazane, its stability was comparable to that of the by-product obtained in the preparation of hexaphenylcyclotrisilazane. Therefore, the lack of stability can probably be attributed to the amine end groups rather than the chlorine atoms on the phenyl rings. Efforts were also made to prepare pure cyclic silazanes with trifluoromethylphenyl and dichlorovinyl side groups, but the compounds were not obtained in pure enough form for hydrolysis data to be significant.

The hydrolysis data are summarized in Tables IV and V. Data in the columns headed "Rate, % per hour" were taken from the curves that were plotted from data on time and amount hydrolyzed, Figures 1-15. The "Rate, % per hour" was the slope of the curve at the point that appeared to give the best representation of the rate. Calculation of rate constants was not practical because of the non-homogeneity of the medium and the continuously changing pH.

Table IV. Relative Rates of Hydrolysis of the More Stable Silylamines

| Silylamine | Hydrolysis in $CCl_4 + H_2O$: Time for 25% hydrolysis, min | Hydrolysis in $CCl_4 + H_2O$: Hydrolysis in first 20 min, % | Hydrolysis in $CCl_4 + H_2O$: Rate, % per hour[b] | Hydrolysis in $CCl_4 + H_2O + HCl$[a]: Time for 25% hydrolysis, min | Hydrolysis in $CCl_4 + H_2O + HCl$[a]: Hydrolysis in first 20 min, % | Hydrolysis in $C_6H_6 + H_2O + HCl$[a]: Time for 25% hydrolysis, min | Hydrolysis in $C_6H_6 + H_2O + HCl$[a]: Hydrolysis in first 20 min, % | Data plotted in Figure No. |
|---|---|---|---|---|---|---|---|---|
| N-trimethylsilylhexaphenylcyclotrisilazane | | | | 139 | 9 | | | 1 |
| Dianilinodiphenylsilane | | | | | | 5[c] | 40[c] | 2 |
| Hexaphenylcyclotrisilazane | | | | | | 5 | 42 | 3 |
| Amine exchange polymer,[d] No. 2783-93 | | 2.5 | 0 | 2 | 64 | | | 1, 14 |
| Diphenylsilylhydrazine polymer | | 3.5[e] | 0 | | 16.5 | | | 4, 8 |
| 2, 4, 6-Trimethyl-2, 4, 6-triphenylcyclotrisilazane | | 3.5 | 0.2 | | | | | 5 |
| Nonamethylcyclotrisilazane | | 0.8 | 1.2 | <1 | 100 | <1 | 100 | 5 |
| Isopropyltris(isopropylamino)silane | >480 | 1.0 | 2.0 | <1 | 100 | | | 6 |
| N-trimethylsilylhexamethylcyclotrisilazane | 640 | 4.0 | 1.7 | <1 | 100 | | | 7 |
| By-product of hexaphenylcyclotrisilazane preparation, No. 2736-71-2A | | 5.3 | 0.5 | <1 | 56 | | | 1, 12 |
| Amine exchange polymer,[f] No. 2783-55 | | 4.5 | 1.2 | 1 | 88 | | | 4, 15 |
| Bis(p-chlorophenyl)silazane mixture | | 6.5 | 2.4 | 1 | 61 | | | 4, 8 |
| Di-tri silazane residue,[g] (Fraction 4) | | 4.0 | | <1 | 98 | | | 1, 12 |
| 2, 2, 4, 4, 6, 6, 8, 8-Octamethyl-1, 5-dioxa-3, 7-diazacyclooctasilane | | 2.2 | 3.1 | <1 | 100 | | | 9 |
| Di-tri silazane[h] (Fraction 3) | | 4.9 | 31 | <1 | 100 | | | 11 |
| Dimethylsilazane polymer,[i] No. 2783-75-5 | 144 | 11 | 4.5 | <1 | 100 | | | 11 |

[a] One equivalent of acid added for each equivalent of amine expected.

[b] At steady-state condition as judged by slope of line after steady state was reached.

[c] Values based on UV absorption for aniline determinations.

[d] Hexamethylcyclotrisilazane + Methylamine-silicon tetrachloride product.

[e] Possibly influenced by impurities or minor components.

[f] Hexamethylcyclotrisilazane + methylamine-silicon tetrachloride product.

[g] Still residue from reaction of ammonia with an equimolar amount of dimethyldichlorosilane and methyltrichlorosilane.

[h] Fraction 3, from reaction of ammonia with an equimolar amount of dimethyldichlorosilane and methyltrichlorosilane.

[i] Dimethylsilazane polymer, obtained in low yield by treating dimethyldichlorosilane with ammonia at -50°C.

Table V. Relative Rates of Hydrolysis of the Less Stable Silylamines

| Silylamine | Hydrolysis in $CCl_4 + H_2O$: Time for 25% hydrolysis, min | Hydrolysis in $CCl_4 + H_2O$: Hydrolysis in first 20 min, % | Hydrolysis in $CCl_4 + H_2O$: Rate, % per hour | Hydrolysis in $C_6H_6 + H_2O$: Time for 25% hydrolysis, min | Hydrolysis in $C_6H_6 + H_2O$: Hydrolysis in first 20 min, % | Data plotted in Figure No. |
|---|---|---|---|---|---|---|
| Hexamethylcyclotrisilazane | 23 | 23 | 38[a] | 15 | 30 | 5, 10 |
| Ethylenediamine silazane | 15 | 21 | | 6 | 36 | 6, 10 |
| Dimethylsilazane polymer[b], No. 2783-109-2 | 5 | 42 | | | | 14 |
| 1, 3, 5-Trimethyl-2, 2, 4, 4, 6, 6-hexakis(methylamino)-cyclotrisilazane | | | | 1 | 91 | 10 |
| Bis(methylamino)diphenylsilane | 3 | 80 | 600[c] | | | 7 |
| 1, 3-Bis(methylamino)pentamethyldisilazane | <1 | 92 | 2,700[c] | | | 7 |
| Dianilinodimethylsilane | <1 | 100 | 3,000[c] | | | 13 |
| Bis(methylamino)dimethylsilane | <1 | 100 | 4,920[c] | | | 8 |

[a] At steady-state conditions as judged by slope of line after steady state was reached.

[b] Still residue from addition of dimethyldichlorosilane to liquid ammonia without solvent.

[c] Based on linear portion of rate curve, in the time interval of 0 to 1 min.

2. Method of comparing rates of hydrolysis

We first planned to adapt the method of Rochow[10] to our needs for comparing hydrolytic stabilities. Rochow used the Karl Fischer Reagent to determine the amount of water that disappeared from a mixture of water, acetic acid, ether, and silylamines that were made from dimethyldichlorosilane and ethylenediamine. In our preliminary experiments, we obtained results somewhat similar to those that were reported[10] for the ethylenediamine derivative. However, hexaphenylcyclotrisilazane apparently hydrolyzed only slightly in 5 days, and the end-points of the Karl Fischer titrations were unstable. Concurrently with the preliminary experiments, we studied the literature on the behavior of silanols with the Karl Fischer Reagent and concluded that the Rochow Method should not be used with our diversified silazanes. The difficulty lies in the fact that silanols, which are products of the hydrolysis of silylamines, react with the Karl Fischer Reagent and with themselves. Gilman and Miller[11] showed that the following reaction occurs:

$$\text{(a)}\quad \underset{\text{silanol}}{R_3SiOH} + \underset{\text{Karl Fischer reagent}}{I_2 + SO_2 + 2\,CH_3OH} \longrightarrow R_3SiOCH_3$$

Only highly hindered compounds failed to react. The condensation of silanols to form silyl ethers occurs in this manner:

$$\text{(b)}\quad 2R_3SiOH \longrightarrow R_3SiOSiR_3 + H_2O$$

If enough were known about the rates of reactions (a) and (b), it might be possible to use the Karl Fischer reaction to measure the extent of hydrolysis of silylamines:

$$R_3SiNH_2 + H_2O \longrightarrow R_3SiOH + NH_3$$

However, we believed that other methods would be more suitable for our studies, because we wanted to compare a variety of silylamines with different R groups.

## B. Experimental Details

### 1. Methods of comparing rates of hydrolysis

#### a. General procedures

The Rochow Method[10] was tried for studying the hydrolytic stability of silylamines by the following procedure: The Karl Fischer Reagent was standardized against water. A calculated weight of sample was dissolved in benzene to make a solution of which 4 ml would be equivalent to approximately 18 mg of water. Aliquots, 4 ml, of the benzene solution were added to 10 dry flasks each containing 10 ml of ether, 21 mg of glacial acetic acid, and 50 mg of water. At the same time, blank samples were prepared with 4 ml of benzene plus the ether, acids, and water. Time was measured from the time the last drop of benzene solution was added to each flask. The flasks were stoppered and placed in a bath at 27°C, and samples were removed at intervals. Only one sample was taken from each flask to keep contamination from atmospheric moisture as low as possible. Each sample was diluted with 10 ml of pretitrated methanol-acetic acid solution and titrated to the first red end-point that remained 10 seconds. The milligrams of water consumed by hydrolysis was equal to the milligrams of water in the blank minus the milligrams of water in the sample. Table VI summarizes the data.

Table VI. Rates of Hydrolysis as Determined by Karl Fischer Reagent

| Sample | Description | Sample weight, mg | $H_2O$ (theory) required for complete hydrolysis, mg | Time, hours | Water consumed mg | Water consumed % |
|---|---|---|---|---|---|---|
| 2614-109-V | hexaphenylcyclotrisilazane | 211.4 | 19.3 | 0.5 | 2.3 | 12 |
| | | | | 3 | 3.4 | 18 |
| | | | | 16 | 3.6 | 19 |
| | | | | 21 | 4.2 | 22 |
| | | | | 120 | 3.5 | 18 |
| | | | | 120 | 4.2 | 22 |
| 2614-149-II | nonamethylcyclotrisilazane | 81.5 | 16.8 | 0.5 | 3.0 | 18 |
| | | | | 1.5 | 4.7 | 28 |
| | | | | 3.5 | 6.1 | 36 |
| | | | | 5.5 | 6.6 | 39 |
| 2614-149-III | hexamethylcyclotrisilazane | 111.2 | 27.3 | 0.5 | 3.4 | 13 |
| | | | | 1.5 | 4.4 | 16 |
| | | | | 2 | 6.7 | 25 |
| | | | | 3 | 9.8 | 36 |
| | | | | 4 | 11.3 | 42 |
| | | | | 5 | 12.4 | 46 |
| | | | | 18 | 19.2 | 70 |
| | | | | 21 | 19.7 | 72 |
| | | | | 120 | 26.0 | 95 |
| 2614-149-VI[a] | $-\overset{CH_3}{\underset{CH_3}{Si}}-NH-CH_2CH_2NH-$ | 123.6 | 19.1 | 0.5 | 3.2 | 17 |
| | | | | 1 | 4.2 | 22 |
| | | | | 1.5 | 4.6 | 24 |
| | | | | 2.5 | 5.8 | 30 |
| | | | | 5 | 8.3 | 43 |
| | | | | 14 | 14.4 | 75 |
| | | | | 18 | 14.4 | 75 |
| 2614-149-VII[b] | hexamethylaminotrimethylcyclotrisilazane | 84.0 | 13.1 | 0.5 | 7.2 | 55 |
| | | | | 1.5 | 9.1 | 70 |
| | | | | 3 | 11.4 | 88 |

[a] Ethylenediamine silazane.

[b] 1, 3, 5-trimethyl-2, 2, 4, 4, 6, 6-hexakis(methylamino)cyclotrisilazane.

Fading of the end point was significant, because it indicated continuing production of water in the sample even after the Karl Fischer Reagent had reacted with all of the free water. Hence, it is clear that the titration was not a simple measure of the water that had not reacted with silazane.

The method that was adopted for estimating the hydrolytic stabilities was this: In a 250-ml glass-stoppered bottle were placed 50.0 ml of carbon tetrachloride and approximately 5.0 milliequivalent, accurately weighed, of the silylamine. Water, 100.0 ml, was added, and the bottle was shaken violently for 1 minute. After the two layers separated, 2.0 ml of the water layer was pipetted off, and 2.0 ml of distilled water was added to the remaining water layer. Shaking was resumed and samples were withdrawn in a similar fashion after various periods of time. The withdrawn aliquots were titrated with standardized 0.01 N hydrochloric acid to determine the amounts of ammonia or amine in the water layer. The samples were taken at frequent intervals, and the progress of hydrolysis was shown by the amount of the total ammonia or amine that appeared in the water. When the last sample of the water layer was removed, a sample of the carbon tetrachloride layer was also titrated as a check on the overall calculations.

The standard procedure just described was modified to suit the requirements of the individual silylamines. Hexaphenylcyclotrisilazane was not sufficiently soluble in carbon tetrachloride, consequently benzene was used. Carbon tetrachloride was preferred as the solvent when it could be used, because it is less likely than benzene to produce emulsions. Control experiments indicated that carbon tetrachloride did not hydrolyze sufficiently under the conditions of the procedure to interfere with the results. Several of the silylamines, such as nonamethylcyclotrisilazane and hexaphenylcyclotrisilazane, hydrolyzed so slowly with water that 1 equivalent of hydrochloric acid was added for each equivalent of base to accelerate the hydrolysis. In such cases, the decrease in the amount of titratable acid was the measure of the extent of hydrolysis.

This method was satisfactory for silylamines made from ammonia, or methylamine, but it was not satisfactory for the N-phenyl compounds because of the difficulty of titrating aniline. Therefore, a modification was tried. Instead of titrating the 2-ml aliquot sample of the aqueous acid layer with a simple acid-base titration, each sample was evaporated to near dryness on a hot plate at about 70°C. As soon as the sample appeared to be almost dry, it was placed in a desiccator at room temperature with potassium hydroxide and phosphorus pentoxide for 16 hours. The residue was then titrated with silver nitrate to determine the amount of aniline hydrochloride, and the result was expressed in terms of percent of the sample hydrolyzed. A better method of analysis for aniline was developed later and adopted. It involved the ultraviolet spectrophotometric determination of aniline. This newer method showed that the values formerly determined by the volumetric chloride analysis were essentially correct. However, the spectrophotometric method is preferable, because it is faster, and it is not subject to the error that might be caused by evaporation of aniline hydrochloride.

In the spectrophotometric method, aniline concentrations were determined from the UV absorption in neutralized aliquot samples at 229 m$\mu$, on a spectrophotometric calibration curve. It was found that aniline obeys Beer's law (the absorbance is directly proportional to the concentration), and the distribution of aniline hydrochloride in the benzene hydrochloric acid system was such that the amount of aniline in the benzene phase was negligible. The hydrolysis data on the anilino compounds that are given in Tables IV and V are based on spectrophotometric determinations.

b. Additional data on compounds slow to hydrolyze

N, N', N''-Triphenylhexamethylcyclotrisilazane was not amenable to the general procedure for hydrolytic stability measurements, because it was not soluble in $CCl_4$ or $C_6H_6$. Furthermore, it was found to be insoluble in toluene, acetonitrile, diethyl ether, chloroform, petroleum ether, and water. Two hydrolysis experiments were conducted with this compound in boiling water and in boiling hydrochloric acid. The purified compound, 90 mg, was boiled in 25 ml of water for 30 minutes. Then 69% was recovered and identified by melting point. However, when the purified compound was boiled in 4% aqueous hydrochloric acid, it dissolved in 3-5 minutes and could not be recovered.

The slow hydrolysis rate of dianilinodiphenylsilane was confirmed by recovery of the original compound after dissolving 0.883 g of it in 50 ml of benzene and shaking with 100 ml of water. After the mixture had been shaken at room temperature for 5 hours, 92% of the original compound was recovered.

The hydrolysis rate of hexaphenylcyclotrisilazane in benzene and water was so slow that it could not be pictured conveniently on the graphs with the other materials. When 1.0014 g of hexaphenylcyclotrisilazane was dissolved in 50 ml of benzene and shaken with 100 ml of water, only 0.44% was hydrolyzed in 5 hours, as determined by titration of the water layer. By evaporation of the benzene solution, 99% of the original hexaphenylcyclotrisilazane was recovered (mp 214-216° C). It is of interest to note that the same amount of hydrolysis (0.44%) was measured in the first 10 minutes of shaking with water. Hence, the small amount of base detected by titration must have been due to impurities rather than products of hydrolysis of hexaphenylcyclotrisilazane.

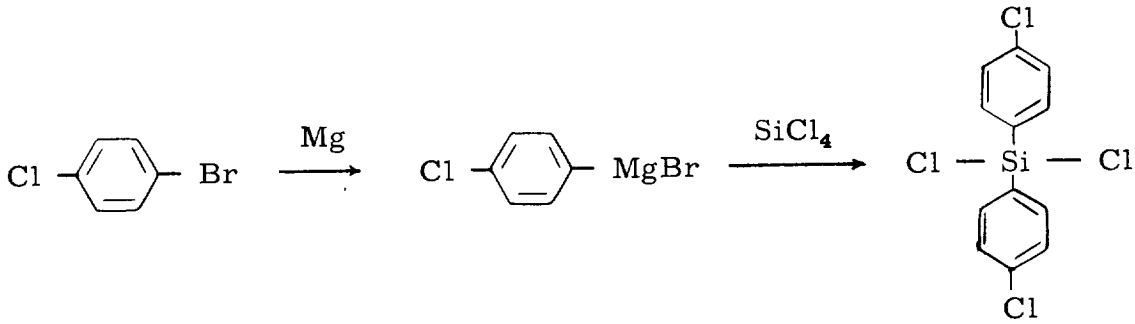
## 2. Methods of synthesis

Several silylamines were prepared primarily to study their hydrolytic stabilities, and the syntheses of these compounds are described in this section.

### a. Silazane with p-chlorophenyl side chains

A silazane with p-chlorophenyl substituents was desired to determine its hydrolytic stability and to determine whether it could be used to reduce the inflammability of heat-barrier coatings (Section III). The p-chloro compound was prepared, but in an impure form, and it was not evaluated in heat barriers because of its low softening point. The plan was to make the p-chlorophenyl silazane by treating bis(p-chlorophenyl)dichlorosilane with ammonia.

Bis(p-chlorophenyl)dichlorosilane was prepared by the method of Chvalovsky and Bazant.[12]



In a 2-liter, 3-neck flask fitted with a stirrer, dropping funnel, and a reflux condenser were placed 24.3 g (1.0 mole) of magnesium turnings and 100 ml of dry ether. The reaction was started with the aid of a few drops of methyl iodide, and then 400 ml of ether was added. Para-chlorobromobenzene, 185.7 g (0.97 mole), dissolved in 500 ml of ether, was added dropwise with stirring over a period of 2 hours. The resulting dark brown mixture was refluxed for an hour and used in the next step of the reaction.

In a 2-liter, 3-neck flask fitted with a stirrer, reflux condenser, thermometer, and dropping funnel were placed 69.5 g (0.41 mole) of silicon tetrachloride and 500 ml of ether. The p-chlorophenyl magnesium bromide solution was added with stirring over a period of 45 minutes, while the temperature was kept below 20°C. The mixture was refluxed for 1.75 hour; and on cooling, the salt settled. The ether layer was rust colored. The ether layer was pipetted off, and the salt layer was extracted first with 275 ml and then with 150 ml of hot ether. The extracts and the main product were combined, and the ether was removed by distillation. The product was distilled and the following fractions were obtained:

1. Bp 90-147°C at 1 mm pressure, 3.3 g, dark red liquid

2. Bp 147-180°C at 1 mm pressure, 53.4 g, tan crystals, mp 54-58°C

3. Bp 160-193°C at 0.5 mm pressure, 2.0 g, tan crystals

4. Residue, dark viscous liquid, 23.3 g

The yield of crude bis(p-chlorophenyl)dichlorosilane based on silicon tetrachloride was 40%. Part of Fraction 2 was recrystallized to yield white crystals, mp 59-63°C. Chvalovsky and Bazant[12] reported 71.2°C as the melting point. On standing for several days in a desiccator, the crude product turned dark blue. The blue material was distilled, and three fractions were obtained. The first fraction, 6 g, boiled from 348-351°C at atmospheric pressure and contained a few crystals; the second fraction, 25.3 g, boiled at 229-234°C and had a melting point of 57-61°C; the residue was a black viscous liquid, 5.7 g, which did not distil at 300°C at 34 mm. Three recrystallizations of the second fraction from Skellysolve "B" yielded 23 g of product melting at 59-62°C. Repeated recrystallizations did not improve the melting point.

Bis(p-chlorophenyl)dichlorosilane, 10 g (0.031 mole), and benzene, 100 ml, were placed in a 200-ml, 3-neck flask fitted with a reflux condenser, thermometer, gas-inlet tube, and magnetic stirrer. The system was flushed with dry nitrogen; and dry ammonia, distilled from liquid ammonia dried over sodium, was passed over the surface of the stirred solution containing the dichlorosilane for 3-5 minutes. Stirring was continued while the solution was held at 70-75°C for 30 minutes. This method of periodic addition of ammonia was intended to assist in the formation of silazane rings. The addition of ammonia was repeated each 30 minutes for 7 hours. At the end of this time, the rate of absorption of ammonia had dropped to zero. The solution stood overnight, and then it was stirred at 70-75°C for 1.5 hour while a positive pressure of ammonia was maintained. The solution was refluxed for 3 hours, cooled, and filtered. The ammonium chloride obtained was 3.2 g (theoretical, 3.3 g). The benzene was removed by distillation through a 1.2 x 30-cm packed fractionating column. The final pot temperature was 150°C at 1.5 mm pressure. None of the product distilled. The residue, 6.6 g, solidified on cooling to a cloudy tan resin that sintered at 64°C. The yield was 80% of the theoretical amount for a cyclic silazane.

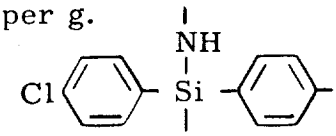
Attempts to crystallize the product were unsuccessful. Elemental analyses and other physical data indicated that the cyclic trisilazane was obtained, but impurities apparently prevented crystallization. The analytical and physical data are summarized in Table VII in the column headed "Second product."

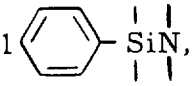
Table VII. Analytical and Physical Data on Bis(p-Chlorophenyl)Silazane

| Elemental composition | First product | Second product | Condensation polymer[a] | Theoretical A | Theoretical B |
|---|---|---|---|---|---|
| Carbon, % | 54.02 | 51.74 | 48.32 | 54.14 | 46.90 |
| Hydrogen, % | 3.70 | 3.95 | 3.33 | 3.41 | 2.62 |
| Chlorine, % | 25.80 | 25.00 | 22.50 | 26.64 | 23.08 |
| Nitrogen, % | 5.01 | 5.32 | 6.55 | 5.26 | 9.12 |
| Silicon, % | 9.10 | 9.20 | 15.10 | 10.55 | 18.28 |
| Total | 97.63 | 95.21 | 95.80 | 100.00 | 100.00 |
| Neutral equivalent | 295 | 277 | | 266.2 | |
| Molecular weight (cryoscopic in cyclohexane) | | 760 | | 798.6 (trimer) | |
| Melting range, capillary | | 36-91°C | | | |
| Thermal stability, ml gas per g produced at 450°C for 1.5 hr[b] | | 4.1 | 0 | | |

[a] Formed by heating the second product until it solidified at 480-500°C.

[b] Method described in the summary report Contract DA-01-009-506-ORD-829 of February 20, 1962, pages 9-11; hexaphenylcyclotrisilazane, 0.4 ml per g.

A  , $C_{12}H_9Cl_2NSi$

B  , $C_6H_4ClNSi$

The reaction just described was the second of three. The three reactions differed only in the rate of addition of ammonia and the temperature. The first reaction was run in the manner that was normally used to make hexaphenylcyclotrisilazane. The ammonia was added as rapidly as it was absorbed, and the temperature was allowed to rise to 65°C. Ammonia absorption was complete in 2 hours, and the reaction mixture was refluxed for 3 hours. The yield was 90% of theoretical, and the product was similar in appearance to the second. The analytical data on this product are in Table VII in the column headed "First product." The third reaction was run in the same manner as the second, except that the final distillation temperature was kept down to 55°C at 180 mm pressure, and the benzene was not completely removed. The semi-liquid product was stored at 0°C and scratched periodically with a glass rod in an effort to induce crystallization, but it did not crystallize.

The condensation polymerization of the silazane with p-chlorophenyl groups is described below in Section V. For the sake of comparison, the elemental composition of the condensation polymer is in Table VII. Data on hydrolytic stability are in Table IV.

b. Silazane with dichlorovinyl side chains

A silazane with dichlorovinyl side chains was desired to determine the effect of chlorine substitution in an aliphatic group on hydrolytic stability and inflammability. The plan was to make a vinyl silazane and then add chlorine to it, but the product was not obtained in sufficiently pure form for deductions to be made about the effect of structure on properties.

The synthesis of 2,4,6-trimethyl-2,4,6-trivinylcyclotrisilazane was attempted by the method that is used for making hexaphenylcyclotrisilazane and hexamethylcyclotrisilazane. In a 500 ml, 3-neck flask fitted with a stirrer, reflux condenser, gas-inlet tube, and thermometer were placed 70.55 g (0.5 mole) of methylvinyldichlorosilane and 250 ml of benzene. Ammonia, which had been dried over sodium, was passed in slowly while the reaction was being stirred for a period of 5 hours. The temperature rose to 70°C, and the solution was stirred under a positive pressure of ammonia for 2 hours after all evidence of reaction had ceased.

After standing over the week end, the clear supernatant solution reacted positively to the Beilstein Test for halogens, and so ammonia was passed in for 1 hour. The temperature rose to 45°C. After being refluxed for 3 hours the solution was filtered, and the Beilstein Test of the filtrate was negative. The ammonium chloride obtained was removed by distillation and the following fractions were obtained:

1. Bp 91°C at 6 mm pressure, 12.8 g, clear liquid
2. Bp 82°C at 2 mm pressure, 4.6 g, clear liquid
3. Residue, pot temperature 200°C at 1.5 mm pressure, 13.6 g, brown grease

By analogy to the boiling point of hexamethylcyclotrisilazane (75°C at 15 mm), Fraction 1 was believed to be the desired product. The neutral equivalent after hydrolysis was 92, theoretical 85.2. The molecular weight as determined cryoscopically in cyclohexane was 240, theoretical 255.5.

Fraction 2 was chlorinated by direct addition of chlorine in carbon tetrachloride solution. In a 100-ml, 3-neck flask fitted with a dry-ice reflux condenser, thermometer, magnetic stirrer, and gas inlet tube were placed 25 ml of carbon tetrachloride and 4.1 g (0.016 moles) of Fraction 1, which was believed to be 2,4,6-trimethyl-2,4,6-trivinylcyclotrisilazane. The reaction vessel and its contents were weighed. Chlorine was passed for 10 minutes over the surface of the solution while it was being stirred. The reaction vessel and its contents had gained approximately a third of the theoretical quantity of chlorine which was 3.4 g (0.048 mole). The reaction mixture had become slightly cloudy. A second 10-minute addition of chlorine added approximately another third of the desired chlorine, but a third 10-minute addition went too far and increased the total chlorine addition to 4.3 g (0.061 moles). Nitrogen was bubbled through the solution for 30 minutes, and the product was held at 2°C over the week end. No change was evident. Centrifugation did not remove the cloudiness, and so most of the carbon tetrachloride was removed in a stream of nitrogen while the product was heated in a

water bath at about 75°C. Benzene, 40 ml, was added, and then centrifugation clarified the solution. The product could not be distilled when the pot temperature was 150°C at 1.5 mm pressure. The undistilled product was a red-brown viscous liquid. It weighed 6.3 g, 84% of the theoretical yield. The analytical composition and molecular weight are in Table VIII. When the product was dissolved in alcohol and water was added, the solution became acidic. Consequently, the compound did not behave in the usual manner of silazanes.

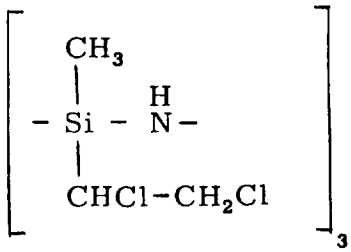
c. Silazane with trifluoromethylphenyl side chains

The synthesis of hexakis(p-trifluoromethylphenyl)cyclotrisilazane was attempted by the method that was used for making hexaphenylcyclotrisilazane. The required silicon halide was made from p-trifluoromethylphenylmagnesium bromide and silicon tetrachloride.

In a 500-ml, 3-neck flask fitted with a stirrer, reflux condenser, and dropping funnel, were placed 5.54 g (0.228 mole) of magnesium turnings and 50 ml of ether. The reaction was started with a few drops of methyl iodide. A solution of 50 g (0.222 mole) of p-trifluoromethylphenylbromobenzene in 125 ml of ether was added dropwise with stirring in the usual manner for a Grignard Reaction. The reaction mixture was refluxed for 1 hour. The product was dark brown in color, and it was used in the next reaction without further treatment.

Table VIII. Elemental Composition and Molecular Weight of the Chlorovinyl Silazane

| | Found | Theoretical[a] |
|---|---|---|
| Elemental analysis, % | | |
| Carbon | 21.12 | 23.08 |
| Hydrogen | 4.43 | 4.52 |
| Chlorine | 51.10 | 45.43 |
| Nitrogen | 6.70 | 8.97 |
| Silicon | 15.40 | 18.00 |
| Total | 98.75 | 100.00 |
| Molecular weight (in cyclohexane) | 520 | 468.3 |



$C_3H_7Cl_2NSi$, cyclic trimer

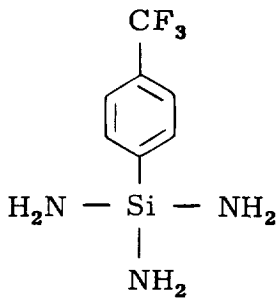
In a 500-ml, 3-neck flask fitted with a reflux condenser, stirrer, and dropping funnel were placed 100 ml of ether and 15.8 g (0.093 mole) of silicon tetrachloride. The Grignard Reagent made as described above was added slowly with stirring over a period of 45 minutes while the reaction mixture was kept cool with an ice bath. No refluxing was evident. The mixture was then heated and refluxed for 1 hour. The magnesium salt was filtered off, and it weighed 28.3 g (theoretical, 31.0 g). The filtered solution was dark brown. Crystals formed in the solution as it stood over the week end. These weighed 6.1 g, and as a liquid product was expected, they were discarded. The product was distilled, and the following fractions were obtained:

1. Bp 98-131.5°C at 1.5 mm, 13.1 g

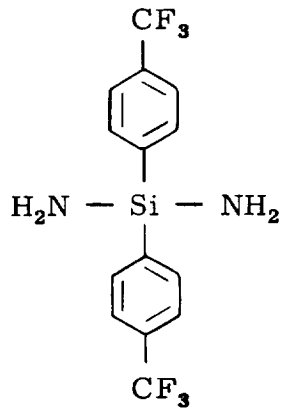
2. Residue, black tar, 18.3 g

Kohl[13] reported the boiling point of bis(p-trifluoromethylphenyl)-dichlorosilane to be 109.5-110°C at 3 mm pressure. The neutral equivalent of Fraction 1 after hydrolysis was 227.9 (theoretical, 194.1).

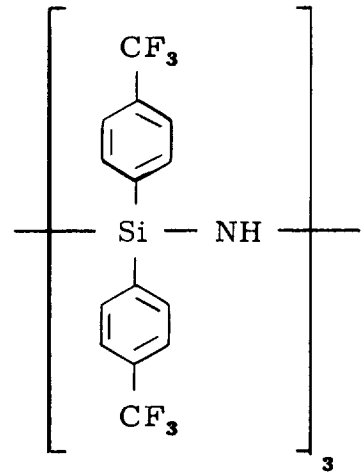
The distilled dichlorosilane, Fraction 1 above, was treated with ammonia in an effort to form the cyclotrisilazane. Fraction 1, 4.8 g (0.0123 mole), was dissolved in 50 ml of benzene, and dry ammonia was passed over the stirred solution for 30 minutes. The solution was refluxed for 3 hours, and the solution was then stirred for 2 additional hours at room temperature while in an atmosphere of ammonia. After 1 hour of refluxing, the mixture stood overnight. The insoluble matter, 1.2 g (theoretical, 1.3 g) was removed by filtration. The benzene was removed by distillation, and the temperature was kept low by reducing the pressure. The final conditions were 25°C at 1.5 mm pressure. The product was a light-tan, cloudy liquid with a neutral equivalent of 109 (theoretical, 333.3). The product was heated at 180°C at 2.5 mm in an effort to condense end-amino groups if any were present, and the neutral equivalent was raised to 125. Evidently the desired compound was not obtained. Three possible formulas with their theoretical neutral equivalents are these:



N.E. - 73



N.E. - 175



N.E. - 333

d. Preparation of bis(methylamino)dimethylsilane

Bis(methylamino)dimethylsilane was prepared by the method of Larsson and Smith.[14] In a 1-liter, 3-neck flask cooled to -15°C and fitted with a stirrer, thermometer, dropping funnel, and reflux condenser were placed 62.2 g (2.0 moles) of methylamine and 400 ml of diethyl ether. The system was swept with dry nitrogen and 54.2 g of dimethyldichlorosilane (0.42 mole) in 60 ml of ether was added with stirring over a period of 1 hour. The temperature was held between -15°C and -20°C by means of a dry ice-acetone bath. After addition of the chlorosilane was complete, the mixture was allowed to warm to room temperature, and then it was refluxed for 45 minutes. When cool, the reaction product was filtered with a Buchner funnel, and the amine hydrochloride was washed on the filter with ether. The filtrates were combined; and the ether was removed by distillation, finally at reduced pressure. The bis(methylamino)dimethylsilane was distilled at 66-67°C at 165 mm pressure. It amounted to 7.3 g (0.062 mole, 15% of theory), and its neutral equivalent was 62.3 (theory, 59.1). Because of the volatility of the compound and its sensitivity to hydrolysis, it was necessary to use a special technique to obtain an accurate value for neutral equivalent. The sample was weighed in a small glass-stoppered vial that was then opened under alcohol in a beaker. An excess of tenth-normal hydrochloric acid was pipetted in quickly, and the excess acid was titrated.

e. Preparation of bis(methylamino)diphenylsilane

Bis(methylamino)diphenylsilane was prepared by the method of Larsson and Bjellerup.[15] Dry ether, 250 ml, was placed in a 1-liter, 3-neck flask fitted with a stirrer, reflux condenser, dropping funnel, and thermometer. The ether was cooled to -15°C, and the flask was swept with dry nitrogen. Methylamine, 62.2 g (2.0 moles), that had been dried by shaking with sodium was added to the ether. Diphenyldichlorosilane, 101.2 g (0.4 mole) was added dropwise with stirring over a period of 1.5 hours, while the reaction temperature was kept at -15°C. After the addition was complete, the reaction mixture was allowed to warm to room temperature while stirring was continued. It was refluxed for 0.75 hour and then filtered. Distillation of the filtrate yielded 78 g, b.p. 144-158°C at 2.5 mm. The distillate was redistilled, and a fraction, 24.0 g, m.p. 18°C, b.p. 154-156°C at 3 mm, was obtained. This agrees with the boiling point observed by Larsson and Bjellerup.[15] The product, bis(methylamino)diphenylsilane, had a neutral equivalent of 126.0 (theory, 121.2).

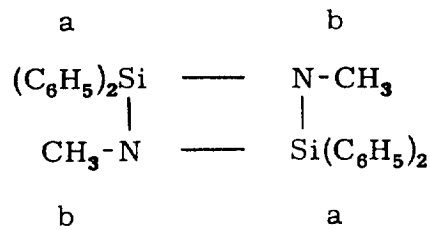
f. Preparation of N,N'-dimethyltetraphenylcyclodisilazane

Bis(methylamino)diphenylsilane was condensed by heating to form N,N'-dimethyltetraphenylcyclodisilazane with the elimination of methylamine. Bis(methylamino)diphenylsilane, 14.7 g (0.06 mole), was refluxed at 315-320°C for 2 hours. Methylamine was evolved slowly. After heating was discontinued, crystals began to form in the melt when the temperature reached 80°C. The crystals, 0.4 g, melted at 208-209°C after two recrystallizations from hexane. The yield was 3% of theoretical. The elemental composition was:

Found: C, 73.30%; H, 6.71%; N, 6.35%; Si, 13.5%

Calculated for $(C_6H_5)_2SiNCH_3$: C, 73.88%; H, 6.20%; N, 6.63%; Si, 13.29%

The molecular weight, as determined by vapor osmometry, was 468 (average of 461 and 474); (calculated for $[(C_6H_5)_2SiNCH_3]_2$, 422.7). Infrared spectra were consistent with that assumed formula. The nuclear magnetic resonance spectrum of a 2% solution in carbon tetrachloride indicated that the protons were in the numerical ratio, a : b = 20 : 5.7, which is consistent with the same formula:




N, N'-dimethyltetraphenylcyclodisilazane

a : b = 20 : 6

Additional quantities were desired for studies of hydrolytic stability, and so a larger preparation of N, N'-dimethyltetraphenylcyclodisilazane was attempted by heating an impure fraction that was obtained from the reaction of diphenyldichlorosilane with methylamine. The main product of that reaction, bis(methylamino)diphenylsilane (preceding preparation, Section e), boiled at 154-156°C at 3 mm. The fraction used for this preparation boiled at 147-154°C at 3 mm. This material, 20.0 g (0.082 mole, assuming $(C_6H_5)_2Si(NHCH_3)_2$ to be the formula) was refluxed at 310-315°C for 8 hours. On cooling, the mass crystallized. It was recrystallized from Skellysolve B and benzene to yield 4.9 g, m.p. 209-220°C. This was the material used for the hydrolytic stability determination (Figure 15), and was probably a mixture of N, N'-dimethyltetraphenylcyclodisilazane and N, N', N''-trimethylhexaphenylcyclotrisilazane.

g. Preparation of dianilinodiphenylsilane

Dianilinodiphenylsilane was prepared by the method of Anderson.[16] In a 300-ml, 3-neck flask fitted with a stirrer, thermometer, reflux condenser, and dropping funnel were placed 50 g (0.54 mole) of aniline and 40 ml of benzene. The system was swept with dry nitrogen, and 20 g (0.079 mole) of diphenyldichlorosilane in 25 ml of benzene was added dropwise with stirring. The temperature rose to 43°C. The mixture was refluxed for 30 minutes, allowed to stand overnight, and filtered. The precipitate was stirred with 125 ml of boiling benzene, and the hydrochloride was removed by filtration. The combined filtrates were evaporated until the volume was 90 ml, and an equal volume of 30-60°C petroleum ether was added. The solution was cooled to 0°C; and, after 2 hours, the white crystals that had formed were filtered off and washed with cold petroleum ether. Traces of solvent were removed in a vacuum desiccator, and the product weighed 16.0 g (0.44 mole, 55% of theory). The melting point was 154-157°C (Anderson[16] reported 153°C, decomposition 413°C). The neutral equivalent was not determined, because the compound was not soluble in alcohol or dilute acid. The carbon-hydrogen content was:

Found: C, 76.74%; H, 5.74%

Theory: C, 78.65%; H, 6.05%

h. Preparation of dianilinodimethylsilane and N, N', N''-triphenylhexamethylcyclotrisilazane

The method of Larsson and Smith[14] was used to prepare dianilinodimethylsilane and N, N', N''-triphenylhexamethylcyclotrisilazane simultaneously. In a 500-ml, 3-neck flask fitted with a thermometer, reflux condenser, stirrer, and dropping funnel were placed 100 ml of carbon tetrachloride and 51.6 g (0.4 mole) of dimethyldichlorosilane. Aniline, 111.7 g (1.2 moles), was added dropwise with stirring over a period of 30 minutes while the temperature rose to 60°C. The mixture was refluxed for 30 minutes, cooled, and filtered. The aniline hydrochloride was washed on the filter with three 25-ml portions of carbon tetrachloride. The product, 28 g of yellow crystals, was distilled at 190-207°C at 11 mm. The

crystals were stirred with four 25-ml portions of petroleum ether (30-60°C) to extract the readily soluble material. The residue was then washed with several small portions of petroleum ether until its melting point became constant at about 250°C (Larsson, 249-250°C). These crystals amounted to 0.8 g of crude, N,N',N''-triphenylhexamethylcyclotrisilazane.

The main body of the product (the petroleum ether-soluble portion) was recrystallized from petroleum ether to yield 10 g of dianilinodimethylsilane in the form of shiny, colorless prisms that melted at 56°C (Larsson,[14] 56°C).

i. Preparation of 1,3-bis(methylamino)pentamethyldisilazane

1,3-Bis(methylamino)pentamethyldisilazane was prepared by the method of Larsson and Smith[14] as follows: In a 5-liter, 3-neck flask fitted with a stirrer, thermometer, reflux condenser, and gas inlet tube were placed 250 g (1.93 mole) of dimethyldichlorosilane and 2.5 liters of benzene. Dry methylamine was passed into the system by allowing it to boil from a flask of liquid methylamine that contained sodium. The reaction mixture was stirred under an atmosphere of methylamine for 4.5 hours. The flask was cooled to prevent the temperature from rising above 30°C. After the reaction mixture stood overnight, the Beilstein Test for halogens in the supernatant liquid was negative. The mixture was refluxed for 3 hours and filtered. The amine hydrochloride was washed twice with 75-ml portions of benzene, and the combined benzene solutions were distilled. The first fraction of the product, 11.1 g, distilled at 29-93°C at 29 mm. The main fraction, 70.4 g, distilled at 93°C at 29 mm (Larsson,[14] 75-76°C at 10 mm). The undistilled portion was 30.7 g. The main fraction was bis(methylamino)pentamethyldisilazane, neutral equivalent, 75.3 g (theory, 68.5). The elemental composition was:

Found: C, 41.08; H, 10.29; N, 19.21; Si, 28.1

Theory: C, 40.92; H, 11.29; N, 20.45; Si, 27.34

The rate of hydrolysis was determined by the standard method, and it was found that the first 75% hydrolyzed very quickly, and then the rate fell to almost zero. The data were verified by titrating a sample of the carbon tetrachloride layer. It was concluded that this unexpected termination of hydrolysis was caused by the presence of a fairly large amount of a cyclic compound in the bis(methylamino)pentamethyldisilazane. Nonamethylcyclotrisilazane is known to hydrolyze very slowly; it boils at 120°C at 22 mm, and it could account for the departure from theory in the elemental analysis. Accordingly, the material was redistilled to purify it. Crude bis(methylamino)pentamethyldisilazane, 48.2 g, was distilled in a 1.2 x 30-cm fractionating column packed with small 6 x 6 mm, perforated stainless-steel plates bent in the form of C's. The center cut, 23.4 g, boiled at 61.0 – 61.5°C at 7 mm pressure. The neutral equivalent was 70.4 (theory, 68.5). The purified compound behaved almost normally when its hydrolysis rate was determined. The hydrolysis rate became very low when 94% had hydrolyzed. Evidently an impurity of higher stability was removed by the fractional distillation.

j. Preparation of isopropyltris(isopropylamino)silane

Isopropyltris(isopropylamino)silane was prepared as follows:

$$\text{i-}C_3H_7Br \xrightarrow{Mg} \text{i-}C_3H_6MgBr \xrightarrow{SiCl_4} \text{i-}C_3H_7SiCl_3$$

$$\text{i-}C_3H_7SiCl_3 \xrightarrow{\text{i-}C_3H_7NH_2} (\text{i-}C_3H_7NH)_3\,Si\,(\text{i-}C_3H_7)$$

Approximately 1 mole of isopropylmagnesium bromide was prepared by the reaction of 1.0 mole of isopropyl bromide with 1.0 mole of magnesium. The product in 250 ml of ether was added dropwise with stirring to 339.8 g (2.0 moles) of silicon tetrachloride in 700 ml of dry benzene over a period of 1.5 hours. The mixture was refluxed for 4 hours, and then the solvent and excess silicon tetrachloride were removed by distillation at atmospheric pressure. The product was 106 g of clear light yellow liquid that was assumed to be trichloroisopropyl silane. Half of the product, 53 g (0.30 mole), of isopropyltrichlorosilane, was added dropwise with stirring to 160.0 g (2.77 moles) of isopropylamine in 500 ml of dry ether while the temperature was held between -5°C and -10°C. The mixture was refluxed for 2.5 hours, cooled, and filtered. The filtrate was distilled to yield the following fractions:

I, 4.0 g, b.p. 90-95°C at 9 mm

II, 44.0 g, b.p. 95-96°C at 9 mm

III, 2.3 g, b.p. 55-82°C at 2 mm

IV, 9.0 g, undistilled at 260°C at 2 mm

The neutral equivalent of Fraction II was 87, whereas the theoretical value for isopropyltris(isopropylamino)silane is 81.8 and for diisopropylbis(isopropylamino)silane is 115.2. The main product was evidently isopropyltris(isopropylamino)silane, 0.18 mole, which was obtained in 18% yield from the isopropyl bromide.

k. Attempt to prepare diisopropylbis(isopropylamino)silane

The preparation of diisopropylbis(isopropylamino)silane was attempted by isopropylation of isopropyltrichlorosilane followed by treatment of the product with isopropylamine. However, a mixture was obtained as the product; and it was not successfully separated into identifiable components.

The isopropyl Grignard Reagent was prepared by treating 7.2 g (0.3 mole) of magnesium with 36.9 g (0.3 mole) of isopropyl bromide in ether. The ether solution of isopropylmagnesium bromide was added dropwise with stirring to 52.4 g (0.3 mole) of isopropyltrichlorosilane (preceding preparation) in 150 ml of benzene. The reaction was refluxed for 5 hours, but no insoluble metal halide appeared, and the Gilman Test for organometallic compounds was positive. Accordingly, the ether was distilled off; and the remaining material, with 100 ml of additional benzene, was refluxed 4 hours at 78°C. In this period, an insoluble salt formed; and the Gilman Test became negative. The reaction mixture was centrifuged, and the resulting clear amber solution was added to 160.0 g (2.77 moles) of isopropylamine in 250 ml of ether while the reaction mixture was held at -5 to -10°C. The mixture was then refluxed for 2 hours, cooled, and filtered. The filtrate was distilled but no pure fraction was obtained. The following fractions were collected:

I, 8.4 g, b.p. 75-80°C at 8.5 mm; neutral equivalent, 213

II, 4.7 g, b.p. 80-87°C at 8.5 mm; neutral equivalent, 136

III, 17.5 g, b.p. 87-90°C at 8.5 mm; neutral equivalent, 92

The theoretical neutral equivalents of the expected compounds were:

triisopropylisopropylaminosilane, 215

diisopropylbis(isopropylamino)silane, 115

isopropyltris(isopropylamino)silane, 82

The neutral equivalents of the fractions suggest that all three compounds were obtained. However, the boiling points were not sufficiently different to permit the conclusion.

1. Preparation of compounds not described elsewhere in this report

The majority of materials discussed in this section on hydrolytic stability were prepared by methods described in this section or elsewhere in this report. The following materials were prepared as described in preceding annual reports: hexamethylcyclotrisilazane,[17] 2,4,6-trimethyl-2.4,6-triphenylcyclotrisilazane,[18] 2,2,4,4,6,6,8,8-octamethyl-1,5-dioxa-3,7-diazacyclooctasilane,[19] nonamethylcyclotrisilazane,[20] and ethylenediamine silazane.[7]

## V. THERMAL STABILITY OF SILICON-NITROGEN COMPOUNDS

### A. Discussion

The thermal stability of silicon-nitrogen compounds has been studied by thermogravimetric analysis and by measuring the amount of permanent gas produced when samples were heated for 1.5 hours at 450°C.

Thermogravimetric analyses showed that some silicon-nitrogen compounds were essentially stable at temperatures approaching 500°C. The most stable silicon-nitrogen compounds were those obtained by thermal condensation, which apparently proceeds by this equation, as discussed in detail in Section VII:

$$n\,(\text{-RR'SiNH-})_x \xrightarrow{\text{heat}} n\,\text{RH or R'H} + (\text{-RSiN-})_{nx} \text{ or } (\text{-R'SiN-})_{nx}$$

The non-polymeric silicon-nitrogen compounds were not amenable to thermogravimetric analysis because of their volatility and their tendency to undergo condensation polymerization with the formation of volatile by-products. The stabilities of the non-polymeric compounds were better studied by determining the extent to which they decomposed to form permanent gases when heated.

Several silicon-nitrogen polymers were prepared for thermogravimetric analysis by heating the following silicon-nitrogen compounds at temperatures above 400°C until they solidified and became infusible:

hexaphenylcyclotrisilazane

methylphenyl silazanes (mixed)

reaction product of methylamine and silicon tetrachloride

bis(p-chlorophenyl) silazane

In addition, two silylhydrazine polymers were prepared and analyzed thermogravimetrically without previously being subjected to condensation polymerization at temperatures above 400°C. They were relatively unstable. The rate of temperature increase was 6°C per minute, and the atmosphere was nitrogen. The data are plotted in Figures 16 and 17. Of the four relatively stable polymers, the one made from hexaphenylcyclotrisilazane was the most stable. It was essentially unchanged by temperatures up to 500°C, and it did not lose weight rapidly until the temperature reached 550°C. The weight leveled off at approximately 75% of its initial value and did not change appreciably on further heating up to 850°C. The residue from heating to 850°C in nitrogen contained carbon, hydrogen, silicon, and nitrogen.

The infusible polymer made from the mixture of methylphenyl silazanes began to lose weight at about 400°C. Its weight became almost constant at about 75% of the initial value when the temperature had reached 700-775°C. The infusible polymer made from silicon tetrachloride and methylamine began to lose weight at 250°C, and it became essentially stable at about 70% of the initial weight at about 600°C. The residue from this polymer was tan, whereas the others were black after being heated to 850°C.

The infusible polymer made by heating the bis(p-chlorophenyl) silazane until it solidified was a dark-brown, friable solid. Thermogravimetric analysis showed it to be less stable in the range of 250-500°C than the condensation polymer made from hexaphenylcyclotrisilazane. However, it became fairly stable in the 650-850°C range at about 63% of its original weight.

Previous reports have contained data on the amount of gas formed while heating silazanes at 450°C.[21,22] Nonamethylcyclotrisilazane was among the most stable silicon-nitrogen compounds previously reported, and it produced appreciably less gas than a sample of octamethylcyclotetrasiloxane. In the past year, several additional compounds were observed, including octaphenylcyclotetrasiloxane, which appeared to be somewhat more stable than octamethylcyclotetrasiloxane. The data in Table IX show that some of the silazanes equal or exceed in stability the siloxanes that were compared in this project. Silylation of hexaphenylcyclotrisilazane was not beneficial to thermal stability, possibly because of the instability of the methyl groups. However, hexamethylcyclotrisilazane produced less gas than N-trimethylsilylhexaphenylcyclotrisilazane, even though it had a higher proportion of methyl groups.

Neither the diphenylsilylhydrazine polymer nor the bis(p-chlorophenyl) silazane ranked high in stability. However, the p-chlorophenyl compound was exceptionally stable after it had undergone condensation polymerization.

Table IX. Thermal Stabilities as Indicated by Gas Formed During Pyrolysis[a]

| Compound | Gas produced, ml per g of sample |
|---|---|
| Nonamethylcyclotrisilazane | 0.03 |
| Octaphenylcycltetrasiloxane | 0.05 |
| Hexaphenylcyclotrisilazane | 0.42 |
| Hexamethylcyclotrisilazane | 0.58[b] |
| Octamethylcyclotetrasiloxane | 0.82[b] |
| N-trimethylsilylhexaphenylcyclotrisilazane | 3.2 |
| Bis(p-chlorophenyl) silazane (not a single compound) | |
| As initially prepared | 4.1 |
| After condensation polymerization | 0 |
| Diphenylsilylhydrazine polymer | 15.2 |

[a] Approximately 0.1 g of sample in an evacuated and sealed glass tube heated at 450°C for 1.5 hour.

[b] Data taken from Annual Summary Report, Contract DA-01-009-506-ORD-829, U. S. Army Ballistic Missile Agency, February 20, 1961, page 11.

## B. Experimental Details

### 1. Thermogravimetric apparatus and procedure

The thermogravimetric analyses of the silicon-nitrogen polymers were performed in a vertical tube in which the sample was in a platinum pan suspended from the arm of an analytical balance. The tube was made of Vycor, a high-silica glass, and it measured 2.6 x 30 cm in the heated area. The tube was heated by a Hoskins Tube Furnace.

Nitrogen was introduced at the bottom of the tube and passed slowly upward except while weights were being measured. The thermocouple entered the bottom of the tube, and the junction was placed just below the platinum pan. The pan was suspended from the balance by a platinum chain that passed through a small hole in the cap of the furnace tube. The cap was joined to the furnace tube by a 29/42 standard-taper joint.

The procedure was as follows: The sample, approximately 0.5 g, was placed in the platinum pan and suspended in the furnace tube. The flow of nitrogen was started, and sample weight was measured every 5 minutes as the temperature was increased at the rate of 6°C per minute. Heat input to the furnace was manually controlled by a variable transformer with the setting increased at a predetermined standardized rate. The results are given in Figures 16 and 17 and Tables X and XI.

### 2. Comparison of thermal stabilities by gas production during pyrolysis

The method of comparing thermal stabilities by measuring the amount of gas produced during pyrolysis was devised after reading the report of Dale and his coworkers,[23] who studied thermal decomposition as indicated by increases in vapor pressure at elevated temperatures. They concluded that hydrogen was the principal gaseous decomposition product from most compounds that contained appreciable amounts of carbon-hydrogen bonds. Consequently, we adopted the relatively simple method of measuring the gas that remained after the sample had been cooled to room temperature. A small sample, approximately 0.1 g, was sealed in a 4.5-ml evacuated, glass tube and heated at 450°C for 1.5 hours. After cooling, the amount of gas was measured by opening the tube under water and transferring the gas to a graduated conical tube. The data are in Table IX.

Table X. Thermogrametric Analyses of Silicon-Nitrogen Polymers in Nitrogen (Temperature increased 6°C per minute)

| Hexaphenylcyclotrisilazane | | Methylphenyl silazane | | Silicon tetrachloride-methylamine | | Bis(p-chlorophenyl) silazane | |
|---|---|---|---|---|---|---|---|
| Temp., °C | Amount remaining, % | Temp., °C | Amount remaining, % | Temp., °C | Amount remaining, % | Temp., °C | Amount remaining % |
| 200 | 100 | 200 | 100 | 200 | 100 | 200 | 100 |
| 245 | 99.9 | 221 | 99.9 | 231 | 99.8 | 215 | 99.4 |
| 290 | 99.6 | 247 | 99.9 | 264 | 99.4 | 241 | 98.5 |
| 331 | 99.4 | 272 | 99.7 | 302 | 97.3 | 269 | 98.0 |
| 366 | 99.3 | 305 | 99.6 | 342 | 92.7 | 302 | 97.7 |
| 404 | 98.9 | 342 | 99.1 | 376 | 88.5 | 329 | 97.0 |
| 440 | 98.4 | 379 | 98.4 | 418 | 82.5 | 352 | 96.0 |
| 480 | 97.8 | 411 | 97.2 | 461 | 76.7 | 394 | 89.8 |
| 519 | 96.4 | 447 | 95.6 | 504 | 73.6 | 435 | 89.0 |
| 556 | 93.6 | 487 | 93.5 | 546 | 72.2 | 476 | 82.0 |
| 600 | 88.9 | 525 | 90.0 | 593 | 71.4 | 511 | 77.2 |
| 641 | 82.8 | 569 | 85.1 | 636 | 70.9 | 571 | 71.1 |
| 682 | 78.5 | 613 | 81.7 | 675 | 70.9 | 599 | 68.2 |
| 720 | 76.5 | 659 | 79.8 | 718 | 70.6 | 644 | 66.6 |
| 761 | 75.5 | 716 | 78.5 | 757 | 70.6 | 687 | 64.9 |
| 805 | 74.8 | 739 | 77.6 | 802 | 70.1 | 715 | 64.0 |
| 843 | 74.6 | 776 | 76.9 | 847 | 69.6 | 765 | 63.4 |
| 850 | 74.5 | | | 850 | 69.5 | 823 | 62.2 |
| | | | | | | 850 | 61.2 |

Table XI. Thermogravimetric Analyses of Silylhydrazines in Nitrogen (Temperature increased 6°C per minute)

| Diphenylsilylhydrazine | | Methylsilylhydrazine (di-tri) | |
|---|---|---|---|
| °C | Amount remaining, % | °C | Amount remaining, % |
| 200 | 100 | 200 | 100 |
| 220 | 99.9 | 220 | 98.9 |
| 244 | 99.8 | 236 | 98.0 |
| 268 | 99.7 | 257 | 97.3 |
| 295 | 94.1 | 280 | 96.3 |
| 326 | 92.0 | 319 | 93.6 |
| 356 | 89.2 | 353 | 91.6 |
| 392 | 80.6 | 362 | 90.0 |
| 436 | 68.9 | 399 | 87.2 |
| 470 | 56.4 | 435 | 84.8 |
| 535 | 40.4 | 469 | 82.6 |
| 556 | 36.0 | 511 | 77.5 |
| 591 | 35.9 | 541 | 70.5 |
| 632 | 35.9 | 586 | 25.0 |
| 674 | 35.6 | 613 | 15.9 |
| 713 | 35.6 | 670 | 15.5 |
| 748 | 35.6 | 720 | 15.2 |
| | | 755 | 14.2 |
| | | 801 | 13.7 |

3. Preparation and performance of the hexaphenylcyclotrisilazane polymer

The hexaphenylcyclotrisilazane polymer was prepared for thermogravimetric analysis by heating recrystallized hexaphenylcyclotrisilazane in a test tube that was loosely closed with aluminum foil. The condensation polymerization of hexaphenylcyclotrisilazane was initially described in the report of the first year's work.[24] The crystals melted, then boiled gently as the tube was heated over a gas flame. When the melt began to solidify, the tube was rotated rapidly in the flame to insure uniform heating. Heating was continued until there was no visible evidence of liquid in the tube or of further reaction. Previous work has shown that the melt solidifies in the temperature range of 525-560°C. The product was a pale-yellow, friable mass that was vitreous when viewed under a microscope.

This polymer was heated and weighed in nitrogen as described above until the temperature reached 845°C. The weight loss at that temperature was 25.4%. Analysis of the residue showed the following elemental composition:

| | |
|---|---|
| Carbon | 46.64% |
| Hydrogen | 2.28% |
| Nitrogen | 10.11% |
| Silicon | 22.80% |
| Remainder | 18.17% |

These results would correspond to the following atomic ratios with silicon as 1.0 :

| | |
|---|---|
| Carbon | 4.8 |
| Hydrogen | 2.8 |
| Nitrogen | 0.9 |
| Silicon | 1.0 |

Evidently the residue is not a simple inorganic material.

The above figure for the remainder—the amount that would normally be assigned to oxygen—is a matter of considerable concern. It is not likely that oxygen amounting to 18% could have been introduced inadvertently. Hence, we believe the analytical methods that were used were unsatisfactory for this refractory material.

4. Methylphenyl silazane polymer

The methylphenyl polymer was made by heating the mixture of methylphenyl silazanes[4] in the manner described for hexaphenylcyclotrisilazane. The results of the thermogravimetric analysis of this polymer are given in Table X and Figure 16.

5. Methylamine-silicon tetrachloride polymer

A polymer was made from the methylamine-silicon tetrachloride reaction product[25] by heating it in the manner described for hexaphenylcyclotrisilazane. Silicon tetrachloride was treated with methylamine, and a crystalline product, mp 116-121°C, which was shown to be a cyclic trisilazane, was isolated. This crystalline compound was polymerized by heating until it solidified to yield the polymer for the thermogravimetric analysis. The results of the analysis are given in Table X and Figure 16.

## 6. Bis(p-chlorophenyl) silazane polymer

The condensation polymerization of the bis(p-chlorophenyl) silazane (Section IV) was carried out in a test tube while air was excluded by introducing a gentle stream of nitrogen through a side arm. Hexaphenylcyclotrisilazane was similarly polymerized for comparison. The two silazanes condensed to infusible, foamed, brittle solids after being boiled for several minutes. However, the chloro compound became almost black before it solidified, whereas the hexaphenyl compound remained almost colorless. The chloro compound started to solidify at 480°C, whereas hexaphenylcyclotrisilazane started to solidify at 560°C.

The condensation polymer made from the bis(p-chlorophenyl) silazane had the elemental composition shown in Table VII; thermogravimetric data are in Table X and Figure 16. The polymer reached a fairly stable state at about 650°C at about 63% of its initial weight.

The bis(p-chlorophenyl) silazane was spread in a thin film on aluminum and cured by heating at 450°C for 15 minutes. The film was slightly darker than films made from hexaphenylcyclotrisilazane, but it had high thermal stability. It crazed but did not flake off even when the aluminum was melted over a flame.

## 7. Procurement of other materials

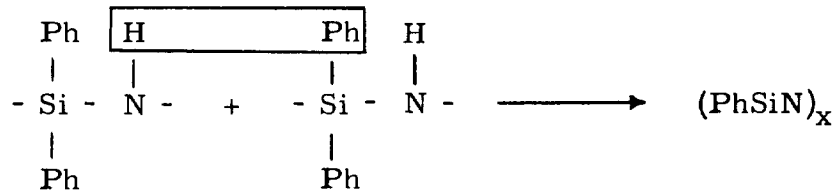
Octaphenylcyclotetrasiloxane was obtained from the General Engineering Laboratory of the General Electric Company. Nonamethylcyclotrisilazane was prepared by the method described in a preceding annual report.[20]

# VI. COATINGS FOR METALS

## A. Discussion

### 1. General considerations

Coatings on metals and ceramics can be made from many silazanes and silylamines by spreading them in thin films on the substrates and heating at temperatures that cause polymerization. The reaction that is believed to be primarily responsible for curing is the condensation polymerization that is represented as follows for hexaphenylcyclotrisilazane:




Other reactions, such as conversion of cyclic to linear structures, condensation of amine end groups, and replacement of nitrogen by oxygen may also be involved to some extent. However, study of the structures of coatings has not progressed far, because it is complicated by the inert and insoluble character of the cured polymers. The principal studies on the reactions involved in curing coatings have been on the polymerization of hexaphenylcyclotrisilazane (Section VII). The major coating studies have been with a by-product that was obtained in the synthesis of hexaphenylcyclotrisilazane from diphenyldichlorosilane and ammonia. Two other silazanes were also evaluated beyond screening trials.

It was standard practice in this project to try each new material as a coating for stainless steel or aluminum. A sample was spread on the metal and heated gently over a flame. If the compound was not volatile, it flowed over the surface as it melted; and then it condensed to a shiny, solid film as heating was continued. Materials that showed some promising feature, such as ease of curing, good stability, or good flexibility, were evaluated more thoroughly as described in this section. The results of similar evaluations of silicon-nitrogen compounds made earlier are described in the preceding annual reports,[26, 27] and results on new materials only are given here.

2. Coatings made with the hexaphenylcyclotrisilazane by-product

Coatings that were resistant to chemicals and high temperatures were produced from a by-product that was obtained in the preparation of hexaphenylcyclotrisilazane. The by-product was superior as a coating agent to partially polymerized hexaphenylcyclotrisilazane,[26] in that it could be applied in thicker layers, it was less brittle, and it had equal or greater thermal endurance after being cured at lower temperatures. The by-product had approximately the same elemental composition as hexaphenylcyclotrisilazane, and it was probably a linear silazane polymer. It probably also contained end-amino groups.

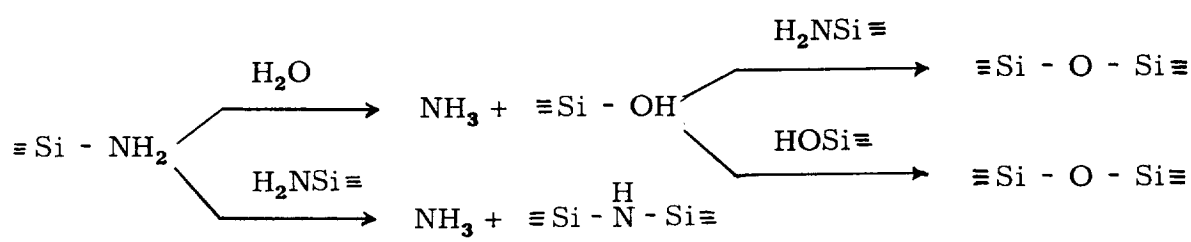
The hexaphenyl by-product could be applied to aluminum in coatings up to 1.25 mils thick, and these remained intact for an hour in air at 500°C. Coatings made from the hexaphenyl prepolymer could be no more than 0.3 mil thick or else they would crack on cooling. This relaxation of the thickness limitation made it much easier to apply a coherent coating to the substrate.

Coatings made from the by-product and cured 1 hour at 110°C withstood boiling water for an hour and protected the aluminum from 19% hydrochloric acid for several minutes. Complete curing was not accomplished in 1 hour at 110°C, and the coatings melted in the range of 200-300°C until after they had been exposed to 300°C for a few minutes.

When an aluminum panel that was partially coated with the hexaphenyl by-product was heated to 550°C for an hour, the uncoated aluminum became yellow-gray while the coated area remained shiny. Coated panels exposed to 550°C for longer periods began to discolor under the coating, and it was doubtful that the coating was protecting the aluminum from oxidation. Panels with 0.25-mil coatings were heated at 550°C for an hour, boiled in water for an hour, and then immersed in 19% hydrochloric acid until the reaction became violent and the uncoated areas became black. The coated areas remained shiny except for a few pinholes. Coatings heated at 550°C and higher for an hour did not tolerate an appreciable amount of flexing.

A sample of the hexaphenyl by-product was fractionated by treating it with diethyl ether which dissolved only part of it. An initial trial with the ether-soluble extract suggested that the extractable material was a better coating agent than the whole by-product. However, this subject has not been pursued further.

A possible explanation for the superiority of the hexaphenyl by-product as a raw material for coatings may lie in the reactivity of end-amino groups and in higher molecular weight. The silazane rings are not easily opened by heat, and hexaphenylcyclotrisilazane polymerizes by splitting out benzene only if it is heated in the vicinity of 450°C. In contrast, the end-amino groups are relatively reactive with themselves and with moisture. Hence, end-amino groups could serve as a route to polymerization by any or all of the following reactions which may occur well below 400°C:




3. <u>Coatings made with the hexaphenylcyclotrisilazane by-product and ethylenediamine silazane</u>

The flexibility of coatings made from the hexaphenylcyclotrisilazane by-product was improved by adding ethylenediamine silazane.[7] The coating formed from a mixture of 9 parts by weight of the hexaphenylcyclotrisilazane by-product and 1 part of ethylenediamine silazane on aluminum proved to be physically stable after the metal panel had been heated in air at 370°C (700°F) for 18 hours. A similar coating without the ethylenediamine silazane crazed and cracked when the coated metal specimen was bent. The ethylenediamine silazane apparently served as a plasticizer for the polysilazane film.

The coating that contained ethylenediamine silazane was also applied to mild steel, on which it proved to be less effective. The cured resin film peeled away from the metal when the metal was bent. The gray appearance of the surface of the stripped film that had been adjacent to the metal, was no doubt caused by a layer of iron oxide. Therefore, the failure of the coating probably resulted from oxidation of the metal rather than brittleness of the coating. In unbent areas, the coating afforded protection from hydrochloric acid.

4. Methyl hydrogen silazane

Coatings were made with the methyl hydrogen silazane,[8] because it was thought to be curable at a lower temperature than hexaphenylcyclotrisilazane and related materials. A series of experiments showed that the methyl hydrogen silazane could be applied to aluminum in a benzene solution and that the coating became solid on curing at temperatures ranging from room temperature to 150°C. The coatings were clear and colorless, but they adhered poorly to aluminum, and they had poor flexibility. When ethylenediamine silazane,[7] 10%, was added to the methyl hydrogen silazane, the resulting coatings could be cured at 120°C; they had better flexibility and adhesion; but they were attacked slowly by 19% hydrochloric acid. Other curing methods and other blends might be more successful. Additional work should be done with methyl hydrogen silazane to study blends with other silazanes and curing at higher temperatures in dry and oxygen-free atmospheres.

5. N-Methyl-Si-phenyl silazane

The by-product obtained in the preparation of N,N'-dimethyltetraphenylcyclodisilazane was made into a coating that appeared to have greater thermal stability than any other we have made. The by-product is a liquid, and its preparation from bis(methylamino)diphenylsilazane is described in Section IV-B-2-f. It was spread on an aluminum panel that was then heated slowly over a gas burner until the panel began to soften. Evidently the temperature was close to 600°C. As cracks appeared in the aluminum, the film cracked also. However, the coating remained largely undamaged. After being cooled rapidly in a stream of water, the badly warped panel was placed in 19% hydrochloric acid for about 10 minutes until the uncoated areas were deeply etched. The coated area remained shiny, except where the aluminum itself had cracked. The panel was then bent to a radius of curvature of about 2 mm, and the coating remained visibly undamaged.

Other experiments indicated that this N-methyl-Si-phenyl coating required a higher temperature for curing than did the coatings made from the hexaphenyl by-product. However, this indication has not been fully investigated or confirmed.

## B. Experimental Details

### 1. Preparation of the hexaphenylcyclotrisilazane by-product

Hexaphenylcyclotrisilazane was prepared by treating diphenyldichlorosilane with ammonia, and the resinous by-product was obtained by evaporating the mother liquors after the crystalline product had been separated. The procedure was as follows: In a 5-liter, 3-neck flask fitted with a stirrer, reflux condenser, and gas inlet tube were placed 3 liters of benzene and 308 ml (376 g, 1.485 moles) of diphenyldichlorosilane. Dry gaseous ammonia was provided for the reaction by allowing it to boil from a flask of liquid ammonia that contained enough sodium to give a blue color. The chlorosilane solution was stirred under an atmosphere of ammonia for 4 hours. The mixture was refluxed for 4 hours and then allowed to cool. The Beilstein Test showed that chloride was absent from the supernatant solution. The ammonium chloride was filtered off, and the occluded silazanes were extracted from it by stirring and filtering four times with 200-ml portions of hot benzene. The benzene solutions were distilled until the pot temperature reached 95°C. The undistilled liquid was repeatedly cooled and filtered to obtain crystalline hexaphenylcyclotrisilazane, 165.5 g (0.28 mole, 56.5% of theory), that melted at 213-215°C. The mother liquor was set aside for a week, and an additional quantity of crystals formed in that period. The crystals were separated by filtration, and proved to be crude hexaphenylcyclotrisilazane, 49.9 g (0.084 mole, 17.0% of theory). The resin content of the mother liquor was determined by evaporating an aliquot of it at 0.05 mm pressure. The yield of resin (a pale-yellow sticky gum) was 55.2 g (0.28 mole), which was 18.8% of theory, if the amine end groups are disregarded, and the formula is assumed to be $(C_6H_5)_2SiNH$. Thus the yield of the combined products was 92.3%.

Hexaphenylcyclotrisilazane and the by-product have been prepared according to the above procedure about ten times, and this preparation was typical. The resinous by-product of an earlier sample was freed of solvent at 0.05 mm pressure and analyzed with the results shown in Table XII. The oxygen was determined by radioactivation analysis by the General Atomic Division of General Dynamics Corporation, San Diego, California. The molecular weight was determined by vapor osmometry by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Table XII. Analysis of Resinous By-Product of Hexaphenylcyclotrisilazane Synthesis

| | Found, % | Theoretical,[a] % |
|---|---|---|
| Carbon | 72.74 | 73.02 |
| Hydrogen | 5.60 | 5.63 |
| Nitrogen | 5.64 | 7.11 |
| Silicon | 12.80 | 14.24 |
| Oxygen[b] | 2.64 | 0 |
| Total | 99.42 | 100.00 |
| Molecular weight[c] | 980 | 592[d] |

a. For $-Si(C_6H_5)_2NH-$.

b. Radioactivation analysis by General Atomic Division of General Dynamics Corporation, San Diego, California.

c. Vapor osmometry by Galbraith Laboratories, Inc., Knoxville, Tennessee. Average of 970 and 990.

d. For hexaphenylcyclotrisilazane, $[Si(C_6H_5)_2NH]_3$.

2. Preparation of coatings with the by-product

Coatings of the resinous by-product of hexaphenylcyclotrisilazane were applied to aluminum panels from a 10% solution in benzene. Application of 0.2 ml of the 10% solution over an area of 15 square centimeters produced a coating that was approximately 0.25 mil thick. In the experiments described below, coatings of 0.25, 0.75, and 1.25 mils in thickness were evaluated.

Little or no difficulty was encountered with cracking of the coatings during exposures to heat, except at 500°C and above. Even after an hour at 500°C, none of the coatings cracked when cooled; but after longer exposures at 500°C the 0.75-mil and the 1.25-mil samples cracked when cooled. The 0.25-mil coating cracked only slightly when cooled after 5 hours at 500°C.

The integrity of the coatings was evaluated by placing the panels in boiling water for an hour and then in 19% hydrochloric acid until the uncoated part of the panel became black. The performance of a coating was considered to be good only if the coated part remained shiny. Coatings that were not cured did not withstand the boiling water and acid treatment. After being cured for 1 hour at 110°C, all of the coatings became slightly cloudy when immersed in boiling water for 1 hour; but they still afforded some protection from the acid. After curing for 1 hour at 300°C, the coatings were visibly unaffected by the boiling water and they protected the aluminum from the acid until the uncoated areas were black and deeply etched. Thus an hour at 110°C is not an adequate cure to obtain maximum chemical stability.

When partly coated panels were heated at 550°C, the aluminum became discolored except under the coating. After an hour at 550°C, only the 0.25-mil coating was visibly uncracked; and it was the only one that withstood the water and acid treatment. However, even after 16 hours at 550°C, microscopic exmination showed that the coatings were still present although they were quite brittle.

Coatings that were cured at 400°C or less for an hour did not craze when the aluminum panels were bent to a radius of about 3 mm. Coatings cured for longer times at 400°C or at higher temperatures crazed when bent to the same extent.

The by-product was fractionated by adding ether to a benzene solution. A white precipitate formed. The mixture was centrifuged, and the clear solution was used to coat an aluminum panel. The coated panel was heated over a gas burner until the aluminum softened and sagged, but the coating remained intact. The coating was not affected by an acid treatment even though it was kept in the acid until the uncoated aluminum was deeply etched.

3. Preparation of coatings with a mixture of the by-product and ethylenediamine silazane

The coating was prepared as follows: 10% solutions of the hexaphenyl by-product and of ethylenediamine silazane[7] were prepared in benzene. These were mixed in a volumetric ratio of 9:1, respectively. An area of 15 square centimeters was marked on each of two 0.033-inch aluminum panels, and 0.4 and 0.6-ml portions of the mixture were applied to the marked areas of the panels. The solvent was allowed to evaporate for 3-4 minutes, and the panels were placed in an oven at 135°C for 30 minutes. The applied films weighed 0.0341 and 0.0544 g. The films were smooth, shiny, colorless, and transparent. They were flexible, but they could be scratched with a fingernail. The panels were then heated in air at 700°F (370°C) for 18 hours. There was no visible change, but the films could no longer be scratched with a fingernail. The final film weights were 0.0132 and 0.0201 g. The panels were bent repeatedly, and no signs of crazing were observed at the point of greatest curvature which had a radius of about 3 mm. The bent panel with the thinner coating was placed in 19% hydrochloric acid for about 5 minutes, and deep etching occurred in all uncoated areas while the coated areas remained bright and shiny. This sample was designated 2736-123-1 and sent to the George C. Marshall Space Flight Center.

The same type of coating was applied to mild steel and cured for 48 hours at 110°C. The coating withstood 75 hours in water with no evidence of rust formation under the coating.

4. Preparation of coatings with the methyl hydrogen silazane

The methyl hydrogen silazane was obtained by the reaction of methyldichlorosilane with ammonia.[8] It was a cloudy viscous liquid that could be dissolved in benzene to form a clear solution.

Several different temperatures were investigated for curing coatings that had been made by spreading a 10% solution of the methyl hydrogen silazane on aluminum. A coating that had been cured in air for a day at room temperature was clear, colorless, and shiny; but it could be scratched with a fingernail. It peeled away from the aluminum after 20 minutes in boiling water. It smoked and cracked when it was heated over a gas flame. A coating that had been cured at 150°C for 4 hours and another that had been cured at 150°C for 22 hours crazed when they were cooled to room temperature.

A benzene solution containing 1% ethylenediamine silazane[7] and 9% methyl hydrogen silazane[8] was prepared to investigate the effect of ethylenediamine silazane on flexibility. Coatings were applied to several aluminum panels and cured at 120°C for 3, 19, and 24 hours. The cured coatings were clear and colorless, and the panels could be bent without cracking the coatings. When the panels were immersed in 19% hydrochloric acid, the coatings were attacked slowly, although considerable protection was afforded the aluminum.

5. Preparation of coatings with the N-methyl-Si-phenyl silazane

Bis(methylamino)diphenylsilane polymerized on heating as described in Section IV-B-2-f , and a small part of the product was the crystalline N, N'-dimethyltetraphenylcyclodisilazane. The remainder was the N-methyl-Si-phenyl silazane of unknown structure, with which coatings were made.

In the first trial, a small amount of the liquid was placed on a stainless steel spatula and heated slowly to red heat over a gas flame. At first the film smoked, and then it became solid. Red heat for about a minute did not destroy it; and the film was intact and flexible after the spatula had been plunged while hot into water. A similar film on an aluminum panel was heated until the aluminum began to soften. After being cooled in a stream of water, the panel was badly warped. It had a few cracks, and the coating was invisible. However, the presence of the coating was confirmed by placing the panel in 19% hydrochloric acid for 10 minutes. The uncoated areas were deeply etched, but the coated areas remained shiny except where the metal had cracked during heating.

In a brief investigation of similar coatings on several additional panels, one on aluminum appeared to be unchanged after being in a furnace at 500°C for 45 minutes. Another, on stainless steel, did not crack when the panel was bent repeatedly after being held at 500°C for an hour. The coating on stainless steel began to volatilize slowly at 650°C and after 18 minutes its presence was no longer detectable.

We believe the thermal endurance of the N-methyl-Si-phenyl coating exceeds that of the coatings made from the hexaphenyl by-product and ethylenediamine silazane. However, the requirements for curing it may be more stringent than those of coatings made with the mixture of the hexaphenyl by-product and ethylenediamine silazane, because several coatings did not appear to be satisfactorily cured at 370°C.

# VII. STUDIES OF THE STRUCTURE OF HEXAPHENYLCYCLOTRISILAZANE POLYMERS

## A. Discussion

Hexaphenylcyclotrisilazane condenses on heating above 450°C to form polymers that are infusible and insoluble and that are potentially useful in coatings, both for protection of metals and for heat-barrier applications.

In the past, the polymerization has been regarded mainly as the elimination of benzene to form Si-N bridges between molecules.

$$n\,(Ph_2SiNH)_3 \longrightarrow 3n\ PhH + (PhSiN)_{3n}$$

No concentrated effort had been made to identify all of the products of the condensation polymerization and this explanation was recognized as being unconfirmed. Furthermore, infrared spectra indicated that Si-H bonds and N-H bonds were present in the infusible polymer, and elemental analyses showed that the reaction did not reach a definite point of completion at the elemental composition PhSiN. Although the intermolecular elimination of benzene between Si-Ph and H-N groups seemed a plausible explanation, it was by no means the only possible explanation. Cross-linking could conceivably occur by bridging through disubstitution in the benzene rings.

To obtain a better understanding of the condensation polymerization of hexaphenylcyclotrisilazane, five subjects were studied:

- identification of the volatile products
- the possibility of disubstitution in benzene rings
- the effect of temperature on the rate of polymerization
- the replacement of Si-C with Si-N bonds during polymerization
- molecular weight changes during polymerization

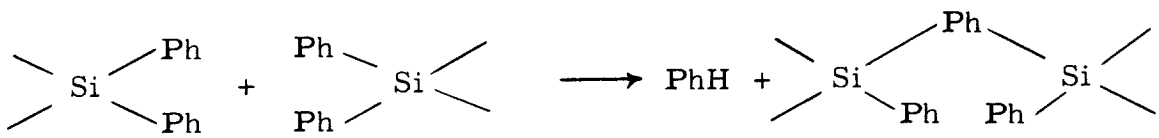
1. Identification of the volatile products

Previous work[28] had shown that the composition of the condensation polymer agreed approximately with the formula, PhSiN, and that benzene was the major volatile material produced during polymerization. To determine the volatile decomposition products more definitely, the condensation polymerization of hexaphenylcyclotrisilazane was carried out in a closed system; and the volatile products were caught in traps cooled by dry ice and liquid nitrogen. About 98% of the volatile products were accounted for. The volatile products contained 97-98% benzene, 1% biphenyl, 1% water, and traces of ammonia and unidentified high-boiling materials. No acetylene, hydrogen, nitrogen, or methane was detected even when the pyrolysis of the hexaphenylcyclotrisilazane was carried to the point at which the solid product became dark brown in color. This lack of gaseous fragments was difficult to explain, and accordingly considerable effort was made to capture them. The explanation may be that carbon is retained by the residue either in the free state or as silicon carbide and that hydrogen is retained either in combination with silicon or with silicon and carbon.

It is obvious that the most important reaction in the thermal polymerization of hexaphenylcyclotrisilazane is the elimination of benzene, probably by the interaction of ≡Si-Ph and H-N≡ groups in adjacent molecules.

## 2. Disubstitution of benzene rings during condensation polymerization

The polymerization of hexaphenylcyclotrisilazane could conceivably occur to some extent by disubstitution in the benzene rings:




To determine whether this occurred, partially polymerized hexaphenylcyclotrisilazane was treated with bromine which was expected to convert the carbon-silicon bonds to carbon-bromine bonds.[29, 30]

$$\text{Ph - Si}\equiv \quad + \quad Br_2 \longrightarrow \quad \text{Ph - Br} \quad + \quad \text{Br - Si}\equiv$$

$$\equiv\text{Si - Ph - Si}\equiv \quad + \quad 2\,Br_2 \longrightarrow \quad \text{Br - Ph - Br} \quad + \quad 2\,\text{BrSi}\equiv$$

The results indicated that disubstitution in benzene rings did not occur to a significant extent. However, brominolysis of unpolymerized hexaphenylcyclotrisilazane in an organic solvent occurred only to the extent of 32% of the expected amount, and that was too low for the evidence to be conclusive. Attempts were made to carry out the brominolysis in bromine water, but a control reaction with hexaphenylcyclotrisilazane yielded an appreciable amount of dibromobenzene, and so the reaction in this medium was not acceptable. Previous workers[29, 30] used the bromine reaction in the study of silanes; and although the method could probably be adapted to silylamines, the value of the information to be gained did not appear to justify further effort.

3. The effect of temperature on rate of polymerization

The rate of polymerization of hexaphenylcyclotrisilazane was found to depend on temperature as expected. However, the relationship had not been studied specifically in the past, and questions were continually being asked about the temperature range for the reaction. Consequently, one method of conducting the polymerization was chosen, and the times required to produce the infusible solid at various temperatures were determined. The results are given in Figure 18 and Table XIII.

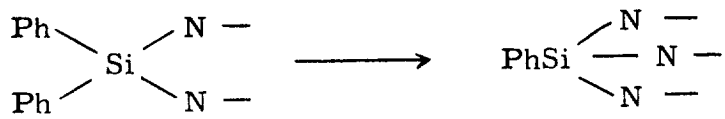
Table XIII. Time-Temperature Relation in Polymerization of Hexaphenylcyclotrisilazane

| Oven temperature, °C | Time to solidify, min | Weight loss, % | Appearance of polymer |
|---|---|---|---|
| 450 | 570 | 37.1 | red-brown, foamed |
| 475 | 266 | 36.8 | tan, foamed |
| 500 | 93 | 32.0 | yellow, foamed |
| 510 | 77 | 32.0 | yellow, foamed |
| 525 | 52 | 31.7 | yellow, foamed |
| 540 | 39 | 31.1 | yellow, foamed |
| 550 | 23 | 29.4 | yellow, foamed |

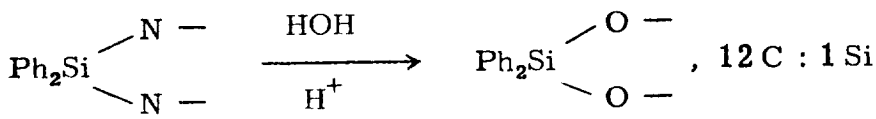
When 1.0 g of hexaphenylcyclotrisilazane in a glass tube was placed in an oven at 450°C, the sample solidified in 9.5 hours. With the oven at 550°C, the sample solidified in 22.5 minutes. It should be emphasized that the temperatures reported are for the oven rather than the samples. Inasmuch as the reaction is endothermic and the samples were cold when placed in the oven, the actual sample temperatures were lower than the oven temperatures. The sample in the oven at 450°C lost 37.1% in weight whereas the theoretical loss to produce PhSiN is 39.6%; the product was a foamed, red-brown solid. The sample in the oven at 550°C lost only 29.4% in weight, and the product was a pale yellow, foamed solid.

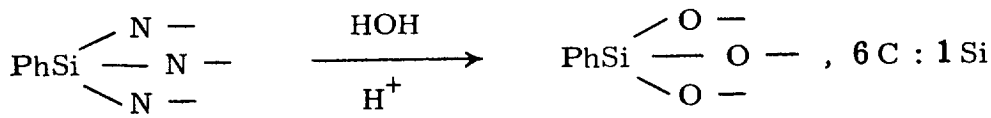
## 4. The replacement of Si-C by Si-N bonds during polymerization

The condensation polymerization of hexaphenylcyclotrisilazane apparently results in each silicon atom becoming attached to three nitrogen atoms:



It was planned to obtain evidence for this transition by hydrolyzing the starting material and the polymer with strong acids and comparing the ratios of carbon to silicon in the resulting products.





Probably the first step in the formation of the trioxysilicon compound is the formation of Si-OH groups, but the subsequent fate of the -OH groups is uncertain. Because of the widespread belief that phenyl-silicon bonds are far more resistant to acid than silicon-nitrogen bonds, very little destruction of carbon-silicon bonds was expected. It was not necessary, although it was desirable, to isolate a pure trioxysilicon compound. These compounds are known to be unstable. They condense to form polymers and mixtures of complex structures. If it could be shown that hexaphenylcyclotrisilazane hydrolyzes to form a material with a carbon to silicon ratio of 12:1, and that the condensation polymer of hexaphenylcyclotrisilazane hydrolyzes to form material with a carbon to silicon ratio of 6:1; we would have additional evidence that three nitrogen atoms were attached to each silicon atom initially.

The first set of samples, after prolonged hydrolysis with 50% sulfuric acid, yielded benzene-soluble products that had carbon to silicon ratios of 11.5:1 for hexaphenylcyclotrisilazane and 7:1 for the condensation polymer. The expected reaction evidently occurred.

5. Molecular-weight changes during polymerization

Several samples were taken during the course of a condensation polymerization of hexaphenylcyclotrisilazane. The molecular weights of successive samples increased as expected. The values were: 560 when the melt was at 512°C, 765 when the melt was at 540°C, and 1400 when the melt was at 554°C.

B. Experimental Details

1. Identification and determination of volatile compounds

To obtain a quantitative material balance, the condensation polymerization of hexaphenylcyclotrisilazane was conducted in a glass distillation apparatus as sketched in Figure 19. The reaction vessel contained a gas inlet tube for the introduction of nitrogen, and the receiver was immersed in a dry ice-trichloroethylene bath. In some experiments, a trap cooled with liquid nitrogen was added downstream from the dry-ice bath. Each portion of the apparatus was tared. Hexaphenylcyclotrisilazane, approximately 1.5 g, was placed in the reaction vessel and weighed. The apparatus was assembled and swept with dry nitrogen. The nitrogen flow was stopped, the receiver was chilled, and the reaction vessel was heated gently with a burner to start condensation of the hexaphenylcyclotrisilazane. The volatile material distilled and condensed throughout the system. When complete solidification occurred in the reaction vessel, heating was stopped; and a gentle flow of nitrogen was started. When all visible liquid had been swept into the receiver, the nitrogen flow was stopped; and each section of the apparatus was weighed after it reached room temperature. The volatile condensation product was analyzed by gas chromatography, and one of the minor chromatographed components was identified by infrared spectroscopy.

The foregoing procedure was derived from several experiments in which the technique was varied to overcome some difficulty. Ice was unsatisfactory for cooling the receiver, because it permitted the loss of 70% of the volatile product. Nitrogen could not be passed through while condensation was occurring, because a smoke formed that was not condensed in the receiver.

Following are the results of an experiment in which 98% of the volatile material was collected in a trap cooled with dry ice and practically all of it was identified:

| | |
|---|---|
| Weight of hexaphenylcyclotrisilazane starting material - | 1.8831 g |
| Weight of infusible polymeric product - (59.5% of starting material, 60.4% is the theoretical amount if PhSiN is formed) | 1.1211 g |
| Amount distilled from starting material - (40.5% of starting material, 39.6% is the theoretical amount if PhSiN is formed) | 0.7620 g |
| Amount of distillate collected - (98.0% of amount distilled, including a droplet of water) | 0.7460 g |

Composition of distillate collected: Organic portion, 99.1% benzene, 0.7% diphenyl plus traces of higher boiling products. In addition there was a small droplet of water. By comparing the size of this droplet with the size of a measured droplet, it was judged to be less than 0.01 ml (1.3% of the distillate or 0.5% of the starting material). Hence, 3.3% of the distillate or 1.4% of the starting material could have been lost as a gas. This amount is insignificant.

In another experiment, the same apparatus was used; but a trap cooled in liquid nitrogen was added to the outlet of the system. Nitrogen ("oil pump grade," Air Reduction Company) was used as the carrier gas, and it was passed through the system slowly at a rate of 2-3 ml per minute for about 20 hours. Unexpectedly, under these conditions, the product was captured by the dry-ice trap; and, in addition, some moisture was condensed from the nitrogen stream. Even though the hexaphenyl polymer was heated far beyond the point at which the infusible solid was produced, the condensed product was principally benzene (98.8%). The solid polymer residue was heated to red heat until it was dark brown. The amounts of products were as follows:

| | |
|---|---|
| Weight of hexaphenylcyclotrisilazane starting material | 2.4448 g |
| Weight of brown infusible polymeric product: (55.8% of starting material, 60.4% is the theoretical amount if PhSiN is formed) | 1.3637 g |
| Amount distilled from starting material: (44.2% of starting material, 39.6% is the theoretical amount if PhSiN is formed) | 1.0811 g |
| Amount of distillate collected in dry ice trap: (101% of amount distilled) | 1.0943 g |
| Composition of distillate collected: Organic portion, 98.8% benzene, 1.1% diphenyl with traces of higher boiling products. In addition there was a droplet of water, estimated to be less than 50 mg (2% of the starting material and 4.6% of the distillate) | |

The droplet of water in the dry-ice-cooled trap introduces a slight uncertainty in the weight balance. However, it was conservatively estimated to be less than 50 mg, which is only 2% of the starting material and 4.5% of the distillate. This amount could account for the 1% excess of the 101% apparent recovery of the distillate, and this indicates that up to 3.5% of some material escaped.

The liquid-nitrogen trap in the experiment just described was capped with a tared balloon after the nitrogen had been passed through for 20 hours. As the trap warmed to room temperature, the balloon was inflated, and the weight gain was found to be 0.2441 g. By gas chromatography the contents were found to be ammonia and small amounts of oxygen and nitrogen in the proportions that they occur in air. No traces of acetylene, carbon monoxide, methane, or hydrogen were found. We believe the observed weight gain can be attributed to the gases detected, plus traces of moisture caught in the joints and the balloon. When the apparatus became thoroughly warmed to room temperature, no condensate was visible.

In two experiments, dry helium was used as the carrier gas to permit detection of any free nitrogen produced. Just enough helium was used to sweep gas out of the system. In one of these experiments, the gas was collected in a gas-sampling bath; and, in the other, the gas was collected over water. No nitrogen was detected.

In another experiment designed to determine the amount of ammonia that was formed, the only condenser used was a trap cooled with ice water; and the uncondensed gases were bubbled slowly through standard sulfuric acid which was maintained at the methyl red end point by adding standard base. The amount of base required showed that only 0.96 mg of ammonia was obtained from 2.2627 g of hexaphenylcyclotrisilazane when the polymerization was stopped as soon as the polymer reached the pale-yellow, infusible stage. Further heating to the dark brown stage produced only another 0.12 mg of ammonia. Thus the ammonia liberated was only about 0.5% of the amount possible based on the total nitrogen content of the sample. A preceding experiment had indicated that the amount of ammonia produced was 6.7% of the total possible. We now believe that the ammonia produced is within the range of the amount that can be formed by inadvertent admission of moisture. Hence, ammonia production is not a significant part of the reaction.

In another experiment hexaphenylcyclotrisilazane was placed in an 18-ml glass tube that was closed with a collapsed rubber balloon. The tube was heated with a burner to convert the silazane to a yellow foamed solid, and then it was heated further to cause slight darkening and insure the maximum opportunity to produce gas. After the system cooled to room temperature, the increase in gas volume was about 10 ml. Gas chromatography showed the gas to be about 65% air that was in the system initially, about 15% hydrogen, about 10% benzene, and about 0.2% methane. The remainder was not identified, but it was present in an amount that was so small as to be inconsequential. Thus, the gaseous materials produced could not be significant indicators of the decomposition mechanisms.

2. Detection of disubstitution in the benzene rings of the polymer

Silicon-carbon bonds in aromatic compounds are cleaved by bromine to yield aryl carbon-bromine bonds, and this reaction can be used as a means of locating the position of attachment of silicon to an aromatic ring. A method similar to that of Benkeser and Torkelson[29] was tried with hexaphenylcyclotrisilazane to determine the yields of mono- and disubstituted bromobenzene in a known compound having only one silicon atom attached to each benzene ring. Hexaphenylcyclotrisilazane, 10.1 g (0.017 mole), was placed in a 250-ml, 3-neck round-bottom flask fitted with a thermometer, condenser, and magnetic stirrer. When carbon tetrachloride, 100 ml, and bromine, 8.2 g (0.051 mole), were added, the temperature rose to 50°C. Stirring was started, and the mixture was refluxed for 5 hours. The sample did not dissolve completely. At the end of this time, a red color showed that bromine was still present in excess. Concentrated hydrochloric acid, 50 ml, was added; and the mixture was refluxed for 2 hours. The white solid dissolved during refluxing, and the red color disappeared. After separation, the water layer was washed with carbon tetrachloride; and the carbon tetrachloride layer was washed with water. The carbon tetrachloride-soluble portion was concentrated to 25 ml by distillation in a 6-inch Vigreux column, and aliquots were analyzed by gas chromatography. The compositions of the aliquots showed that 5.25 g (0.033 mole) of bromobenzene and 0.0075 g ($3 \times 10^{-5}$ mole) of dibromobenzene were present. No attempt was made to distinguish between the isomers of dibromobenzene. Thus the yield of bromobenzene was 32% of the theoretical quantity, and the yield of dibromobenzene was 0.03%.

A similar experiment was performed on the prepolymer made by boiling hexaphenylcyclotrisilazane until the liquid became viscous and appeared to be close to the solidification point. The amount of prepolymer was 1.5545 g (0.013 mole if PhSiN is the formula). The yield of bromobenzene was 0.450 g, 22% of the theoretical yield, and of dibromobenzene was 0.015 g, 0.5% of the theoretical yield. It appears that a trace of disubstitution may have occurred in the benzene rings during polymerization.

The method of Kipping and Cusa[30] was next tried on unpolymerized hexaphenylcyclotrisilazane to determine whether the method was satisfactory. Hexaphenylcyclotrisilazane was sealed in a Pyrex tube with water and an excess of bromine. The tube was heated at 110°C overnight, and the product was extracted with carbon tetrachloride. The amount of bromobenzene found was 39% of the theoretical yield and the amount of dibromobenzene was 0.1%. Hence, this method was a slight improvement, but higher yields were needed for assurance that the amount of dibromobenzene was actually low.

Brominolysis was then attempted at atmospheric pressure with bromine water. In a 100-ml, round-bottom, 3-neck flask fitted with a reflux condenser and a magnetic stirrer were placed 2.0 g (0.0034 mole) of hexaphenylcyclotrisilazane and 6.0 ml (0.33 mole) of water. The stirrer was started and 6.0 ml (18.7 g, 0.234 g atoms) of bromine was added dropwise. The mixture was dark red. After 1.5 hours the excess bromine was removed with sodium thiosulfate solution. The pale yellow suspension was extracted 8 times with 3-5 ml portions of ether, and the combined ether extracts were analyzed for bromobenzene and dibromobenzene by gas chromatography. The yield of bromobenzene was 28%, and the yield of dibromobenzene was 24%. Accordingly, this procedure was unsatisfactory for our purpose for two reasons: the conversion of phenyl-silicon bonds to phenyl-bromine bonds was too low, and the amount of disubstitution that occurred under the conditions of the experiment was too high.

3. The effect of temperature on the rate of polymerization

Hexaphenylcyclotrisilazane, 1.0 g, was placed in a glass tube that measured 15 x 1 cm. The end of the tube was capped with crimped aluminum foil, and the tube was inserted into an oven through a small hole in the door. The tube was placed at an angle so that the melt was in the oven while the upper end of the tube just barely protruded from the oven to permit benzene to escape outside. The material in the tube was examined visually at frequent intervals to determine when solidification occurred. The time required for solidification and the corresponding weight losses were determined at seven temperatures ranging from 450 to 550°C. The data are recorded in Table XIII and Figure 18. In these experiments the melt temperatures were not observed.

4. Hydrolysis of hexaphenylcyclotrisilazane polymers

Hexaphenylcyclotrisilazane, 3.00 g, was refluxed for 4 hours with 75 ml of 50% sulfuric acid. During this time the solid apparently dissolved or disintegrated to form a cloudy solution with no visible particles of a second phase. The liquid was then extracted exhaustively with benzene. The extracted product was dried, finally at 5 microns pressure for 5 hours, to yield approximately 1.5 g of a white, friable powder. The analysis is in Table XIV.

The condensation polymer of hexaphenylcyclotrisilazane was treated similarly. The condensation polymer was formed by heating hexaphenylcyclotrisilazane in a test tube until it solidified to form a pale yellow vitreous solid. The polymer, 1.10 g, was refluxed for 4 hours with 25 ml of 50% sulfuric acid. The resulting liquid was cloudy, and no unreacted polymer was visible. The liquid product was extracted with benzene, and the benzene was removed by evaporation. As the last of the benzene was removed, the color of the residue darkened to purple. After the application of high vacuum, 5 microns pressure for 5 hours, the product weighed approximately 0.5 g. The analysis is in Table XIV.

Table XIV. Elemental Analyses of the Hydrolyzed Hexaphenylcyclotrisilazane and the Condensation Polymer Formed From It.

| | Hydrolysis products of | |
|---|---|---|
| | Hexaphenylcyclotrisilazane | Condensation polymer |
| Carbon, % | 67.36 | 50.22 |
| Hydrogen, % | 5.00 | 5.30 |
| Nitrogen, % | <0.1 | 0.24 |
| Silicon, % | 13.50 | 17.20 |
| Ratio C:Si | 11.5 : 1 (Theory, 12:1) | 6.9 : 1 (Theory, 6:1) |

5. Molecular weight changes during polymerization

Hexaphenylcyclotrisilazane, 10 g, was placed in a test tube that was loosely capped with aluminum foil. The tube was heated with a flame until a thermometer in the tube indicated 512°C. A sample taken at that time was determined to have a molecular weight of 560 (average of 548 and 570). A second sample taken when the temperature reached 540°C had a molecular weight of 765 (average of 752 and 775). A third sample, taken when the temperature reached 554°C, had a molecular weight of 1390 (average of 1380 and 1405).

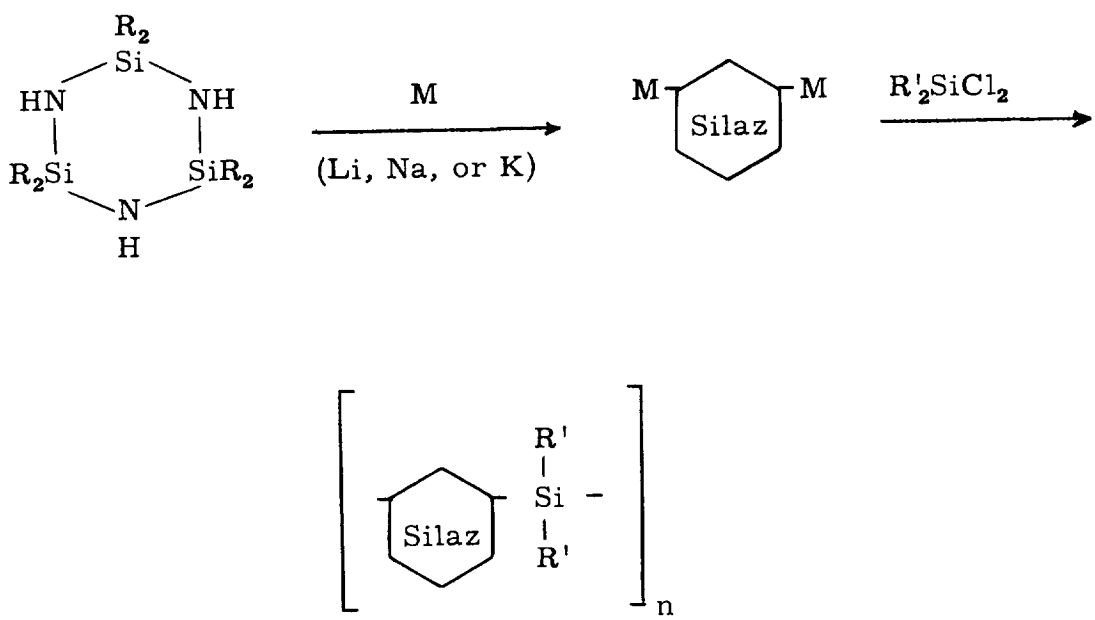
The molecular weights were determined by vapor osmometry by Galbraith Laboratories, Inc.

# VIII. N-SILYLATION OF SILAZANES

## A. Discussion

### 1. Purpose

The N-alkali derivative of silazanes are useful intermediates for the synthesis of a wide variety of compounds, and they offer possible routes to polymers. For example,

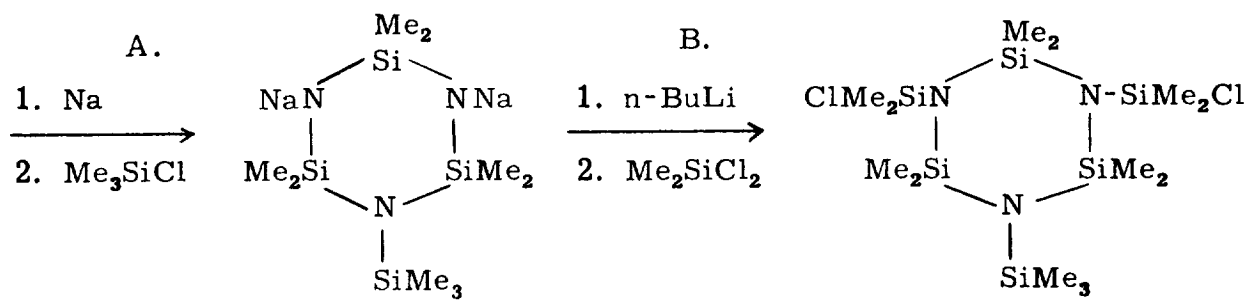



The N-silylation reaction was studied extensively to develop the method for future use in preparing compounds of desired structures.

## 2. Previous work

The literature contains several reports of N-alkali derivatives of silicon-nitrogen compounds.[31] Wannagat and Niederprum[32] used phenyl-lithium to prepare triply silyl-substituted amines and found that they were "strikingly" stable to hydrolysis. Fink[33] found that 1, 2, or 3 of the N-hydrogen atoms in hexamethylcyclotrisilazane could be substituted with Li by the proper use of n-butyllithium.

The lithium derivatives of silylamines are now being investigated in several laboratories. Maselli[34] mentioned that unpublished work was being done by Kruger and Rochow on the reaction of dimethyldichlorosilane with the dilithium derivative of hexamethylcyclotrisilazane. Shaw[35] reported work on the reaction of hexamethyldisilazyllithium with chlorosilanes. The N-tris-silyl compounds were exceptionally stable to heat and moisture. Breed and Elliott[36] reported attempts to prepare N-(trimethylsilyl)-N', N''-bis(chlorodimethylsilyl)hexamethylcyclotrisilazane,




Breed and Elliott developed a satisfactory means of conducting Reaction A but not Reaction B. They preferred the sodium to the lithium derivative for Reaction A, according to the method of Goubeau.[37]

3. Study of methods

We started to prepare N, N', N''-tris(trimethylsilyl)hexamethylcyclotrisilazane by the method of Fink[33] to establish the method and to obtain the compound for studies of hydrolytic and thermal stabilities. We were unable to produce the tris(trimethylsilyl) compound by Fink's method. Instead we obtained what was apparently a mixture of the bis- and tris-(trimethylsilyl) derivatives.

The compound N-trimethylsilylhexamethylcyclotrisilazane was then made by the method of Breed and Elliott.[36] Their method avoided lithium and made the intermediate sodium compound in the presence of styrene, which serves as a hydrogen acceptor.

Unsuccessful attempts were made to prepare N-trimethylsilylhexaphenylcyclotrisilazane by the method of Fink[33] with n-butyllithium. The sodium method of Breed and Elliott,[36] however, yielded 25% to 50% of the theoretical amount of a compound melting at 152-154°C. Ultimate identification of this compound as N-trimethylsilylhexaphenylcyclotrisilazane was complicated by disagreement with Fink[33] about the melting point. Fink reported 80°C as the "softening point." Extensive attempts to purify the compound revealed that the observed melting point was affected by the history of the compound. We observed "softening points" of approximately 73 to 80°C on two samples: One was a fused mixture of hexaphenylcyclotrisilazane and the trimethylsilyl derivative, and the other was the trimethylsilyl derivative alone after it had been held at 200°C for 5 minutes. Both of these samples had cooled from melts to form clear glasses; and the glasses were pulverized for determination of capillary melting points. Hence, the fusion points we observed were not true crystalline melting points. Fink measured his "softening point" after distillation and did not report a recrystallization. This may provide an explanation of our disagreement. In the course of our recrystallizations, we obtained other samples that may have contained solvent. One sample was recrystallized from hexane to a melting point of 152-154°C. Then it was recrystallized from a mixture of dioxane and diethyl ether to a melting point of 115-117°C. NMR spectra showed that this sample contained dioxane. Further recrystallization from hexane raised the melting point of the material to 155-156°C, and NMR spectra indicated that the ratios of the different protons agreed with the expected ratios for the pure compound. Solution of the compound in benzene followed by reprecipitation with ethanol led to crystals that melted at 170-173°C, but NMR spectra indicated the presence of ethanol.

We now believe the determinations of the melting points and softening points of N-trimethylsilylhexaphenylcyclotrisilazane were complicated by the existence of the solid in different physical forms. Furthermore, the compound had a strong tendency to cling tenaciously to solvents.

While attempting to resolve our disagreement with Fink, we prepared the trimethylsilyl derivative with the aid of potassium. The potassium method was not only more convenient but led to a higher yield, 63%. Styrene was not required to promote the reaction of hexaphenylcyclotrisilazane with potassium.

### 4. Properties of the silylated cyclic silazanes

The N-trimethylsilyl derivatives of hexamethylcyclotrisilazane and hexaphenylcyclotrisilazane were more stable to hydrolysis than their parent compounds (Section IV). The increase in stability cannot be explained adequately by simple steric shielding of a single nitrogen atom, because the hydrolysis rates of the silyl derivatives were lower from the very beginning of hydrolysis and not merely in the latter third.

## B. Experimental Details

### 1. Silylation of hexamethylcyclotrisilazane

#### a. Metalation with n-butyllithium

The reports of Fink[33] were studied to determine the best method of synthesis. Nevertheless, in three attempts, we failed to obtain the N, N', N''-tris(trimethylsilyl)hexamethylcyclotrisilazane. Instead we apparently obtained a mixture containing largely the N, N'-bis(trimethylsilyl) derivative.

The procedure was as follows: In a 200-ml, 3-neck flask fitted with a magnetic stirrer, reflux condenser, thermometer, and dropping funnel was placed 8.65 g (0.135 mole, 10% excess) of n-butyllithium in heptane solution (41.0 ml). The n-butyllithium was purchased from the Lithium Corporation of America, and the manufacturer's assay was confirmed by titration.[38] Hexamethylcyclotrisilazane, 9.0 g (0.041 mole), was added dropwise with stirring to the butyllithium solution over a period of 45 minutes. Addition of each drop caused the formation of gas and insoluble matter. When the reaction mixture became too thick for efficient stirring, 10 ml of benzene was added, and the solution was refluxed for 1 hour. After cooling, 14.6 g (0.135 mole) of trimethylchlorosilane was added over a period of 20 minutes. The solution was then refluxed for 3 hours. Upon cooling, the mixture settled into two layers; the upper two-thirds being clear. About half of the clear layer, 25 ml, was pipetted into a 45-ml stainless steel bomb and heated at 132°C for 7 hours. The other half of the clear layer, 25 ml, was pipetted into another bomb and heated at 175°C for 7 hours. The two autoclaved mixtures were centrifuged to remove the insoluble lithium chloride, and the solutions were distilled separately. Their boiling ranges were essentially the same. The distillable fractions were clear liquids boiling at 110-135°C at 3 mm pressure. The combined distillable products amounted to 6.4 g. The residues, 3.6 g, were cloudy, viscous, orange liquids that did not distill at 182°C at 3 mm.

Fink[33] reported that the tris-silyl compound boiled at 333°C at 723 mm pressure, and the bis-silyl compound boiled at 261°C at 730 mm. These boiling points are approximately equivalent to 160°C at 3 mm pressure for the tris-silyl compound and 103°C at 3 mm for the bis-silyl compound. The index of refraction of our distilled product was $n_D^{20}$ 1.4459. Fink reported the indexes were $n_D^{20}$ 1.4823 for the tris-silyl and $n_D^{20}$ 1.4422 for the bis-silyl.

The distilled products were combined and treated with n-butyllithium and trimethylchlorosilane in an effort to attach another trimethylsilyl group. The method was this: The clear distillable liquid, 6.4 g (0.022 mole, if disubstituted) in 20 ml of benzene, was added to 1.69 g (0.026 mole) of n-butyllithium in 7.5 ml of heptane solution. A small amount of gas was evolved. The clear solution was refluxed for 30 minutes, then it was cooled, and 2.89 g (0.026 mole) of trimethylchlorosilane was added. After refluxing for 30 minutes, the reaction mixture was cloudy. It was autoclaved at 130°C for 5.5 hours. After being cooled, the product was centrifuged; and the resulting clear liquid was distilled. Only 1.5 g of distillable product, boiling at 110-135°C at 2 mm pressure, was obtained. The undistillable, viscous residue weighed 4.3 g. The additional treatment evidently caused polymerization.

The reaction of hexamethylcyclotrisilazane with n-butyllithium and trimethylchlorosilane was repeated except that hexane was added instead of benzene to facilitate stirring. The results of the second reaction were essentially the same as those of the first. The distilled compound was analyzed for carbon and hydrogen and the results (Table XV) indicated that it was the tris compound. However, the neutral equivalent, boiling range, and index of refraction indicated that it was a mixture of the bis and tris compounds. The distilled liquid product was again treated with n-butyllithium and trimethylchlorosilane, and again polymerization was largely the result.

The third attempt to prepare N,N',N''-tris(trimethylsilyl)-hexamethylcyclotrisilazane was conducted at a higher dilution, and the composition of the intermediate lithium derivative was also checked.

In a 1-liter, 3-neck flask fitted with a magnetic stirrer, reflux condenser, thermometer, and dropping funnel were placed 9.0 g (0.041 mole) of hexamethylcyclotrisilazane and 250 ml of dry Skellysolve. The solution was cooled to -10°C. To this was added 8.26 g (0.129 moles, 5% excess) of n-butyllithium in heptane solution (40.2 ml) which had been diluted with 200 ml of Skellysolve. The n-butyllithium was added over a period of 1.5 hours while the temperature of the reaction was kept below -10°C. After the addition of the n-butyllithium, the reaction was allowed to warm to room temperature.

Table XV. Elemental Analyses of Trimethylsilyl Derivatives of Hexamethylcyclotrisilazane

| | Found | | Theoretical for | | |
|---|---|---|---|---|---|
| | Second reaction | Third reaction | A | B | C |
| Carbon, % | 41.21 | 41.60 | 39.61 | 41.31 | 32.83 |
| Hydrogen, % | 10.49 | 9.72 | 10.25 | 10.40 | 9.64 |
| Nitrogen, % | - | 10.51 | 11.55 | 9.64 | 19.14 |
| Silicon, % | - | 37.0 | 38.59 | 38.65 | 38.39 |
| Neutral equivalent | 134.9 | 140.9 | 121.3 | 145.4 | 73.2 |

A. Bistrimethylsilyl derivative.

B. Tristrimethylsilyl derivative.

C. Hexamethylcyclotrisilazane, $C_6H_{21}Si_3N_3$.

To check the composition of the mixture at this point, a 5-ml sample was removed from the solution which had a volume of approximately 500 ml. The solvent was evaporated in a stream of dry nitrogen, and 107.1 mg of white powdery residue was obtained. Theoretically, the amount of residue would have been 174 mg if no reaction had occurred and the residue had been a mixture of hexamethylcyclotrisilazane and butyllithium. The theoretical amount of residue for the trilithium derivative of hexamethylcyclotrisilazane was 101 mg.

Trimethylchlorosilane, 13.47 g (0.129 moles, 3% excess) was added to the solution in the reaction flask over a period of 0.5 hour and the solution was refluxed for 1.5 hours. After cooling, a 35-ml portion of the solution was pipetted into each of four stainless steel reaction vessels. The vessels were closed and heated at 112°C for 16 hours. The four autoclaved mixtures were centrifuged to remove the insoluble lithium chloride, and the clear liquids were combined and distilled. The main fraction boiled at 113-123°C at 8 mm pressure; it weighed 5.5 g. The residue, 3.8 g, was a cloudy, viscous, brown liquid that did not distil at 165°C at 8 mm. The elemental analyses and neutral equivalents are given in Table XV. The index of refraction of the distilled product was $n_D^{20}$ 1.4410. Evidently the product was a mixture of the bis- and tris-derivatives.

b. Metalation with sodium

N-Trimethylsilylhexamethylcyclotrisilazane was prepared by the method of Breed and Elliott.[36] In a 200-ml, 3-neck flask fitted with a thermometer, magnetic stirrer, reflux condenser, and dropping funnel were placed 50 ml of purified dioxane and 1.0 g (0.046 mole) of metallic sodium. The dioxane had been purified by successive treatments with hydrochloric acid and with potassium hydroxide, then it was refluxed with sodium until the sodium remained shiny. The dioxane-sodium mixture was refluxed and stirred until the sodium was well dispersed, and then a mixture of 10.0 g (0.046 mole) of hexamethylcyclotrisilazane and 4.79 g (0.046 mole) of freshly distilled styrene was added over a period of 25 minutes. Refluxing was continued for 3 hours while the sodium went almost completely into solution. The reaction was cooled to 30°C, and 4.96 g (0.046 mole) of trimethylchlorosilane in 5.0 ml of dioxane was added over a period of 10 minutes while the temperature rose to 70°C. The mixture was refluxed for 2 hours, cooled, and

centrifuged. It was distilled through a 1.2 x 30-cm column packed with 6 x 6-mm, perforated, stainless-steel plates bent in C-form. Four fractions were obtained:

I, 0.1 g, b.p. 45-53°C at 0.5 mm

II, 2.0 g, b.p. 53-55°C at 0.5 mm, $n_D^{23.3}$ 1.4599, $n_D^{25}$ 1.4590

III, 7.6 g, b.p. 55-60°C at 0.5 mm, $n_D^{23.3}$ 1.4593, $n_D^{25}$ 1.4584

IV, 2.7 g, not distillable at 115°C at 0.5 mm

Breed and Elliott[9] reported $n_D^{26}$ 1.4561-1.4596 (for several preparations) as the index of refraction of N-trimethylsilylhexamethylcyclotrisilazane.

The neutral equivalent of Fraction III could not be determined by the conventional method because of slow hydrolysis. However, after prolonged stirring with excess acid the neutral equivalent was found to be 97.5 (theory, 97.2). NMR spectra, as discussed below, confirmed the identification.

## 2. Silylation of hexaphenylcyclotrisilazane

### a. Metalation with n-butyllithium

Fink[33] described the preparation of N-trimethylsilylhexaphenylcyclotrisilazane by treating hexaphenylcyclotrisilazane with n-butyllithium and reacting the product with trimethylchlorosilane. In one attempt, 15.9 g (0.027 mole) of hexaphenylcyclotrisilazane in benzene was treated with 1.72 g (0.027 mole) of n-butyllithium. The mixture was stirred at room temperature for 16 hours; then the solvent was distilled, and the residue was heated at 190°C at 2 mm pressure for 3 hours. At this point, the amount of residue and its decomposition point, 205-207°C, agreed with Fink. The residue was mixed with trimethylchlorosilane, 2.91 g (0.027 mole), in benzene and autoclaved at 200°C for 6 hours with occasional shaking. The product was distilled at 1 mm pressure; and a fraction, 6.1 g, boiling at 291-303°C was obtained. It melted at 47-52°C. This may have contained a small amount of the desired trimethylsilyl derivative, but recrystallization yielded largely hexaphenylcyclotrisilazane.

Other attempts to prepare N-trimethylsilylhexaphenylcyclotrisilazane by the use of freshly prepared n-butyllithium, and by autoclaving at various temperatures (112-200°C) likewise failed. Consequently, another method was sought.

b. Metalation with sodium

Goubeau[37] suggested the use of styrene to promote the reaction of sodium with silylamines. Styrene functions as a hydrogen acceptor, and Breed[36] adapted the method to make a trimethylsilyl derivative of hexamethylcyclotrisilazane. We applied the method to hexaphenylcyclotrisilazane in the following manner: In a 300-ml, 3-neck flask fitted with a reflux condenser, magnetic stirrer, thermometer, and dropping funnel were placed 60 ml of purified dioxane and 0.4 g (0.02 mole) of metallic sodium. The mixture was refluxed and stirred until the sodium was well dispersed. A solution containing hexaphenylcyclotrisilazane, 11.8 g (0.02 mole), 80 ml of dioxane, and 2.08 g (0.02 mole), of freshly distilled styrene was added slowly over a period of 1.25 hours. Refluxing was continued for 3 hours while the sodium dissolved almost completely. After the solution was cooled to 30°C, 2.17 g (0.02 mole) of trimethylchlorosilane in 5 ml of dioxane was added over a period of 10 minutes. No exothermic reaction was detected. The reaction mixture was refluxed for 1.5 hours and then centrifuged. The dioxane was distilled off leaving an orange-colored glassy residue. The solid was dissolved in hot toluene and centrifuged to separate a solid crystalline phase and a clear solution.

A laborious fractional crystallization was performed on both the solid and liquid phase with Skellysolve "B" (essentially n-hexane) as the solvent. The fractional crystallization yielded numerous separate batches of products that were combined and ultimately refined to the following fractions:

I, 2.7 g, m.p. 152-154°C, possibly N-trimethylsilylhexaphenylcyclotrisilazane

II, 5.5 g, m.p. 110-190°C, mixture of product and starting material

III, 3.6 g, m.p. 212-214°C, hexaphenylcyclotrisilazane

11.8 g total

Fraction I consisted of well-defined crystals that were soluble in most organic solvents, particularly benzene, Skellysolve "B", tetrahydrofuran, acetone, and ether. They were only slightly soluble in ethanol. Fraction I, as described above, had been recrystallized to constant melting point from Skellysolve "B". The elemental composition and molecular weight were:

Found: C, 71.26%; H, 6,19%; N, 6.31%; Si, 16.2%; molecular weight (vapor osmometry), 674, 680.

Theory: C, 70.53%; H, 6.22%; N, 6.33%; Si, 16.92%; molecular weight, 664.1

The elemental composition was not close enough to theory for positive identification, and the melting point did not agree with Fink's, and so metalation with potassium was tried.

c. Metalation with potassium

Potassium was used to make the mono-silyl derivative of hexaphenylcyclotrisilazane in the following manner: In a 500-ml, 3-neck flask fitted with a magnetic stirrer, reflux condenser, thermometer, and dropping funnel were placed 60 ml of purified dioxane and 1.3 g (0.0338 mole) of metallic potassium. This mixture was heated to reflux, and 20.0 g (0.0338 mole) of hexaphenylcyclotrisilazane dissolved in 180 ml of purified dioxane was added over a 1-hour period. The resulting solution was refluxed for 3 hours. At the end of this time almost all of the potassium had reacted. The solution was cooled, and 3.67 g (0.0338 mole) of trimethylchlorosilane dissolved in 10 ml of dioxane was added over a 10-minute period. A white precipitate, presumably KCl, formed during the following 2 hours of refluxing. The reaction product was cooled and centrifuged. The KCl precipitate was washed twice with dioxane, and its yield was 2.4 g (theory, 2.5 g).

The product was distilled to remove the dioxane, and the undistilled portion was dissolved in Skellysolve B (essentially n-hexane) and filtered to remove the insoluble hexaphenylcyclotrisilazane. The recovered starting material, 3.2 g (16% of the starting material) melted at 206-213°C. The trimethylsilyl derivative was recrystallized in this sequence: three times from Skellysolve B, once from diethyl ether, once from dioxane, and three times from Skellysolve B. The crystalline product melted at 161-164°C and weighed 14.1 g, which amounted to a 63% yield. Infrared spectra revealed no hexaphenylcyclotrisilazane.

A small portion, about 0.5 g, of the purified product was dissolved in benzene and precipitated by the addition of absolute ethanol. The recovered and dried crystals melted at 170-173°C. The infrared spectra of the recovered substance showed that it was free of hexaphenylcyclotrisilazane, but the NMR spectra suggested that some ethanol was present.

d. Identification of N-trimethylsilylhexaphenylcyclotrisilazane

The necessity of resolving our disagreement with Fink about the melting point of N-trimethylsilylhexaphenylcyclotrisilazane was discussed above. The experiments described below confirmed our view that we had the same compound as Fink, but that the observed melting point depends on several factors.

As a means of freeing this mono-trimethylsilyl derivative of solvent, a small portion of the product obtained by the sodium method was sublimed at about 100°C at a pressure of approximately 0.02 mm. On heating the sublimed compound in a capillary melting point tube, it appeared to change form at 80°C; but it did not melt completely until the temperature reached 155°C.

In another experiment, about 0.1 g of the compound made by the sodium method (m.p. 152-154°C) was fused in a test tube. The melted compound was allowed to boil before it was solidified by slow cooling. This residue began to fuse at 73°C when heated in a capillary tube, and a clear melt had formed when the temperature reached 75°C.

For the compound, N-trimethylsilylhexaphenylcyclotrisilazane, which he purified by fractional distillation, Fink[33] reported a "softening point" of 80°C. Judging from the elemental analysis as reported by Fink, it is possible that he had a mixture containing as much as 30% hexaphenylcyclotrisilazane and 70% of the trimethylsilyl derivative. A mixture of this composition was prepared by fusion of the two compounds. While melted, the liquid was stirred to assure homogenity of the melt. The resultant non-crystalline, solidified mass had a "softening point" of 75°C.

Several recrystallizations of the trimethylsilyl derivative from diethylether and then from a mixture of dioxane and ethanol yielded crystals melting at 114-117°C. NMR spectra revealed dioxane in a chloroform solution of the crystals, and so they were recrystallized twice from Skellysolve B and then held at 0.03 mm pressure for 2 days. The resulting crystals melted at 155-156°C. The elemental composition and molecular weight were:

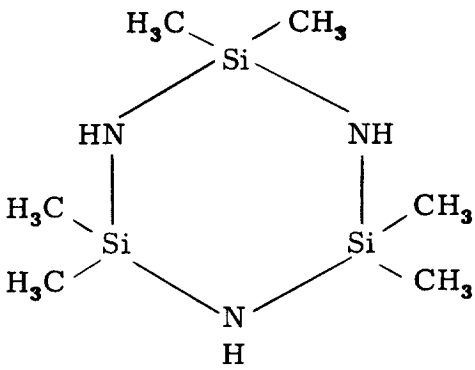
Found: C, 70.87%; H, 5.97%; N, 6.65%; Si, 16.6%; molecular weight (vapor osmometry), 663, 681

Calculated: C, 70.53%; H, 6.22%; N, 6.32%; Si, 16.92% molecular weight, 664.1

NMR spectra showed that the integral ratio of the different protons was 30 : 1.9 : 9.1 (expected, 30 : 2 : 9). Consequently, we consider that the compound we prepared was identified as N-trimethylsilylhexaphenylcyclotrisilazane.

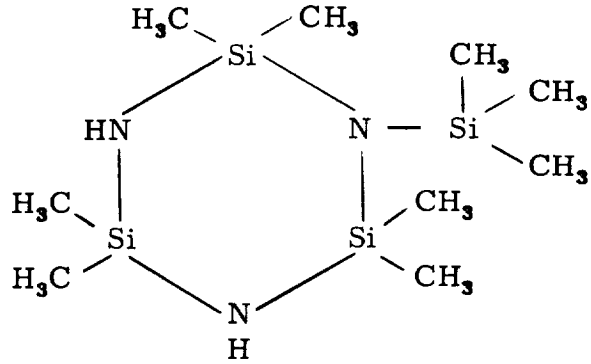
3. Nuclear magnetic resonance and infrared spectra of silylated silazanes

Spectroscopic data were desired for the silylated silazanes because of uncertainties about the identities resulting from our disagreement with Fink's[33] melting point. Hence, infrared and NMR spectra of the following compounds were obtained:



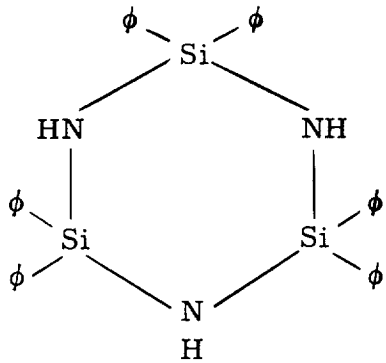
I.

Hexamethylcyclotrisilazane



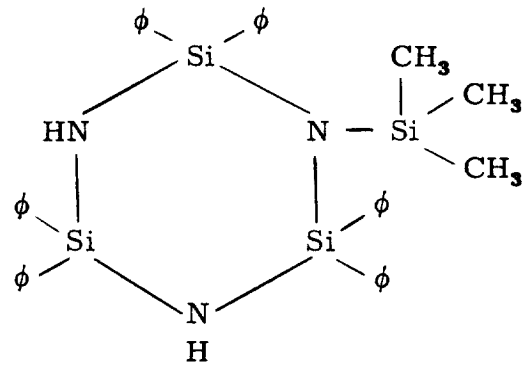
II.

N-Trimethylsilylhexamethylcyclotrisilazane



III.

Hexaphenylcyclotrisilazane



IV.

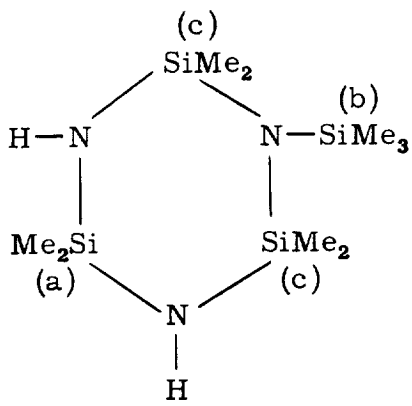
N-Trimethylsilylhexaphenylcyclotrisilazane

Proton magnetic resonance spectra were determined for I, II, III, and IV, with a Varian A-60 nuclear magnetic resonance spectrometer. Carbon tetrachloride was the solvent for I, II, and IV. Compound III was dissolved in chloroform-d, (dueterochloroform, $CDCl_3$). The concentrations of the solutions were 5-10%, as the solubility of the compound allowed.

Chemical shifts are quoted in cycles per second from tetramethylsilane. A positive shift is downfield from tetramethylsilane, a negative shift upfield.

The spectrum of Compound I showed a single sharp absorption at 3 cps (cycles per second). This was attributed to the methyl groups, all of which were expected to be equivalent. In addition, there was a low, broad absorption centered at about 50 cps and overlapping the methyl absorption. This is absorption by protons attached to nitrogen.

Compound II showed three sharp bands at 4, 8, and 11 cps. These bands were attributed to methyl protons in three different environments as indicated:




a = 4 cps
b = 8 cps
c = 11 cps

These assignments were borne out by the integral ratio of these bands

$$a : b : c = 2 : 3 : 4$$

In addition, the spectrum of II showed a broad absorption at about 34 cps from protons attached to nitrogen.

The spectrum of III showed a multiplet at about 441 cps, attributed to protons attached to the phenyl rings. In addition, there was absorption at about 94 cps, and this was assigned to the protons attached to nitrogen. The ratio of the integrals of these bands was 10.4 : 1.0 (phenyl protons to N-H protons), which agrees reasonably well with the known structure.

The spectrum of IV showed a single, sharp peak at -16 cps, assigned to the methyl protons. There was a broad band at 100 cps, assigned to N-H protons. The phenyl absorption consisted of a multiplet centered at 443 cps, and a single peak at 424 cps. (This indicates phenyl groups in different magnetic environments.) The area under the multiplet at 443 cps was equivalent to four phenyl groups. The peak at 424 cps was equivalent to the remaining two phenyl groups. Integration of the spectrum gave a ratio of 30 : 1.9 : 9.1 (phenyl protons to NH protons to methyl protons, theory 30 : 2 : 9).

Infrared spectra of III and IV were consistent with the assumed structures to the limited extent that frequencies can be assigned. We expect to obtain more information in future work. Hexaphenylcyclotrisilazane, III, has two strong absorption bands at 1200 $cm^{-1}$ and 945 $cm^{-1}$. These bands were absent from the spectrum of IV. Consequently, the evidence was that no more than a small amount of III was present in IV.

# IX. THE USE OF DI-, TRI-, AND TETRAFUNCTIONAL CHLOROSILANES IN POLYMERIZATION

## A. Discussion

Reactions of tri- and tetrafunctional chlorosilanes with methylamine and ammonia were studied in attempts to make polymers. The plan was to circumvent the tendency of silylamines to cyclize, when purely difunctional reagents are used, by introducing tri- and tetrafunctional chlorosilanes which would cause chain branching and make it possible for molecules to continue to grow even after some branches were terminated by cyclization. Solid polymers were produced by these methods, but none had the high softening points and high strengths desired.

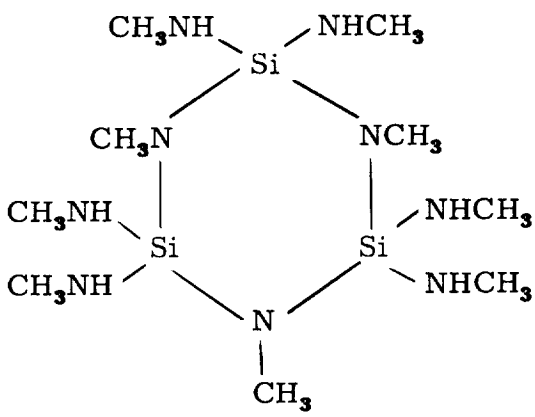
As a first step in the extension of work on trichlorosilanes, three reactions were run in which mixtures of dimethyldichlorosilane and methyltrichlorosilane were treated with methylamine rather than with ammonia as in experiments previously reported.[39] The yields of undistillable polymer produced varied from 11-22%, which were considerably lower than expected. The similar series of reactions with ammonia produced from 27% to 90% yields of undistillable polymer. Evidently steric hindrance by the methyl group on the nitrogen reduced the amount of polymer formed. It was thought that the distillable product must have contained an appreciable number of end-amino groups, so further polymerization was attempted by refluxing it for 25 hours at 205-210°C. Some methylamine was lost, and about 13% of the product remaining was a light yellow oil that did not distil at 173°C at 0.15 mm pressure. The conclusion was that some polymerization occurred, but the molecular weight was not significantly increased by the operation.

When methyltrichlorosilane alone was treated with methylamine, the product was an oil that released methylamine on heating at gradually increasing temperatures up to 350°C to yield a transparent, colorless material that was a gum at room temperature and that was soft when warm. This product was expected to be a modification of the compound that was obtained by the reaction of methylamine with silicon tetrachloride and that polymerized on heating to an infusible, insoluble wax. The new material, made from methyltrichlorosilane, polymerized on heating to yield a thermoplastic product. On even longer heating at high temperature, its softening point increased and its solubility in benzene decreased; but it remained clear and almost colorless. It had some merit as a coating agent for metals, but it did not appear superior to other materials (Section VI), and so it was not studied in detail.

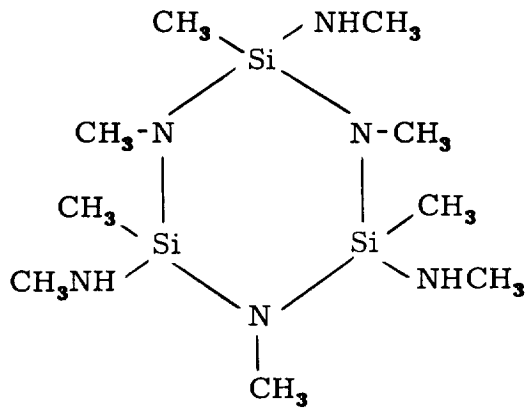
The closest approach to a desirable polymer of this type was made by the reaction of methylamine with a mixture of silicon tetrachloride and methyltrichlorosilane. The initial reaction product was heated to 380°C; and, on cooling, it formed a clear, resinous, colorless, brittle solid that softened at 150-175°C. After 30 minutes in boiling water, the resin retained essentially its original shape; but its surface was deeply cracked and cloudy. It began to disintegrate after 3 minutes in boiling 4% hydrochloric acid, and it disintegrated completely in 10 minutes.

In the course of the work on the polyfunctional chlorosilanes, a crystalline product was isolated from the reaction of silicon tetrachloride with methylamine. The compound was identified as 1,3,5-trimethyl-2,2,4,4,6,6-hexakis(methylamino)cyclotrisilazane. It was unstable to both heat and moisture and polymerized readily to a highly stable friable solid. A crystalline compound was also isolated from the reaction of methyltrichlorosilane with methylamine. It was so unstable that it was not identified, although it had the correct neutral equivalent for material with the repeating unit, $CH_3(CH_3NH)SiNCH_3$.

It melted with decomposition, probably condensation polymerization, in the range of 90-110°C. Elemental analysis and molecular weight determinations were not attempted, because the crystals appeared to change slowly at room temperature in spite of efforts to exclude air and moisture. The crystalline compound may be 1,2,3,4,5,6-hexamethyl-2,4,6-tris(methylamino)cyclotrisilazane.




1,3,5-trimethyl-2,2,4,4,6,6-hexakis(methylamino)cyclotrisilazane




1,2,3,4,5,6-hexamethyl-2,4,6-tris(methylamino)cyclotrisilazane

B. Experimental Details

1. Reaction of methylamine with a mixture of dimethyldichlorosilane and methyltrichlorosilane (9 : 1 molar ratio)

In a 500-ml, 3-neck flask fitted with stirrer, thermometer, reflux condenser, and gas inlet tube were placed 11.6 g (0.09 mole) of dimethyldichlorosilane, 1.5 g (0.01 mole) of methyltrichlorosilane, and 200 ml of dry benzene. Methylamine was passed in through the gas inlet tube, and a positive pressure of methylamine was maintained on the reaction with the aid of a balloon on top of the condenser. The temperature was kept below 35°C. Methylamine was passed in with stirring for 1 hour. As no further reaction appeared to be taking place, the reaction mixture was refluxed for 3 hours. A Beilstein Test for halogens in the supernatant liquid was positive, so methylamine was passed in for another 2 hours. The Beilstein Test was then negative. The reaction mixture was filtered without further refluxing, and the benzene was removed from the filtrate by distillation. The product was distilled under reduced pressure, and 4.5 g of product was obtained including 1.0 g of undistilled brown oil. This oil was 22% of the total product. The distillation data are in Table XVI-A.

2. Reaction of methylamine with a mixture of dimethyldichlorosilane and methyltrichlorosilane (3 : 1 molar ratio)

In a 1000-ml, 3-neck flask fitted with a stirrer, thermometer, reflux condenser, and gas inlet tube were placed 29.0 g (0.225 mole) of dimethyldichlorosilane, 11.2 g (0.075 mole) methyltrichlorosilane, and 600 ml of dry benzene. Methylamine was passed through the gas inlet tube for 2 hours while the reaction mixture was being stirred and the temperature was kept below 35°C. The reaction mixture was refluxed for 3 hours. After standing overnight under an atmosphere of nitrogen, the clear supernatant layer was positive to the Beilstein Test for halogens. Consequently, methylamine was passed in for two additional hours; the Beilstein Test was then negative. The reaction mixture was filtered, and the benzene was removed from the filtrate by distillation. The product was distilled, and the results are given in Table XVI-B. The total product was 21.9 g of which 2.8 g or 13% was undistillable oil.

Table XVI. Distillation of Products from the Reactions of Methylamine with Mixtures of Dimethyldichlorosilane and Methyltrichlorosilane

| Fraction number | Pressure, mm, Hg | Vapor temperature, °C | Pot temperature, °C | Weight, g |
|---|---|---|---|---|
| A. Ratio of di- to trichloride, 9:1 | | | | |
| 1 | 10 | 75-78 | 80-100 | 2.7 |
| 2 | 3.5 | 79-80 | 100-135 | 0.8 |
| 3 | 1 | residue, gray-brown oil | | 1.0 |
| Total | | | | 4.5 |
| B. Ratio of di- to trichloride, 3:1 | | | | |
| 1 | 14 | 90-97 | 98-107 | 11.2 |
| 2 | 10 | 96-97 | 104-115 | 2.5 |
| 3 | 8 | 99-102 | 109-113 | 5.4 |
| 4 | 1.5 | residue, brown oil | | 2.8 |
| Total | | | | 21.9 |
| C. Ratio of di- to trichloride, 1:1 | | | | |
| 1 | 16 | 88-94 | 107-109 | 1.3 |
| 2 | 16 | 94-101 | 109-116 | 5.1 |
| 3 | 11 | 94-102 | 106-116 | 5.8 |
| 4 | 11 | 102-114 | 116-125 | 5.7 |
| 5 | 8 | 112-119 | 125-132 | 4.5 |
| 6 | 8 | 119-125 | 132-140 | 5.3 |
| 7 | 4 | 108-115 | 124-140 | 1.3 |
| 8 | 1 | 97-108 | 120-135 | 2.0 |
| 9 | 1 | residue, brown oil | | 4.0 |
| Total | | | | 35.0 |

3. Reaction of methylamine with a mixture of dimethyldichlorosilane and methyltrichlorosilane (1 : 1 molar ratio)

In a 500-ml, 3-neck flask fitted with a stirrer, gas inlet tube, reflux condenser, and thermometer were placed 250 ml of benzene, 25.8 g (0.2 mole) of dimethyldichlorosilane and 29.9 g (0.2 mole) of methyltrichlorosilane. Methylamine was passed in slowly for 6 hours while the temperature was kept below 35°C. After the mixture had stood overnight, methylamine was passed in again for 6 hours. A positive pressure of amine was kept on the reaction by means of an inflated balloon on the reflux condenser. The hydrochloride was removed from the reaction by filtration, and more methylamine was passed in for 3 hours with stirring. The remainder of the hydrochloride was filtered off, and the product was distilled according to the data of Table XVI-C. The total product was 35 g of which 11% was undistillable oil.

4. Attempt to polymerize distillable products of methyltrichlorosilane reactions

Two distilled products from the reaction of methylamine with mixtures of dimethyldichlorosilane and methyltrichlorosilane were combined and refluxed to determine if they would polymerize at an elevated temperature. It was reasoned that if cyclization did not terminate each chain, end-amino groups would result from the excess of methylamine that had been used, and further polymerization could be induced by end-group condensation. Hence, Fractions A-1 and B-1 of Table XVI were combined and refluxed for 25 hours at 205-210°C. Methylamine was evolved slowly, and the liquid became slightly cloudy and yellow. The product was then fractionated by distillation, and 72% of the weight of starting material was recovered. Forty percent boiled in the same range as the starting material, 23% boiled higher (95-173°C at 0.15 mm pressure), and 13% was an oil that did not distil at 173°C at 0.15 mm. Evidently some polymerization occurred but not to the desired extent.

5. Reaction of methylamine with methyltrichlorosilane

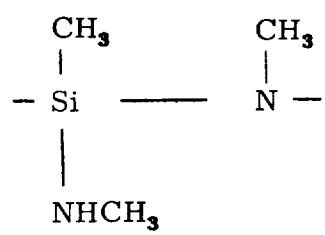
The reaction of methyltrichlorosilane with methylamine was carried out as follows: In a 1-liter, 3-neck, round-bottom flask fitted with a stirrer, thermometer, reflux condenser, and gas inlet tube were placed 74.8 g (0.5 mole) of methyltrichlorosilane and 700 ml of dry benzene. Methylamine was supplied by allowing it to distill from a flask containing liquid methylamine and a small amount of sodium. The benzene solution was stirred under an atmosphere of methylamine for 1.5 hour, and then it was filtered to remove the excessive amount of solid that was causing stirring to be ineffective. Stirring of the filtrate under methylamine was resumed and continued for 1.5 hours. The mixture was refluxed for 2 hours, and then allowed to settle. The Beilstein Test revealed that halogens were absent from the clear supernatant liquid. The reaction mixture was filtered, and most of the benzene was removed from the filtrate by distillation under reduced pressure, the temperature being kept below 80°C. The crude reaction product containing some benzene was heated in an open test tube over a gas flame. The melt temperature rose gradually over a period of 3.2 hours from 100°C to 380°C. Bubbling occurred throughout the entire period as the melt became more viscous. On cooling to room temperature, a soft, cloudy solid was obtained. Further heating for 0.3 hour raised the melt temperature to 410°C. The cooled product was a hard, transparent, amber, brittle solid that became soft when heated to 100°C. It was soluble in benzene. Attempts were then made to distill the crude reaction product. The pressure was reduced to 18 mm, and as the pot temperature rose to 58°C, the odor of methylamine was detectable in the pump exhaust. The pressure was lowered to 8 mm, and the temperature was raised slowly to 130°C, but apparently nothing distilled except methylamine. Later a small amount of insoluble resin was found in the dry-ice trap of the distilling apparatus.

The undistilled liquid was refluxed at atmospheric pressure for 7 hours during which time the temperature gradually rose to 350°C. The odor of methylamine was strong throughout the refluxing period. The liquid cooled to a tough, sticky gum that was colorless and transparent. When heated on a steel spatula, it solidified to a vitreous coating of excellent thermal stability.

A small amount of the gum was heated further in an atmosphere of nitrogen. It foamed and became progressively more viscous showing that it was capable of further polymerization.

Another reaction of methylamine with methyltrichlorosilane was run in the same manner, except that the temperature was never allowed to rise above 80°C. Reduced pressure was used, but the distillation was stopped while a small amount of benzene remained in the product. When cooled, most of the product crystallized.

The crude crystals were recrystallized twice from benzene while care was taken to avoid heating above 60°C. The product had a neutral equivalent of 52.9 and a melting point of 90-110°C with decomposition. No further attempts were made to refine or to analyze the product, because it appeared to be somewhat unstable even at room temperature in a nitrogen atmosphere. The neutral equivalent would be 51.1 for a compound with this repeating unit:




The product may have been the corresponding cyclic trisilazane.

6. Repetition of the reaction of ammonia with dimethyldichlorosilane and methyltrichlorosilane (1 : 1 molar ratio)

The preceding annual report[39] described the initial experiments that produced undistillable polymers by treating mixtures of methyltrichlorosilane and dichlorodimethylsilane with ammonia. The procedure was repeated to obtain material for studies of hydrolytic stability.

In a 5-liter, 3-neck flask fitted with stirrer, reflux condenser, thermometer, and gas-inlet tube, were placed 1800 ml of benzene, 64.53 g (0.5 mole) of dimethyldichlorosilane, and 74.74 g (0.5 mole) of methyltrichlorosilane. The solution was stirred, and ammonia was passed in for 4.5 hours while the temperature was kept below 50°C. During the entire addition of ammonia, a balloon was kept on the condenser to maintain a positive pressure of ammonia. After being refluxed for 3 hours the reaction mixture was cooled and filtered. The clear supernatant liquid was negative to the Beilstein Test for halogens. The following fractions were obtained:

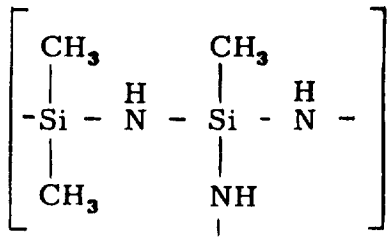
| | | |
|---|---|---|
| Fraction 1: | 6.0 g, | b.p. 45-125°C, 2 mm pressure |
| Fraction 2: | 7.1 g, | b.p. 125-195°C, 2 mm pressure |
| Fraction 3: | 10.4 g, | b.p. 195-245°C, 2 mm pressure |
| Fraction 4: | 15.2 g, | residue, not volatile at 320°C, 2 mm pressure |
| | 38.7 g | |

The neutral equivalents of Fraction 3 and of the residue were 71.5 and 72.4, respectively (theoretical, 48.8). The data on these two fractions, including the results of elemental analyses, are summarized in Table XVII. The data on hydrolytic stability are in Section IV.

Table XVII. **Elemental Composition and Neutral Equivalents of Silazanes Made with Equimolar Mixture of Di-and-Tri Chlorosilanes**

| Element | Found, % | Theoretical, %[a] |
|---|---|---|
| **Fraction 3** | | |
| Carbon | 23.01 | 24.62 |
| Hydrogen | 7.45 | 8.26 |
| Nitrogen | 22.93 | 28.73 |
| Silicon | 40.7 | 38.39 |
| Total | 94.09 | 100.00 |
| Neutral equivalent | 71.5 | 48.8 |
| Molecular weight (cryoscopically in benzene) | 900 | |
| **Fraction 4** (residue) | | |
| Carbon | 24.09 | 24.62 |
| Hydrogen | 7.19 | 8.26 |
| Nitrogen | 21.24 | 28.73 |
| Silicon | 42.3 | 38.39 |
| Total | 94.82 | 100.00 |
| Neutral equivalent | 72.4 | 48.8 |
| Molecular weight (cryoscopically in benzene) | 2500 | |

a



$C_3H_{12}N_3Si_2$

7. Identification of the crystalline reaction product made from silicon tetrachloride and methylamine

When silicon tetrachloride was treated with methylamine in earlier studies,[40] a crystalline, benzene-soluble, moisture-sensitive, heat-sensitive product was obtained; but it was not identified. This compound was needed for studies of the influence of structure on properties and for attempts to achieve high molecular weight products by amine exchange. Hence, the synthesis was repeated to obtain additional quantities of material.

The compound was thought to be the cylic trimer. However, the initial elemental composition[40] did not agree precisely with the theoretical values. The preparation was repeated with special precautions to exclude moisture during recrystallizations, and the data of Table XVIII were obtained. The agreement of the actual and theoretical analytical values confirmed the identity as the cyclic trimer, 1,3,5-trimethyl-2,2,4,4,6,6-hexakis(methylamino)cyclotrisilazane.

8. Reaction of methylamine with a mixture of methyltrichlorosilane and silicon tetrachloride (4:3 molar ratio)

A mixture of silicon tetrachloride and methyltrichlorosilane was aminated in the following manner: 31.9 g (0.19 mole, 0.75 equivalent) of silicon tetrachloride and 37.4 g (0.25 mole, 0.75 equivalent) of methyltrichlorosilane were dissolved in 1 liter of benzene and stirred under an atmosphere of methylamine for 8.5 hours. The mixture was refluxed for 1.5 hours, cooled, and filtered. The benzene was removed by distillation at reduced pressure. The product, 45 g, was a clear, colorless oil.

Table XVIII. Elemental Composition and Physical Data on 1, 3, 5-Trimethyl-2, 2, 4, 4, 6, 6-hexakis(methylamino)cyclotrisilazane

| | Found | | Theoretical for $(C_3H_{11}N_3Si)_3$ |
|---|---|---|---|
| | Previous[a] | Latest | |
| Elemental analysis | | | |
| Carbon, % | 33.75 | 29.64 | 30.73 |
| Hydrogen, % | 9.70 | 9.40 | 9.46 |
| Nitrogen, % | 35.59 | 35.05 | 35.85 |
| Silicon, % | 23.1 | 23.2 | 23.96 |
| Total | 102.14 | 97.29 | 100.00 |
| Molecular weight (cryoscopic in cyclohexane) | 370 | 430 | 351.7 |
| Neutral equivalent (hydrolyzed) | 43 | 42 | 39.1 |
| Melting point, °C | 116-121 | 116-122 | |

[a] Earlier work to identify this compound was described in the Annual Summary Report, Contract NAS 8-1510, dated February 28, 1962, page 10.

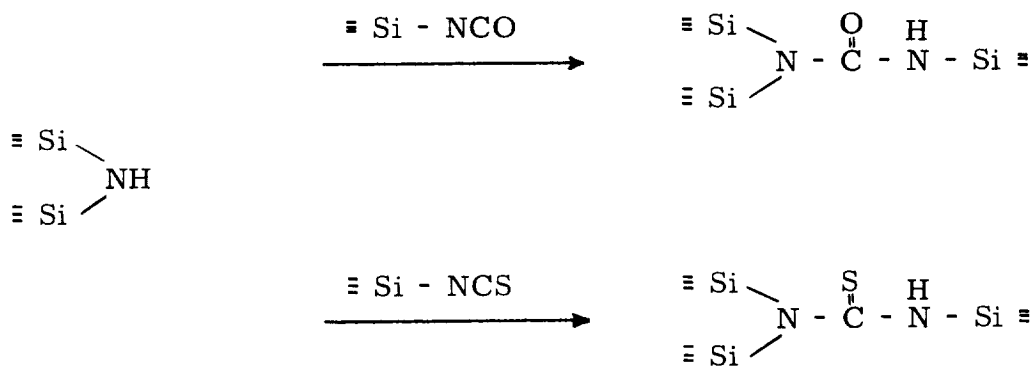
Several attempts were made to polymerize the colorless oil by heating in a test tube. The liquid foamed when the temperature first went above 300°C. Continued heating caused a gradual increase in viscosity, and finally the melt solidified when the temperature reached about 420°C, although accurate temperature measurement was not possible because of excessive foaming. Repeated attempts to produce a clear, resinous solid with a high softening point were only partially successful. The highest softening point obtained was in the range of 150-175°C; and the cool polymer was brittle, clear, and colorless. Successful polymerization by this method appeared to be limited by high viscosity in the range of 300-400°C which caused most of the material to be in the form of foam.

Additional attempts were made to polymerize the mixture of silylamines obtained by the reaction of methylamine with methyltrichlorosilane and silicon tetrachloride. The intention was to determine whether polymerization by heat could be conducted slowly enough to produce an unfoamed solid with a high softening point. Small amounts of the liquid silylamine were placed in three glass tubes which were then swept with nitrogen and capped with crimped aluminum foil. The tubes were heated at temperatures of 180°C, 250°C, and 300°C until the liquids solidified. The tubes were examined periodically to learn whether any non-foamed solid had been produced. In no case was a non-foamed solid formed. An infusible foam formed above the liquid in each tube, and the foam increased in quantity until all of the liquid had foamed and solidified. The non-foamed liquids were highly viscous before they foamed and solidified. The periods required to reach the solidified states at the various temperatures were: 300°C, 7 hours; 250°C, 22 hours; 180°C, 65 hours. The sample heated at 180°C did not become completely solid in 65 hours, but most of it had foamed and solidified at that time, and there seemed to be no purpose in heating it longer.

# X. SILICON-NITROGEN COMPOUNDS WITH AMIDE LINKAGES

## A. Discussion

Silicon isocyanates and isothiocyanates were of interest because of their anticipated ability to form new types of silicon-nitrogen compounds with amide linkages that might have useful physical and chemical properties.




Silicon isocyanates and isothiocyanates reacted with the silylamines as expected; but the products had low molecular weights; and, as yet, no evidence of outstanding stability has been obtained.

A third type of reaction was reported by Hurwitz, Park, and de Benneville[41] who treated acetamide in triethylamine with triphenylchlorosilane.

$$CH_3\overset{O}{\overset{\|}{C}}NH_2 + (C_6H_5)_3SiCl \longrightarrow CH_3\overset{O}{\overset{\|}{C}}-\overset{H}{N}-Si(C_6H_5)_3$$

Their patent mentioned nothing about hydrolytic and thermal stability. We wished to make polymers by treating difunctional chlorosilanes with diamides, but the preferred first step appeared to be to determine whether the sought-after structure would be stable. Acetamide and diphenyldichlorosilane were available, and so they were reacted by the Hurwitz method. The product obtained was believed to be diphenyldiacetamidosilane, although it was not fully characterized.

$$2CH_3\overset{O}{\overset{\|}{C}}NH_2 + (C_6H_5)_2SiCl_2 \longrightarrow CH_3\overset{O}{\overset{\|}{C}}-\overset{H}{N}-\underset{\underset{C_6H_5}{|}}{\overset{\overset{C_6H_5}{|}}{Si}} - \overset{H}{N} - \overset{O}{\overset{\|}{C}}CH_3$$

The crystalline compound melted at 120-125°C, and it became liquid within a few minutes when exposed to atmospheric moisture. Time was not available to confirm the identity and to compare the moisture sensitivity of the product with that of other silicon-nitrogen compounds as described in Section IV.

## B. Experimental Details

### 1. Reaction of dimethylsilicondiisocyanate with hexamethylcyclotrisilazane

The first reaction of dimethylsilicondiisocyanate with hexamethylcyclotrisilazane was conducted as follows: Dimethylsilicondiisocyanate, 2.0 g (0.014 mole), 3.09 g (0.014 mole) of hexamethylcyclotrisilazane, and 10 ml of dry benzene were placed in a 50-ml, 3-neck flask fitted with a thermometer, condenser, and magnetic stirrer. The system was flushed with nitrogen, and then nitrogen was introduced slowly through a capillary tube acting as an ebullator. The solution was refluxed for 6 hours. The color became pale yellow, but no other evidence of reaction was seen. The product was distilled carefully through a 6-inch Vigreux column. After the benzene was removed, the first drop of higher-boiling material distilled at 28°C at 15 mm pressure. Thereafter the boiling point rose steadily until the vapor temperature reached 102°C at 0.2 mm pressure while the pot temperature was 165°C. The distillate weighed 1.6 g and the residue weighed 2.1 g. The yield should have been 5.09 g if the isocyanate and silazane reacted in the conventional manner.

It was evident that the product was different from the starting material, but information was needed on the nature of the product. Titration of the two fractions with standard acid revealed that the titratable base in the products was 56% of that in the starting materials, whereas the weight was 73%. Hence titratable base had disappeared. The only end-point in an electrometric titration of the distillate was at pH 3.5; but there were two end-points, one at 6.5 and one at 3.5, for the residue. Silazanes exhibit only one end-point at about 5.5. Neither starting material could have been present in the undistillable product, which contained less titratable base than a simple silazane. These observations might be explained by assuming reaction of the isocyanate with the silazane to fix some of the nitrogen in a non-titratable form.

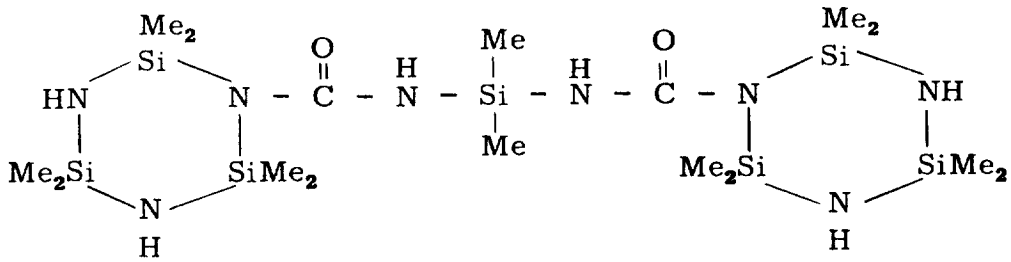
The molecular weight of the distillate, as measured cryoscopically in cyclohexane was 310 (average of 318 and 306). The molecular weight of the residue was 350 (average of 346 and 353). The data on the reaction products are summarized in Table XIX.

Table XIX. Products from the First Reaction of Dimethylsilicondiisocyanate and Hexamethylcyclotrisilazane

| | Volatile product | Residue | Theoretical[a] A | Theoretical[a] B |
|---|---|---|---|---|
| **Elemental analysis** | | | | |
| Carbon, % | 34.02 | 33.43 | 33.06 | 33.21 |
| Hydrogen, % | 7.21 | 8.02 | 8.32 | 7.52 |
| Nitrogen, % | 16.49 | 17.45 | 19.28 | 19.36 |
| Oxygen, % (by difference) | 18.68 | 14.30 | 5.51 | 8.85 |
| Silicon, % | 23.6 | 26.8 | 33.83 | 31.06 |
| Neutral equivalent | | | 145.3 | 361.7 |
| First end-point, pH 6.5 | - | 267 | | |
| Second end-point, pH 3.5 | 183 | 130 (total titration) | | |
| Molecular weight | 310 | 350 | 581.3 | 361.7 |

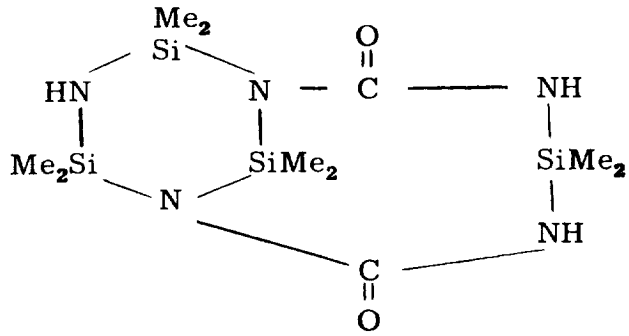
[a] For

A.



$C_{16}H_{48}N_8O_2Si_7$

B.



$C_{10}H_{27}N_5O_2Si_4$

In a second reaction, an attempt was made to obtain a higher molecular weight by omitting the solvent. Equimolar quantities of hexamethylcyclotrisilazane (2.0 g, 0.014 mole) and dimethylsilicondiisocyanate (3.09 g, 0.014 mole) were mixed and heated at 160°C for 8 hours. The product was distilled to yield 1.9 g of distillate with a molecular weight of 280 and 2.2 g of residue with a molecular weight of 530. The change in conditions did not produce a significant improvement.

2. Reaction of dimethylsilicondiisocyanate with 2,2,4,4,6,6,8,8-octamethyl-1,5-dioxa-3,7-diazacyclooctasilane

A fresh batch of the oxa-azacyclooctasilane was prepared by the method described in a previous report.[19]

In a 25-ml, 3-neck flask fitted with a thermometer, reflux condenser, nitrogen ebullator, and magnetic stirrer were placed 2.0 g (0.014 mole) of dimethylsilicondiisocyanate and 4.1 g (0.014 mole) of the oxa-azacyclooctasilane. Moisture was excluded, and the system was flushed with nitrogen. The reactants were refluxed at 146°C for 8 hours. The product was distilled, and the following fractions were obtained: 2.1 g, bp 77-100°C at 5 mm pressure; and 3.7 g, not distillable at 155°C at 5 mm.

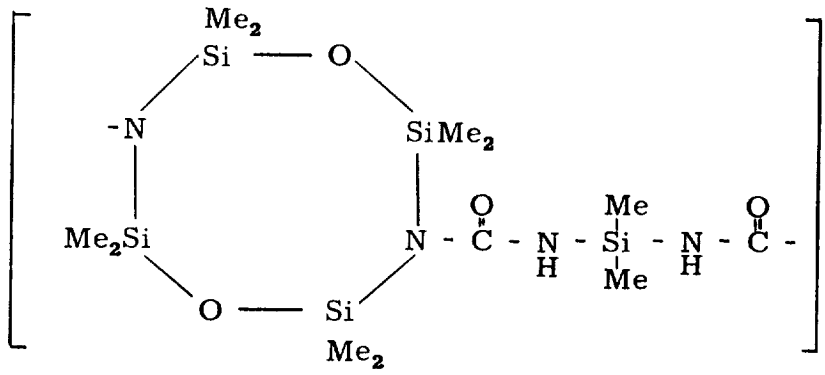
The molecular weight of the distilled part was 320 and that of the remainder was 500, as determined cryoscopically in cyclohexane. Consequently, it appears that the distillate was largely unreacted oxa-azacyclooctasilane.

The undistilled product, 3.7 g, did not distill at 155°C at 5 mm pressure, but 2.7 g of it did distill at 279-305°C at atmospheric pressure leaving 0.8 g of residue. The residue was a brown viscous liquid that appeared to be decomposing at 305°C. The molecular weight of the second distilled fraction was 400, as estimated cryoscopically in cyclohexane. The data obtained on the various fractions of the product from this reaction are given in Table XX.

Table XX. Product Obtained by the Reaction of Dimethylsilicondiisocyanate with 2, 2, 4, 4, 6, 6, 8, 8-Octamethyl-1, 5-dioxa-3, 7-diazacyclo-octasilane

| | Fraction 1 | Fraction 2 | Residue | Theoretical[a] |
|---|---|---|---|---|
| B.P., °C | 77-100 | 279-305 | >305 | |
| Pressure, mm Hg | 5 | atm | atm | |
| Weight, g | 2.1 | 2.7 | 0.8 | |
| Carbon, % | 34.04 | 34.80 | 33.50 | 32.99 |
| Hydrogen, % | 7.85 | 7.16 | 7.97 | 7.38 |
| Nitrogen, % | 11.58 | 12.34 | 10.63 | 12.83 |
| Silicon, % | 32.0 | 29.9 | 30.10 | 32.15 |
| Oxygen, %[b] | 14.53 | 15.80 | 17.80 | 14.65 |
| Molecular weight | 320 | 400 | | 436.86 |
| Neutral equivalent | 198 | 280 | | c |

[a] For



, $C_{12}H_{32}N_4O_4Si_5$

[b] By difference.

[c] Probably not titratable as a base.

3. Preparation of dimethylsilicondiisothiocyanate

Some uncertainty was involved in determining the method for preparation of dimethylsilicondiisothiocyanate. The preparation of dimethylsilicondiisothiocyanate was described by Anderson,[42] who treated silver isothiocyanate with dimethyldichlorosilane. We were not able to find a source of a material that was called silver isothiocyanate. However, it was apparent from a search of the literature that only the iso form of the silver thiocyanates exists, and that form has been called silver thiocyanate by most writers. The only other source of information found on the siliconisothiocyanates or siliconthiocyanates was the patent of Joyce[43] who prepared dimethylsilicondithiocyanate from lead thiocyanate. Thus, we have the method and data of Joyce on the "thio" compound and the data of Anderson on the "isothio" compound. The two writers gave approximately the same melting and boiling points for the two compounds. The compound we made by the Joyce method had the correct molar refraction as calculated for the thio compound by Anderson. Anderson calculated the molar refractions for both compounds, but he made only the isothio compound. By heating the thio compound made by the Joyce method, we apparently converted it to the isothio compound, because the product had the correct molar refraction, according to Anderson, for the isothio compound. The conversion of organic thiocyanates to isothiocyanates is well known.[44]

In accordance with the method of Joyce[43], 50 g (0.388 mole) of dimethyldichlorosilane was dissolved in 400 ml of benzene in a 1-liter, 3-neck flask fitted with a thermometer, stirrer, and reflux condenser. Lead thiocyanate, 129.35 g (0.40 mole) was added in four equal portions at 30-minute intervals with stirring; and the mixture was refluxed for 3 hours. The product, 46.4 g (0.27 mole), distilled at 82-86°C at 5 mm pressure. This boiling point is equivalent to the 216-218°C at atmospheric pressure reported by Joyce.[43] Joyce called this compound dimethylsilicondithiocyanate. Anderson[42] described both the thio and isothio compounds and gave their molar refractions. According to Anderson,[42] the molar refraction of the thio compound was 45.64, which agrees with the observed value, 45.87, for the compound we made by the method of Joyce.

Hofmann[44] converted organic thiocyanates to isothiocyanates by heating. Accordingly the dimethylsilicondithiocyanate was refluxed for 8 hours at 220°C and then distilled to obtain 37.4 g of product boiling at 74-77°C at 2.5 mm. The molar refraction of the product was 49.58, which is reasonably close to Anderson's value of 50.07 for dimethylsilicondiisothiocyanate.

4. Reaction of dimethylsilicondiisothiocyanate with hexamethylcyclotrisilazane

In a 25-ml, 3-neck flask fitted with a stirrer, thermometer, and reflux condenser were placed 4.39 g (0.02 mole) of hexamethylcyclotrisilazane and 3.59 g (0.02 mole) of dimethylsilicondiisothiocyanate. The solution was refluxed for 7 hours at 220°C. The solution became yellowish-brown, but no solid formed. The product was distilled, and the boiling point gradually increased from 120°C at 1.5 mm to 215°C at 1.5 mm while 5.8 g distilled. The residue, 0.5 g, would not distill at 320°C at 1.5 mm. After cooling it was a viscous brown liquid. The distillate had an acid reaction in water, and the residue had a neutral equivalent of 342. Reaction between the isothiocyanate and the silazane undoubtedly occurred, but satisfactory polymerization did not.

5. Reaction of dimethylsilicondiisothiocyanate with 2,2,4,4,6,6,8,8-octamethyl-1,5-dioxa-3,7-diazacyclooctasilane

In a 25-ml, 3-neck flask fitted with a stirrer, thermometer, reflux condenser, and gas inlet tube were placed 5.89 g (0.02 mole) of 2,2,4,4,6,6,8,8-octamethyl-1,5-dioxa-3,7-diazacyclooctasilane and 3.59 g (0.02 mole) of dimethylsilicondiisothiocyanate. The solution was heated for 9 hours at 160°C. The solution became yellowish-brown, but no solid formed. The product was distilled, and the boiling point gradually increased from 115°C at 1.0 mm to 200°C at 1.0 mm while 7.3 g distilled. The residue, 1.7 g, did not distill at a pot temperature of 270°C at 1 mm. The residue was a viscous, dark brown liquid. The distilled fraction formed an acidic solution when placed in a mixture of ethyl alcohol and water. The neutral equivalent of the residue was 384. Again reaction occurred, but polymerization did not.

6. Reaction of diphenyldichlorosilane with acetamide

The Hurwitz procedure[41] was applied to acetamide and diphenyldichlorosilane as follows: In a 500-ml, 3-neck, round-bottom flask fitted with a thermometer, stirrer, reflux condenser, and dropping funnel were placed 5.0 g of acetamide (0.08 mole), 20.0 g of triethylamine (0.20 mole), and 200 ml of benzene. To this, 10.7 g (0.04 mole) of diphenyldichlorosilane in 100 ml of benzene was added dropwise with stirring over a period of 30 minutes while the temperature was kept at 0-4°C. The mixture was refluxed for 2 hours, the amine hydrochloride salt was filtered off, and about half of the benzene was removed by distillation. When the solution was cooled, white needle-like crystals formed. A small portion of these was recrystallized twice from benzene in a nitrogen atmosphere to yield material melting at 115-125°C and containing 9.6% nitrogen (theory, 9.4%). This analytical result was encouraging, and so the entire batch was recrystallized three times from benzene to yield 4.0 g, m.p. 120-125°C. However, the elemental analysis did not confirm the expected structure.

Found: C, 56.80%; H, 6.18%; N, 7.78%

Calculated for $(CH_3CONH)_2Si(C_6H_5)_2$: C, 64.40%; H, 6.08%; N, 9.39%

The crystals were soluble in acetone, but in water they turned to a wax-like mass. They were stable in the dry air of a desiccator, but they liquefied within a few minutes in the laboratory air. When heated on a spatula, the material smoked and gave no evidence of polymerizing.

When the crystalline material was heated in a test tube with a thermometer, it began to evolve gas or boil at 230°C. At 250°C the odor of acetamide was apparent, and a second liquid phase began to appear. Evidently the thermal stability was not outstanding.

# XI. ATTEMPTED FORMATION OF SILAZANES THROUGH SILICON ISONITRILES

## A. Discussion

Dimethyldiisocyanosilane was desired as an intermediate for making silicon-nitrogen polymers by the following type of reaction.

$$(CH_3)_2Si(NC)_2 + NH_3 \longrightarrow \left[ - Si(CH_3)_2 - \overset{H}{N} - \right]_n$$

This reaction is comparable to the reaction of ammonia with chlorosilanes. However, it was thought possible that the tendency to cyclize might be less with the isocyanosilanes than with the chlorosilanes, and there might be some advantage in avoiding the hydrochloric acid that is produced by the chlorosilanes.

The possibility of forming silicon-nitrogen polymers by this method was suggested by the work of McBride and Beachell[45] who made polymeric siloxanes by the reaction of dimethyldiisocyanosilane with water.

The preparation of dimethyldiisocyanosilane proved to be tedious; and so it was necessary to confine the experiments to one each with ammonia, methylamine, and ethylenediamine. The first two produced only high-boiling oils. The reaction with ethylenediamine produced an elastomeric material with high thermal stability but low strength. It resembled the materials previously made by heating ethylenediamine silazane in air.

## B. Experimental Details

### 1. Preparation of dimethyldiisocyanosilane

Dimethyldiisocyanosilane was prepared by treating dimethyldibromosilane with silver cyanide according to the method of McBride and Beachell.[45] Two methods have been used to prepare dimethyldibromosilane. One was the brominolysis of dimethyldiphenylsilane, which was described by McBride and Beachell.[45] The other is the method of Rochow[46], who treated silicon with methyl bromide in the presence of copper.

$$2\ MeBr + Si \xrightarrow[300^\circ C]{Cu} Me_2SiBr_2$$

Silicon was pulverized to pass a 40-mesh screen, and then it was mixed in the ratio of 80 : 20 with finely powdered copper. The mixture was placed in an 18-mm Pyrex tube so that the packed length was 30 cm. A thermocouple was located at the center of the packed section of the tube. The tube was swept with methyl bromide and heated in a tube furnace to 290-295°C. Methyl bromide was passed through at the rate of about 0.5 cu ft per hour. The product was condensed in a dry-ice trap and distilled to obtain the dimethyldibromosilane. Precise yield figures were not obtained, because the tube was not repacked after each run, and the object was to prepare the compound rather than to develop the method. The process could be controlled fairly well by observing whether a condensable liquid formed in the tube downstream from the packed section. Finally 63 g of dimethyldibromosilane, b.p. 112-114°C, was accumulated.

Dimethyldibromosilane, 54.5 g (0.25 mole), was dissolved in 150 ml of benzene in a 500-ml, 3-neck flask fitted with a stirrer, thermometer, and reflux condenser. Silver cyanide, 73.0 g (0.55 mole), was added with stirring over a period of 1.5 hours while the temperature increased from 24-40°C and the color became bright yellow. The mixture was refluxed for 2.5 hours and then allowed to settle. The supernatant liquid was decanted, and the residue was washed with three 100-ml portions

of warm benzene. The liquids were combined and distilled in a 1.2 x 30 cm column packed with glass helices to yield the following fractions:

I, 15.6 g, b.p. 40-81°C at 75 mm

II, 3.6 g, b.p. 81-83°C at 75 mm, m.p. 78-85°C

III, 3.3 g, residue

Fraction II was dimethyldiisocyanosilane, 0.033 mole (11% yield).

2. Reaction of dimethyldiisocyanosilane with ammonia, methylamine, and ethylenediamine

The reaction with ammonia was carried out in a 100-ml, 3-neck flask. Dimethyldiisocyanosilane, 2.5 g (0.023 mole), in 50 ml of benzene was stirred in an atmosphere of ammonia for 1.75 hour. A precipitate formed, and the mixture was refluxed for 2.5 hours. The reaction mixture was centrifuged to yield 0.6 g of precipitate, whereas the theoretical amount for complete conversion to ammonium cyanide would have been 2.0 g. The solvent was removed from the filtrate by distillation, and 1.3 g of light brown oil that did not distill at 180°C was obtained. There was no evidence of polymerization as indicated by high viscosity. Only 0.2 g of the 1.3 g failed to distill at 150°C at 5 mm pressure. The products were probably volatile silazanes.

The experiment with methylamine was conducted in the manner just described for ammonia. The light brown, oily product weighed 0.9 g. It did not distill at 190°C; but all of it distilled at less than 127°C at 5 mm. Hence, no significant polymerization occurred with either ammonia or methylamine.

The experiment with ethylenediamine was conducted as follows: Ethylenediamine, 4.15 g (0.069 mole) was added with stirring to 2.5 g of dimethyldiisocyanosilane dissolved in 50 ml of benzene. The addition required 0.75 hour, and the mixture was refluxed for 3 hours. The reaction mixture was separated into two layers by centrifugation. The solvent was removed from the benzene layer by distillation. All of the volatile material had distilled when the vapor temperature reached 40°C at 50 mm pressure. A reddish rubbery residue, 0.6 g, remained in the pot. It had very little strength, but it did not fully decompose on a spatula at red heat.

# XII. SILYLHYDRAZINE POLYMERS

## A. Discussion

Hydrazine was studied as a possible starting material for making silicon-nitrogen polymers. Because of its tetrafunctionality and composition, it offered possibilities for making high-molecular-weight polymers that would be relatively non-combustible. The direct reaction of hydrazine with methyl- and phenyl-substituted chlorosilanes produced polymers, but the molecular weights were too low for their physical properties to be valuable. The hydrolytic stability of the polymer formed by the reaction of hydrazine with diphenyl silylhydrazine was relatively high, but in the absence of interesting physical properties work on the hydrazine derivatives was not continued.

### 1. Diphenylsilylhydrazine polymer

A polymer made from diphenyldichlorosilane and hydrazine proved to be approximately as stable to moisture as hexaphenylcyclotrisilazane. It was not completely hydrolyzed by boiling for 6 hours with 0.1 N sulfuric acid. It underwent condensation polymerization to a brittle solid with a loss of 32% in weight when it was heated to 500°C, and the total loss was 39% when it was heated to red heat. On heating the polymer in a sealed tube at 450°C for 1.5 hours, 15.2 ml of permanent gas per gram of polymer was evolved; this value classes the polymer as having low thermal stability (Section V). The product of condensation polymerization was a brown, friable, infusible solid. We did not succeed in making high-quality coatings on aluminum with this material.

2. Methylsilylhydrazine (di-tri) polymer

A polymer was made from hydrazine and an equimolar mixture of dimethyldichlorosilane and methyltrichlorosilane. The trifunctional silicon compound was added to increase the chances of obtaining a high-molecular-weight polymer. The product was soluble in benzene until the last stages of the preparation. When the temperature was raised and the pressure was lowered to remove the last traces of benzene, the product solidified; and it was thereafter infusible and only partially soluble in acetone or benzene. This behavior suggested the presence of reactive hydrazine end groups which condensed to form a cross-linked polymer. A thermogravimetric analysis (Section V) showed that this compound lost 30% of its weight on being heated to 530°C, and then it rapidly lost an additional 55% on being heated to 630°C. Evidently the thermal stability of the methylsilylhydrazine made with a mixture of di- and tri-functional compounds is not outstanding.

B. Experimental Details

1. Diphenylsilylhydrazine polymer

The diphenylsilylhydrazine polymer was prepared in the following manner: In a 500-ml, 3-neck flask equipped with a stirrer, dropping funnel, and reflux condenser were placed 15.85 ml (16.03 g, 0.5 mole) of hydrazine and 150 ml of dry benzene. The hydrazine was previously dried by fractional crystallization until the freezing point reached 1.2°C. According to Audrieth,[47] this freezing point indicates 99.2 +% purity. The system was swept with dry nitrogen. The hydrazine-benzene mixture was stirred, and 34.6 ml (42.2 g, 0.166 mole) of diphenyldichlorosilane was added in drops over a period of 1.5 hour while the temperature rose to 50°C. The mixture was refluxed for 2 hours. The Beilstein Test for halogens was positive, and so 1 ml (1.01 g, 0.03 mole) of hydrazine was added. After an hour of refluxing the Beilstein Test was negative. The product was filtered; the benzene was removed by distillation, and 38 g of pale-yellow, cloudy solid was obtained. The final pot conditions were 150°C at 3 mm pressure. On heating in a capillary melting-point tube, the powdered solid began to sinter at 85°C and flow at 100°C. The molecular weight was determined cryoscopically in benzene to be 1100. The results of the elemental analysis of the diphenylsilylhydrazine polymer are in Table XXI. Because it had a

molecular weight of 1100, its volatility was believed to be low enough for a thermogravimetric analysis to be performed on the original polymer as obtained from the hydrazine-chlorosilane reaction. However, the weight loss on heating to 740°C, as shown in Section IV, was 65%. In contrast, when the polymer was heated to red heat in a test tube, the loss was only 39%. Obviously, heating in the test tube resulted in further polymerization of some volatile components that were lost under the conditions of the thermogravimetric analysis.

In an effort to gain insight into the nature of the thermal condensation of the diphenylsilylhydrazine, a batch was heated to 430°C, and a sample was taken for determination of elemental composition and molecular weight (Table XXI). It appeared that the molecular weight had gone down rather than up. Continued heating to red heat produced a foamed, brown solid that contained the original elements: carbon, hydrogen, silicon, and nitrogen. The analytical results (Table XXI) were not informative because of the failure to account for all of the material in the sample, except in the case of the prepolymer that was obtained by heating to 430°C. This is regarded as another example of the difficulty in obtaining reliable analytical data on the silicon-nitrogen compounds. For the purpose of checking the low value reported for nitrogen (6.84%) in the original polymer, we attempted to hydrolyze it by refluxing 0.2123 g (1.00 milliequivalent if $Ph_2SiN_2H_2$ was the formula) for 6 hours with 2.38 milliequivalents of standard 0.0953 N sulfuric acid. Back titration with standard alkali required 2.01 milliequivalents to the first end point at pH 5.3 and 0.46 milliequivalents to the second end point at pH 9.7. According to this titration, the hydrazine freed by hydrolysis was 0.46 milliequivalents or 46% of the amount that was believed to have been added. The elemental analysis found 51.8% of the amount expected. Although the result from titration appears to support the analytical figure, neither is acceptable, because both the nitrogen and carbon contents of the polymer heated to 430°C were higher than those of the original polymer without corresponding decreases in the hydrogen contents.

Table XXI. Analytical Data on the Diphenylsilylhydrazine Polymers

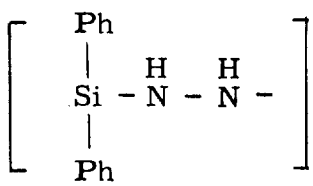
| Elemental analysis | Found: Original product[a] | Found: Partly polymerized[b] | Found: Fully polymerized[c] | Theoretical[d] |
|---|---|---|---|---|
| Carbon, % | 60.30 | 71.42 | 56.09 | 67.88 |
| Hydrogen, % | 5.94 | 5.32 | 3.19 | 5.70 |
| Nitrogen, % | 6.84 | 10.00 | 6.38 | 13.19 |
| Silicon, % | 14.60 | 13.00 | 22.50 | 13.23 |
| Total | 87.68[e] | 99.74 | 88.16[e] | 100.00 |
| Molecular weight (cryoscopic) | 1100 | 1000 | | 212.33 (repeating unit) |

[a] Original polymer obtained by reaction of diphenyldichlorosilane and hydrazine.

[b] Original polymer heated to 430° C.

[c] Original polymer heated to red heat.

[d] For



, $C_{12}H_{12}N_2Si$

[e] These figures are the best available, but they are believed to be low.

2. Reaction of hydrazine with a mixture of methyltrichlorosilane and dimethyldichlorosilane (1:1 molar ratio)

The reaction of hydrazine with the mixture of methyltrichlorosilane and dimethyldichlorosilane was expected to proceed according to this equation:

$$8H_2NNH_2 + CH_3SiCl_3 + (CH_3)_2SiCl_2 \longrightarrow \begin{array}{c} CH_3 \\ | \\ -Si \\ | \\ CH_3 \end{array} \begin{array}{c} \\ \\ H\ H \\ -N-N- \\ \\ \end{array} \begin{array}{c} NH\text{-}NH\text{-} \\ | \\ Si \\ | \\ CH_3 \end{array} -NH\text{-}NH- + 5H_2NNH_2 \cdot HCl$$

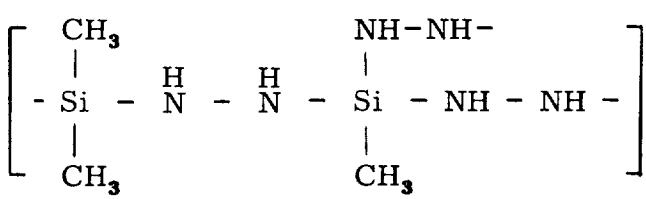
The reaction was conducted as follows: In a 500-ml, 3-neck flask fitted with a stirrer, thermometer, dropping funnel, and reflux condenser were placed 16.03 g (1.59 ml, 0.5 mole) of dry hydrazine and 150 ml of benzene. Methyltrichlorosilane, 9.97 g (7.8 ml, 0.066 mole) and dimethyldichlorosilane, 8.62 g (8.0 ml, 0.066 mole) were dissolved in benzene in the dropping funnel. The hydrazine was dispersed in the benzene by stirring; the system was swept with dry nitrogen; and the silane mixture was added slowly, with vigorous stirring, over a period of 1 hour. The temperature rose to 45°C. The reaction mixture was refluxed for 2 hours. The salts were allowedto settle, and the Beilstein Test revealed that no chloride was present in the supernatant liquid. The salts were separated by centrifugation, and the benzene was removed from the clear liquid product by distillation. When the benzene was almost gone and the pot temperature was 125°C, the product was a white sticky mass. Reduction of the pressure to 1.5 mm at 35°C caused the residue to foam and harden to a friable, white powder that was only partially soluble in benzene or acetone. It softened but did not melt on heating. During a thermogravimetric analysis (Section IV), the polymer lost approximately 85% of its weight on being heated to 800°C. Analytical data are in Table XXII. The molecular weight was not measured, because the polymer was not soluble. No attempts to make satisfactory coatings were successful.

Table XXII. Analytical Data on the Methylsilylhydrazine (di-tri) Polymer

| Elemental analysis | Found[a] | Theoretical[b] |
|---|---|---|
| Carbon, % | 26.83 | 18.83 |
| Hydrogen, % | 7.44 | 7.90 |
| Nitrogen, % | 11.40 | 43.93 |
| Silicon, % | 36.30 | 29.34 |
| Total | 81.97 | 100.00 |

[a] Original polymer obtained by reaction of methyltrichlorosilane and dimethyldichlorosilane with hydrazine.

[b] For



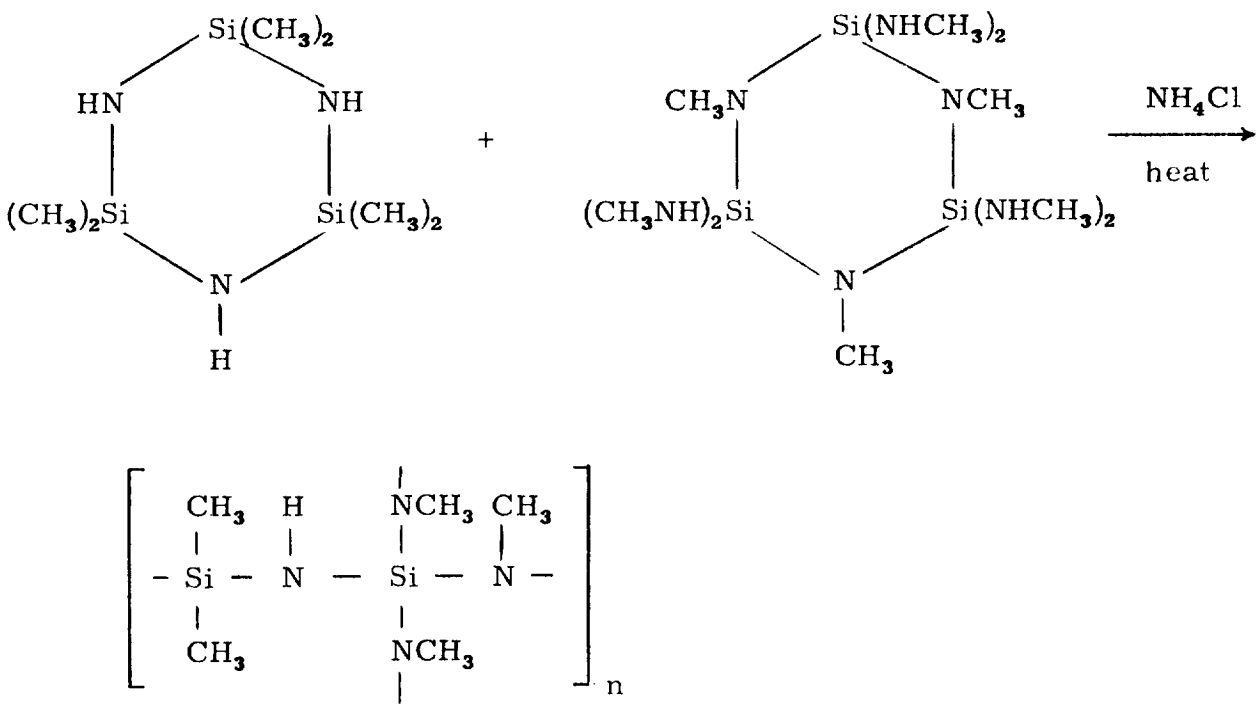
, $C_3H_{15}N_6Si_2$

# XIII. POLYMERIZATION BY AMINE EXCHANGE AND END-GROUP CONDENSATION

## A. Discussion

Earlier studies of amine-exchange reactions as a method of forming high-molecular-weight silylamine polymers showed promise,[48] and the investigation of these reactions was continued.

Hexamethylcyclotrisilazane was treated with 1, 3, 5-trimethyl-2, 2, 4, 4, 6, 6-hexakis(methylamino)cyclotrisilazane (Section IX) in the presence of ammonium chloride. The hexamethylamino compound was expected to provide opportunities for forming a branched polymer of high molecular weight. The equation below represents one of the possibilities for rearrangement into polymeric forms.



Ammonium chloride can serve as a catalyst to facilitate ring opening and rearrangement to form polymers. Polymers can also be formed by the elimination of methylamine between $CH_3NH$- end groups. Ammonia can be eliminated and replaced by methylamine after the hexamethylcyclotrisilazane rings open. It is likely that all of these reactions proceed simultaneously and that the polymerization is complex.

One amine-exchange product was a viscous, cloudy, red oil; and another was a soft, red-brown solid. The two reactions differed principally in that a higher ratio of the hexamethylamino compound and higher temperatures were used in the second. The molecular weights of the products were, respectively, about 1500 and 1700. Both underwent condensation polymerization on heating to form brittle solids. When the exchange products were heated as thin films on aluminum, the resulting coatings proved to have excellent thermal stability; but they had a tendency to crack or craze on curing. It was necessary to heat the films to red heat before they were fully converted to solids. Less drastic heating produced gels. The thermal stability of the gel material appeared to be unusual even for the silazanes.

Both polymers were less stable to hydrolysis than the phenyl-substituted silazanes, but they were more stable than the other alkyl-substituted silazanes including nonamethylcyclotrisilazane. Results of the hydrolysis experiments are in Section IV.

The work was extended by attempting to polymerize nonamethylcyclotrisilazane. It is desirable to obtain a fully methylated silazane polymer, even of low molecular weight, because nonamethylcyclotrisilazane, which is a fully methylated silazane trimer, has been demonstrated to have a high degree of stability to hydrolysis.

Three attempts were made to polymerize nonamethylcyclotrisilazane. The first was by an amine-exchange reaction with 1,3,5-trimethyl-2,2,4,4,6,6-hexakis(methylamino)cyclotrisilazane catalyzed by ammonium chloride. The maximum temperature used was 235°C. The main product had high thermal stability, but it was insoluble and infusible and would be difficult to make into useful forms. However, the reaction demonstrated that the ring of nonamethylcyclotrisilazane could be opened. The second was an attempt to improve on the first by using a lower temperature, 75°C, with no catalyst. The nonamethylcyclotrisilazane did not react; and the hexamethylamino compound homopolymerized. The third attempt was by rearrangement of nonamethylcyclotrisilazane with methylamine hydrochloride as the catalyst. About half of the product was an unidentifiable brown polymer that was not soluble in benzene. It melted when heated strongly, and it was friable even after being fused and resolidified.

An attempt was also made to induce polymerization by condensation of the end-amino groups of bis(methylamino)pentamethyldisilazane. Bis(methylamino)pentamethyldisilazane was refluxed for 38 hours at 205-210°C. About 20% of it polymerized to a nondistillable oil, and about 75% of it was converted to a slightly higher boiling material that has not been identified.

End-group condensation of bis(methylamino)diphenylsilane was described in Section IV. Some polymeric and some crystalline cyclic material was formed. It is obvious that polymerization can be accomplished by end-group condensation; but, as yet, no linear high polymers with attractive properties have been obtained by these methods.

B. Experimental Details

1. Amine-exchange reactions with 1,3,5-trimethyl-2,2,4,4,6,6-hexakis(methylamino)cyclotrisilazane

The first amine-exchange reaction was conducted as follows: In a 100-ml, 3-neck flask fitted with a magnetic stirrer, thermometer, and reflux condenser, 3.0 g (0.0085 mole) of 1,3,5-trimethyl-2,2,4,4,6,6-hexakis(methylamino)cyclotrisilazane, 15.0 g (0.068 mole) of hexamethylcyclotrisilazane, and 0.2 g (0.0037 mole) of ammonium chloride were placed. The mixture was heated with stirring to 140-150°C, and gas was evolved. After 2.5 hours at 140-150°C, 0.2 g (0.0037 mole) of ammonium chloride was added, and heating was continued to maintain 140-150°C for a total of 6 hours. Gas evolution was continuous, although it was much more rapid just after the ammonium chloride was added. After standing overnight, the temperature was raised to 190-210°C for 5 hours. Another 0.2 g (0.0037 mole) of ammonium chloride was added, and the mixture was held at 260-270°C for 3.5 hours. The resulting mixture was viscous at room temperature and red-brown in color. It was dissolved in 50 ml of xylene and centrifuged to clarify it. The xylene was removed by distillation; the final pot conditions were 190°C at 1 mm pressure. The yield was 11.2 g of red-brown, viscous liquid.

An attempt was made to determine the neutral equivalent of the amine-exchange polymer. The polymer was stirred in absolute ethanol for 30 minutes before solution was complete. Then 2.0 ml of water was added, and titration was started. Because of drifting of the pH, approximately 1.5 hours was required to complete the titration. The value obtained for the neutral equivalent was 136.6, whereas the theoretical value for hexamethylcyclotrisilazane is 73.1 and for the hexamethylamino compound is 39.1. The expected neutral equivalent was between 39.1 and 73.1. Consequently, part of the nitrogen was lost or made unavailable by the reaction. Elemental analyses are in Table XXIII. For reference purposes, this polymer was numbered 2783-55.

The hydrolytic stability of the polymer, determined as described in Section IV, was higher than that of either starting material. After 26 minutes, when hydrolysis was 4.8% complete, as judged by the neutral equivalent, the water layer became a gel. A similar gel did not form when the stability study was conducted in acid.

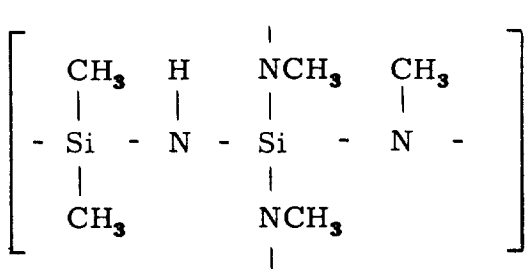
Table XXIII. Elemental Compositions of Products from Amine Exchange Reactions of Hexamethylcyclotrisilazane and 1, 3, 5-trimethyl-2, 2, 4, 4, 6, 6-hexakis(methylamino)cyclotrisilazane

| Element | Found: First product[a] | Found: Second product[b] | Theoretical[c] |
|---|---|---|---|
| Carbon, % | 32.34 | 26.50 | 31.86 |
| Hydrogen, % | 8.71 | 7.72 | 8.56 |
| Nitrogen, % | 14.83 | 16.55 | 29.75 |
| Silicon, % | 39.3 | 37.45 | 29.83 |
| Total | 95.18 | 88.22 | 100.00 |
| Neutral equivalent | 136.6 | 113.0 | 47.09 |
| Molecular weight (vapor osmometry)[d] | 1500 | 1700 | |

[a] Amine exchange polymer 2783-55

[b] Amine exchange polymer 2783-93

[c] For



[d] Galbraith Laboratories, Inc.

When the amine-exchange polymer was dissolved in benzene and spread on aluminum, it did not cover the surface evenly. The appearance suggested a nonhomogeneous solution with aggregates of partially dissolved polymer. By heating the panel over a burner, the coating could be cured in stages of increasing hardness. Probably the molecular-weight range was very great, and low-molecular-weight portions were lost in the initial stages of curing. Heating in a test tube caused condensation polymerization to a vitreous, brittle solid ultimately, but the test tube reached red heat before a solidification was complete.

The molecular weight as determined by vapor osmometry was 1500.

The second amine-exchange reaction was conducted as follows: In a 100-ml, 3-neck flask fitted with a reflux condenser, magnetic stirrer, and thermometer, were placed 3.4 g (0.0097 mole) of 1,3,5-trimethyl-2,2,4,4,6,6-hexakis(methylamino)cyclotrisilazane, 12.8 g (0.055 mole) of hexamethylcyclotrisilazane, and 0.2 g (0.0037 mole) of ammonium chloride. After 2 hours at 200°C, 0.2 g (0.0037 mole) of ammonium chloride was added, and stirring was continued at 200°C for a total of 4 hours. Gas evolution was continuous, but it was much more rapid just after each addition of ammonium chloride. After standing overnight, 0.2 g (0.0037 mole) of ammonium chloride was added, and the mixture was stirred at 240°C for 2 hours; then 0.2 g (0.0037 mole) of ammonium chloride was added, and the temperature was raised to 310°C for 4 hours. Another 0.2 g (0.0037 mole) of ammonium chloride was added, and heating was continued at 310°C for 4 additional hours. Then 0.2 g (0.0037 mole) of ammonium chloride was added, and the solution was stirred at 320-340°C for 2 hours; and another 0.2 g (0.0037 mole) of ammonium chloride was added, and the solution was stirred at 320-340°C for 3 hours. The resulting mixture was a red-brown solid at room temperature. It was dissolved in 60 ml of xylene and refluxed for 2 hours. The xylene solution was centrifuged to clarify it. The xylene was removed by distillation, the final pot conditions being 215°C at 4 mm. The yield was 6.4 g of a red-brown soft solid. The analytical data are in Table XXIII. For reference purposes this polymer was numbered 2783-93.

The hydrolytic stability of the product, determined as described in Section IV, was higher than the stability of either starting material. After 80 minutes, when hydrolysis was 2.5% complete as judged by the neutral equivalent, the water layer became a gel. When the stability measurement was made in acid, a similar gel formed in 158 minutes.

The polymer formed a thermally stable film when it was cured on aluminum. The molecular weight was found to be 1700 by vapor osmometry.

2. Exchange reactions between nonamethylcyclotrisilazane and 1,3,5-trimethyl-2,2,4,4,6,6-hexakis(methylamino)cyclotrisilazane

In a 50-ml, 3-neck flask fitted with thermometer, magnetic stirrer, and reflux condenser were placed 2.0 g (0.007 mole) of nonamethylcyclotrisilazane, 3.4 g (0.0097 mole) of 1,3,5-trimethyl-2,2,4,4,6,6-hexakis-(methylamino)cyclotrisilazane, and 0.2 g (0.0037 mole) of ammonium chloride. While the mixture was heated with stirring at 80-90°C, gas was evolved slowly. After heating 2 hours at 80-90°C, 0.2 g (0.0037 mole) of ammonium chloride was added, and the temperature was raised to 135°C. After 1 hour at 135°C, 0.2 g (0.0037 mole) of ammonium chloride was added, and the temperature was raised to 235°C for 0.5 hour. This caused a strong evolution of gas and the sample foamed and partly solidified. The reaction product was cooled, and 30 ml of benzene was added and refluxed for 1 hour. The benzene was removed by centrifuging and decanting, and the insoluble solid material that was left weighed 6.0 g after drying. The solid product could not be melted on a spatula in a gas flame. On distillation of the benzene solution, 0.2 g of nonamethylcyclotrisilazane, 10% of the starting material, was obtained, and 0.2 g of undistillable residue remained.

A reaction with nonamethylcyclotrisilazane was also run without ammonium chloride as catalyst. In a 25-ml, 2-neck flask fitted with stirrer, thermometer, and reflux condenser were placed 0.5 g (0.0019 mole) of nonamethylcyclotrisilazane and 0.3 g (0.0008 mole) of 1,3,5-trimethyl-2,2,4,4,6,6-hexakis(methylamino)cyclotrisilazane. The mixture was heated at 65-75°C for 6 hours. The liquid became cloudy, but there was no apparent increase in viscosity. The sample was mixed with 20 ml of benzene and centrifuged. The benzene solution was decanted leaving 0.25 g of insoluble material. When the benzene was evaporated, 0.5 g of crystals, melting at 31-32°C, was obtained. This was obviously nonamethylcyclotrisilazane, which had not reacted.

3. Catalyzed rearrangement of nonamethylcyclotrisilazane

In a 25-ml, 3-neck flask fitted with a thermometer, stirrer, and reflux condenser were placed 2.6 g (0.009 mole) of nonamethylcyclotrisilazane and 0.2 g (0.0029 mole) of methylamine-hydrochloride. The mixture was heated to 180-190°C, and the hydrochloride turned brown. After 1.5 hours of stirring at 180-190°C, 0.2 g (0.009 mole) additional hydrochloride was added, and heating was continued at this temperature for 3 hours. After standing overnight, another 0.2 g (0.009 mole) of the hydrochloride was added and heating was continued at 200-220°C for 5 hours. The temperature was then raised to 250°C for 0.5 hour. The reaction was cooled, 20 ml of dry ether was added and the mixture was centrifuged. The ether solution was decanted into a 5-ml beaker. The ether was evaporated and the residue was distilled in a small sublimation apparatus with a cold-finger condenser. The distillate was nonamethylcyclotrisilazane, 0.8 g. A brown oil, 0.3 g, that could not be distilled at 0.2 mm pressure and 100°C was left behind. When heated on a spatula to red heat, the oil produced a brittle coating where the film was thin, and a gel-like material where it was thick.

4. Polymerization of bis(methylamino)pentamethyldisilazane by end-group condensation

Bis(methylamino)pentamethyldisilazane was prepared as described in Section IV. A 10-g sample of it was refluxed for 38 hours at 205-210°C. The product, which was slightly yellow, was distilled. Fraction I, 7.4 g, distilled at 103-114°C at 22 mm; it had a neutral equivalent of 90.0. Fraction II, 2.0 g, did not distill at 295°C at 3.5 mm; it had a neutral equivalent of 114. These may be compared with nonamethylcyclotrisilazane which distills at 50-52°C at 0.4 mm (estimated 120°C at 22 mm) and has a neutral equivalent of 87.2. All cyclic fully methylated silazanes would have the same neutral equivalent. It is difficult to explain the formation of nonamethylcyclotrisilazane except by disproportionation.

# XIV. THE EFFECT OF REACTION CONDITIONS ON POLYMERIZATION DURING THE FORMATION OF SILAZANES

## A. Discussion

Various reaction conditions were tried in attempts to produce polymeric silazanes by the reaction of dimethyldichlorosilane with ammonia. In the past, cyclic trimers or tetramers, rather than polymers, have been produced preferentially.

$$(CH_3)_2SiCl_2 + NH_3 \longrightarrow \left[(CH_3)_2SiNH\right]_{3 \text{ or } 4} + NH_4Cl$$

The earlier reactions were carried out in benzene with little or no effort to control the temperature, which varied between 30°C and 75°C. The products consisted of hexamethylcyclotrisilazane and octamethylcyclotetrasilazane roughly in the ratio of 3:1 with about 1% of undistillable polymer.

Published information[49-51] on the preparation of other polymers suggested that reactions at lower temperatures might favor the formation of polymers. Table XXIV summarizes the data on experiments at lower temperatures. The results show that no significant amount of polymer was formed, nor was there a significant change in the ratio of tetramer to trimer at the various temperatures that were tried.

Table XXIV. Effect of Temperature on the Reaction of Dimethyldichlorosilane with Ammonia in Toluene

| Reaction temperature, °C | Distribution of product, % | | |
|---|---|---|---|
| | Hexamethylcyclotrisilazane | Octamethylcyclotetrasilazane | Undistillable polymer |
| 38° to 55°C | 58 | 38 | 4 |
| 3° to 8°C | 69 | 31 | 0 |
| -60° to -70°C | 63 | 34 | 3 |

The concentrations of reactants were also varied and the solvent was eliminated in attempts to produce polymers rather than cyclic compounds. In one reaction, ammonia gas was added to liquid dimethyldichlorosilane; and 23% of the product was an undistillable oil. In another reaction, dimethyldichlorosilane was added to liquid ammonia; and 74% of the product was an undistillable oil. It appears that the lack of solvent favored polymerization, but not to the desired extent since the products were oils. Furthermore, only about one-half of the theoretical amount of each product was isolated.

## B. Experimental Details

### 1. Reaction at low temperature

In a 2-liter, 3-neck flask fitted with stirrer, reflux condenser, and gas inlet tube were placed 129.1 g (1.0 mole) of dimethyldichlorosilane and 840 ml of toluene. The solution was cooled to -60 to -70°C in a dry ice-acetone bath. At this temperature, ammonia was passed in with stirring for 4 hours. The solution was then stirred at 0-5°C for 4 hours and allowed to stand over a week-end at room temperature under an atmosphere of ammonia. The ammonium chloride was filtered off, and the clear supernatant toluene solution was found to be negative to the Beilstein Test for halogens. The toluene was removed at reduced pressure while the temperature was kept below 35°C.

The product consisted of 63% hexamethylcyclotrisilazane and 34% octamethylcyclotetrasilazane. In addition, there was 3% of undistillable polymer. The polymer was a cloudy oil that did not distill at 285°C at 3 mm pressure. Its neutral equivalent was 174; and its molecular weight was approximately 1500, as estimated cryoscopically in benzene. According to the nitrogen found (10.3%), the neutral equivalent was higher than expected (136). This difference indicates that some of the silicon-nitrogen bonds were very slow to hydrolyze.

The hydrolytic stability of the polymer was determined as described in Section IV, and was higher than that of hexamethylcyclotrisilazane. After 144 minutes, the polymer was only 25% hydrolyzed in water. By contrast, hexamethylcyclotrisilazane was 25% hydrolyzed in water in 23 minutes. In acid, the hydrolysis of the polymer was complete in 1 minute. For reference purposes, the polymer was designated 2783-75-5.

2. Reaction at intermediate temperature

In a 2-liter, 3-neck flask fitted with a stirrer, reflux condenser, thermometer, and gas-inlet tube were placed 129.1 g (1.0 mole) of dimethyldichlorosilane and 750 ml of toluene. The solution was cooled to 3-5°C in an ice bath. At this temperature, ammonia was passed in with stirring for 5.5 hours. After standing overnight under an atmosphere of ammonia, the clear supernatant toluene solution gave a positive Beilstein Test for halogens. Ammonia was passed in for an additional 7 hours at 3-5°C with stirring. The Beilstein Test for halogen was then negative. The solution was heated with stirring at 30-35°C for 3.5 hours, and then it was cooled and filtered. The toluene was removed by distillation at atmospheric pressure.

The product consisted of 69% hexamethylcyclotrisilazane, and 31% octamethylcyclotetrasilazane. There was no undistillable polymer.

3. Reaction at elevated temperature

In a 2-liter, 3-neck flask fitted with stirrer, reflux condenser, thermometer, and gas-inlet tube were placed 129.1 g (1.0 mole) of dimethyldichlorosilane and 840 ml of toluene. Ammonia was passed in for 4 hours, and the temperature was allowed to rise to 55°C. After 3 hours of refluxing, the clear, supernatant toluene solution was positive to the Beilstein Test for halogens. The mixture was cooled to room temperature, and ammonia was passed in for 2 hours while the temperature rose to 38°C. After filtering, the toluene filtrate was hazy. While more ammonia was being passed in for 45 minutes, the solution cleared. The solution was filtered without refluxing, and the toluene filtrate remained clear. The product contained 58% hexamethylcyclotrisilazane and 38% octamethylcyclotetrasilazane. In addition there was 4% of undistillable polymer.

4. Reactions without solvent

a. Addition of ammonia to dimethyldichlorosilane without solvent

In a 25-ml, 3-neck flask fitted with a stirrer, thermometer, and gas-inlet tube was placed 12.9 g (0.1 mole) of dimethyldichlorosilane. Dry ammonia was passed for 1 minute over the surface of the stirred liquid at intervals of 10 minutes over a period of 3 hours. At one point the temperature rose to 75°C; however, the temperature was kept below 45°C for most of the reaction. At the end of 3 hours, a balloon filled with ammonia was placed on the condenser, and the solution was stirred for 2 hours. The product, after standing over the week-end, was dissolved in 60 ml of benzene and filtered. It was evident from a Beilstein Test that all of the halogen had not reacted. More ammonia was passed in for 1.5 hour, and the temperature rose to 48°C. The solution was stirred for 1 hour, and the ammonium chloride was filtered off. The benzene was removed at reduced pressure.

The total product was 4.7 g (theory for $-(CH_3)_2SiNH-$, 7.3 g). The product consisted of 47% hexamethylcyclotrisilazane, 30% octamethylcyclotetrasilazane, and 23% undistillable polymer. The final pot conditions were 140°C at 1.5 mm pressure. The polymer was a cloudy oil.

b. Addition of dimethyldichlorosilane to liquid ammonia

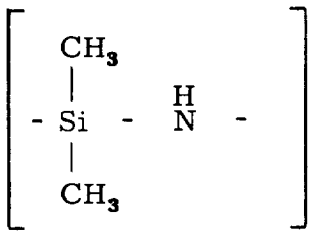
In a 200-ml, 3-neck flask fitted with a dry ice-acetone condenser, stirrer, and dropping funnel was placed approximately 100 ml of dry liquid ammonia. Dimethyldichlorosilane, 12.9 g (0.1 mole), was added slowly over a period of 15 minutes. The solution was stirred for 2.5 hours. After the mixture had stood overnight the liquid ammonia was allowed to evaporate, and the residue was mixed with 100 ml of benzene. The solution was refluxed for 2 hours, and the ammonium chloride was filtered off. The benzene was removed at reduced pressure. A small portion of the product, 1.1 g, boiled at 87-93°C at 20 mm. The remainder, 3.1 g, was undistillable at 120°C at 1.5 mm. The theoretical yield of $-(CH_3)_2SiNH-$ was 7.3 g. The results of an elemental analysis are in Table XXV.

The hydrolytic stability was determined as described in Section IV. After 5 minutes, the polymer had hydrolyzed 25% in water. The hydrolysis was complete in 1 minute in acid solution. For reference purposes, the polymer was designated 2783-109-2.

Table XXV. Elemental Analysis of Polymeric Product Obtained by the Addition of Ammonia to Dimethyldichlorosilane

| | Found | Theoretical[a] |
|---|---|---|
| Carbon, % | 29.29 | 32.80 |
| Hydrogen, % | 7.51 | 9.64 |
| Nitrogen, % | 12.26 | 19.17 |
| Silicon, % | 34.65 | 38.39 |
| Total | 83.71 | 100.00 |
| Neutral equivalent | 168.3 | 73.15 |

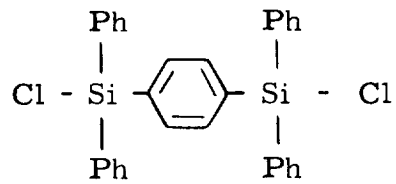
[a] For



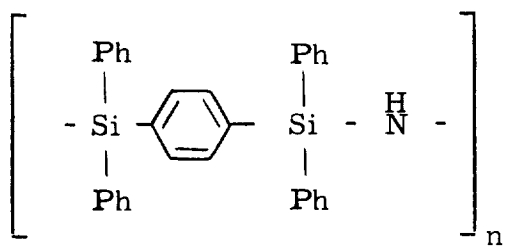
## XV. SILICON-NITROGEN POLYMERS CONTAINING AROMATIC BRIDGES

Inasmuch as aromaticity is an effective contributing factor to thermal stability and carbon-silicon bonds are amply stable, an attempt was made to prepare silicon-nitrogen polymers in which the Si-N units were connected by aromatic bridges.

The method of Newing[52] was used in an attempt to prepare 1,4-bis(diphenylchlorosilyl)benzene,



The Grignard Reagent of 1,4-dibromobenzene was prepared in tetrahydrofuran, and the solution was added to diphenyldichlorosilane. Crystals were obtained as described by Newing. They were assumed to be 1,4-bis(diphenylchlorosilyl)benzene, but they were not fully characterized. The crystals were dissolved in benzene and treated with ammonia to form the silylamine. The expected structure was



The product was a soft solid that flowed when warmed slightly. It boiled and darkened when heated to 300°C. On continued heating to 380°C, no evidence of further polymerization was observed. Time did not permit further examination of the product.

B. Experimental Details

1,4-Dibromobenzene, 141 g (0.6 mole) was added to 29.2 g (1.2 moles) of magnesium in 300 ml of tetrahydrofuran. After reaction was complete, the solution was added to 303 g (1.2 moles) of diphenyldichlorosilane in 500 ml of tetrahydrofuran. The tetrahydrofuran was distilled off, and 1200 ml of heptane was added. The mixture was warmed, the magnesium salts were removed by filtration, and the filtrate was cooled. A gray-white solid mass appeared after several days. Recrystallization was attempted without success from ether, benzene, hexane, and tetrahydrofuran. The difficulty was that the solid product was only partially soluble, and the part that did dissolve was slow to crystallize. Finally, the solid was stirred with 400 ml of benzene and centrifuged. An aliquot was evaporated in a nitrogen stream to determine the amount of dissolved solid, which showed that 26.9 g was in solution. This benzene solution was stirred under an atmosphere of ammonia for 3.5 hours while the temperature rose to 40°C. The mixture was refluxed for 2.5 hours, cooled, and centrifuged. The precipitate was washed three times with 50 ml portions of hot benzene. The benzene solutions were combined, and the benzene was removed by distillation. The residue was held at 175°C at 0.5 mm pressure for an hour to remove the last traces of low-boiling material. The product was a cloudy yellow solid that was sticky.

The product decomposed without polymerizing further when it was heated on a spatula. When heated in a test tube it boiled, probably with decomposition, at 300°C. Continued heating to 350-380°C caused the mass to smoke and become black. On cooling, the mass was slightly harder and tougher than it was initially, but it softened at less than 100°C. No evidence of moisture sensitivity was seen, but thermal stability did not appear to be high.

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April 29, 1963
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# APPENDIX

Figures 1 through 19

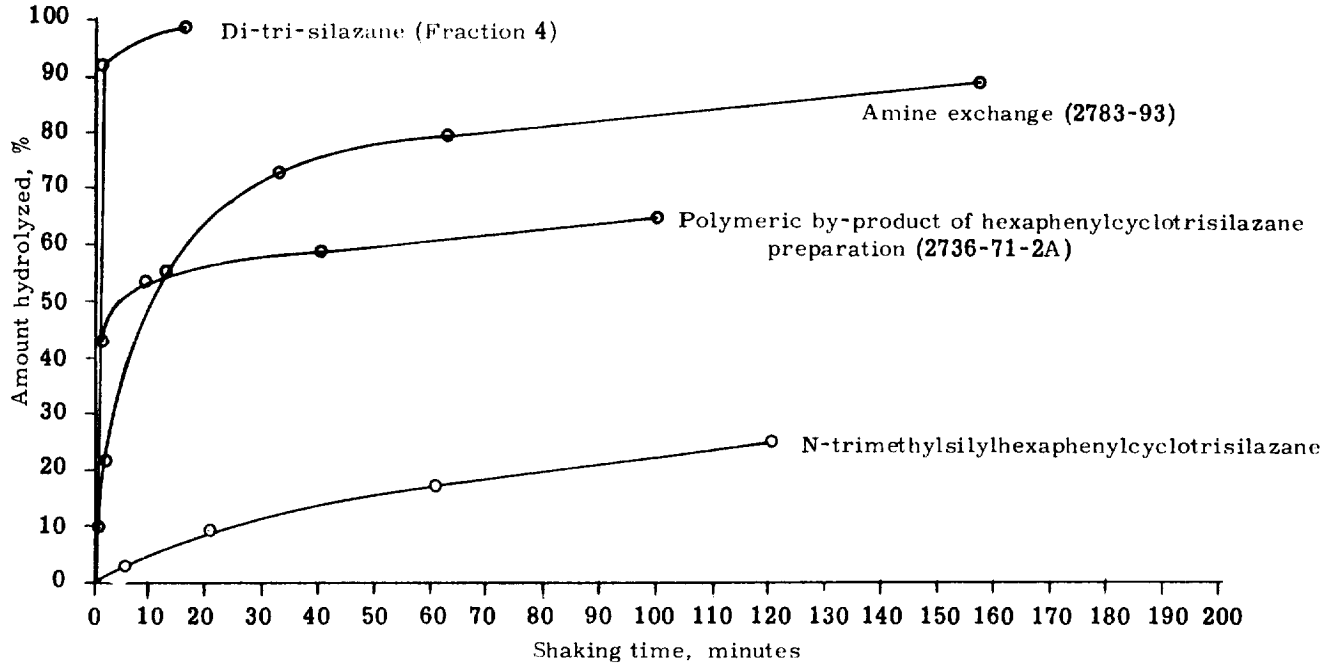


Figure 1. Hydrolysis in Carbon Tetrachloride and Hydrochloric Acid

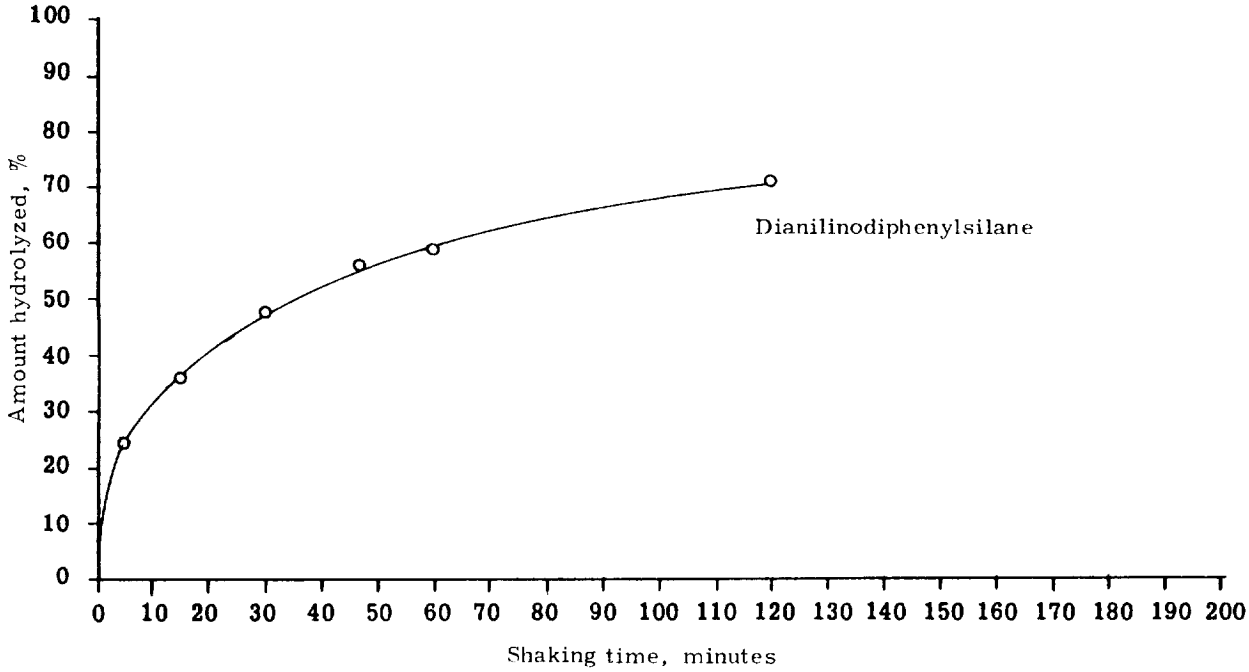


Figure 2. Hydrolysis in Benzene and Hydrochloric Acid.

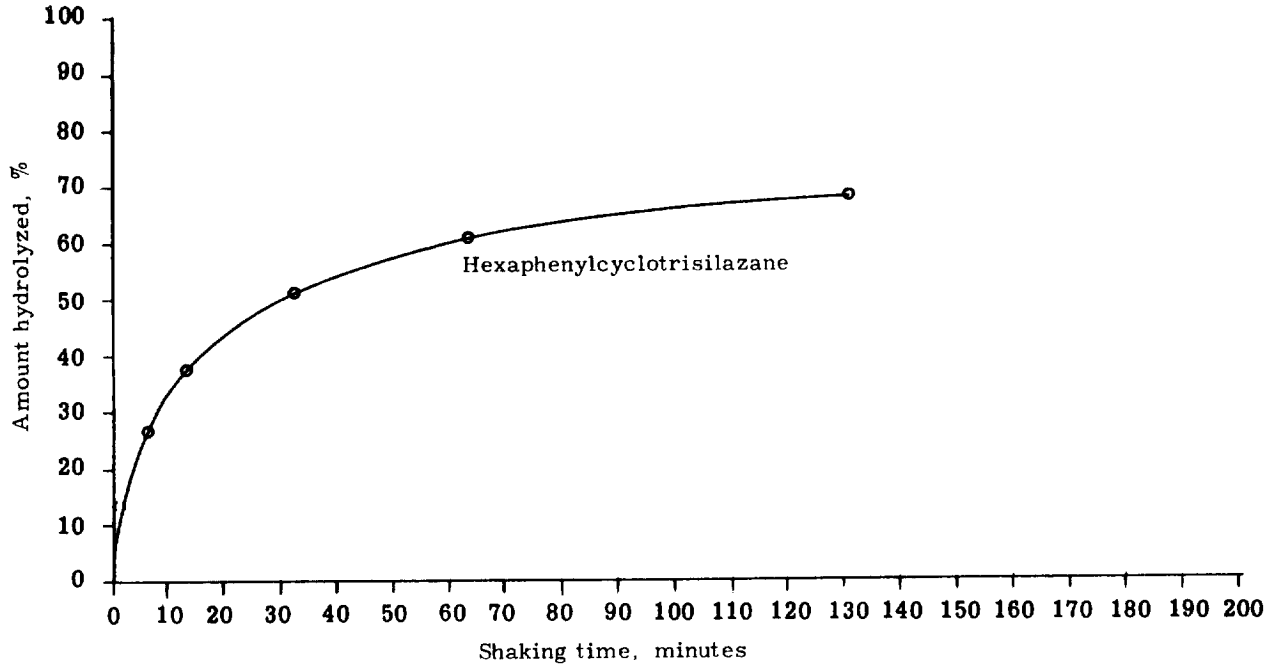


Figure 3. Hydrolysis in Benzene and Hydrochloric Acid

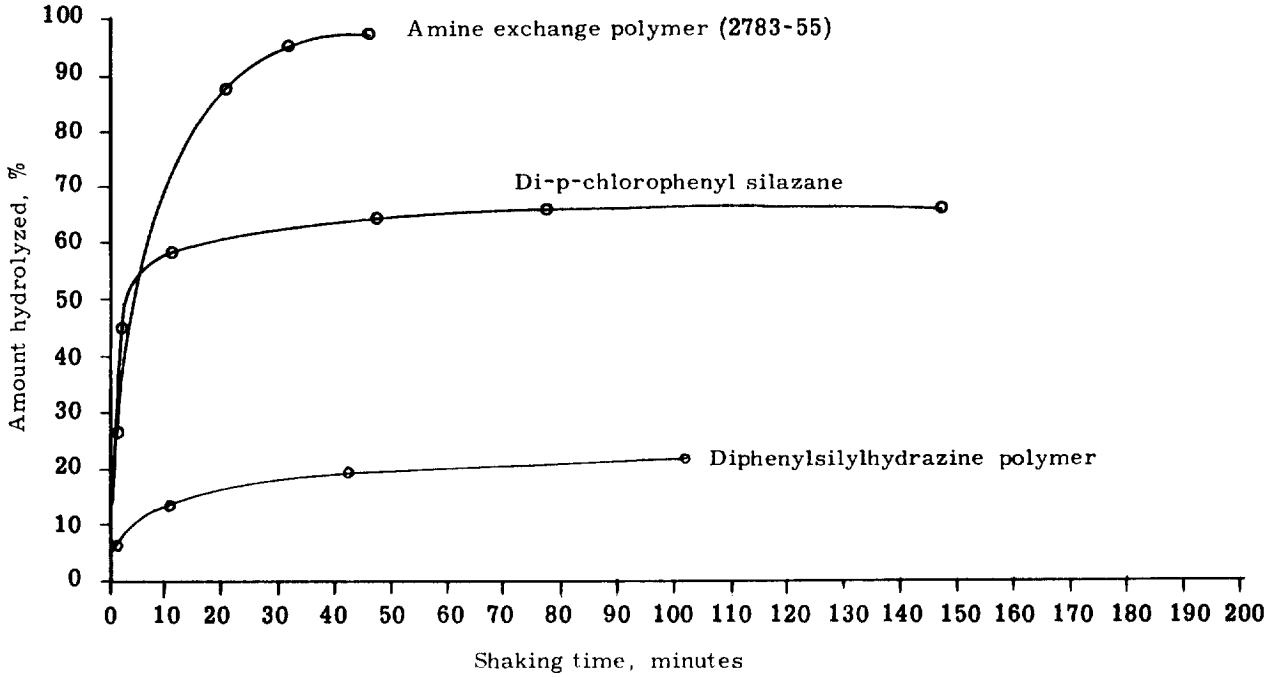


Figure 4. Hydrolysis in Carbon Tetrachloride and Hydrochloric Acid

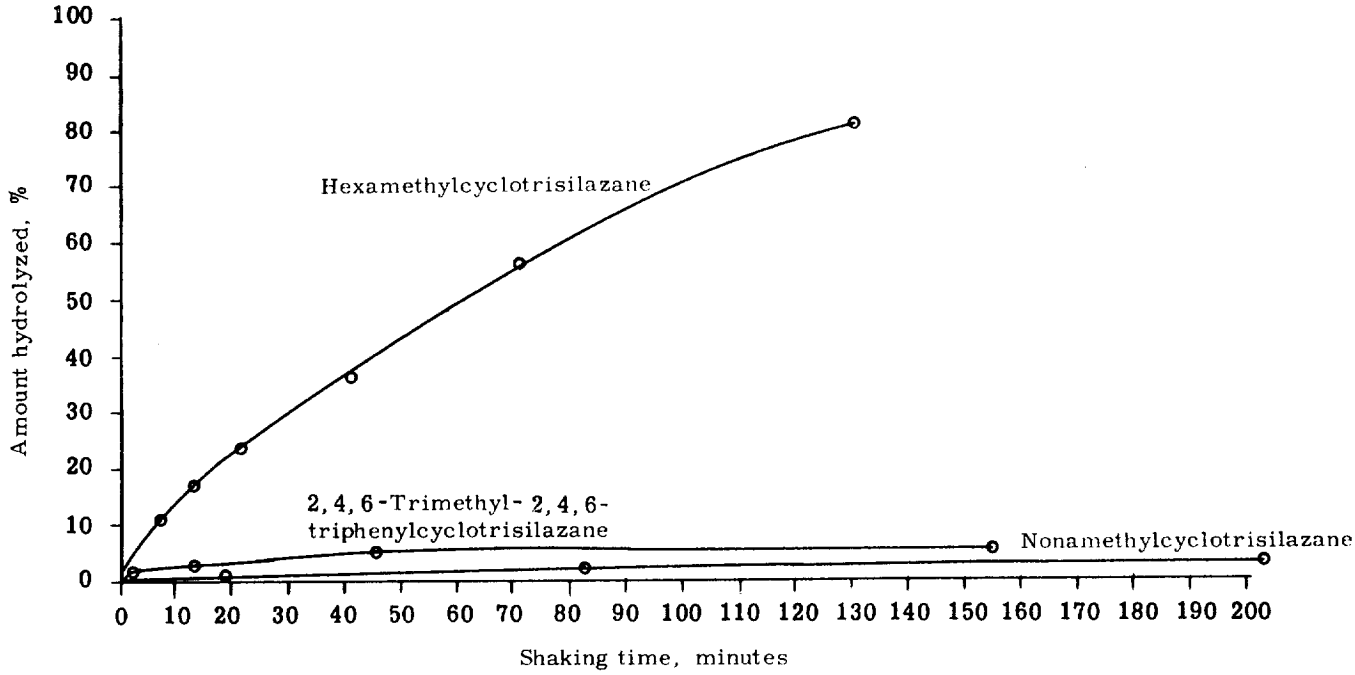


Figure 5. Hydrolysis in Carbon Tetrachloride and Water

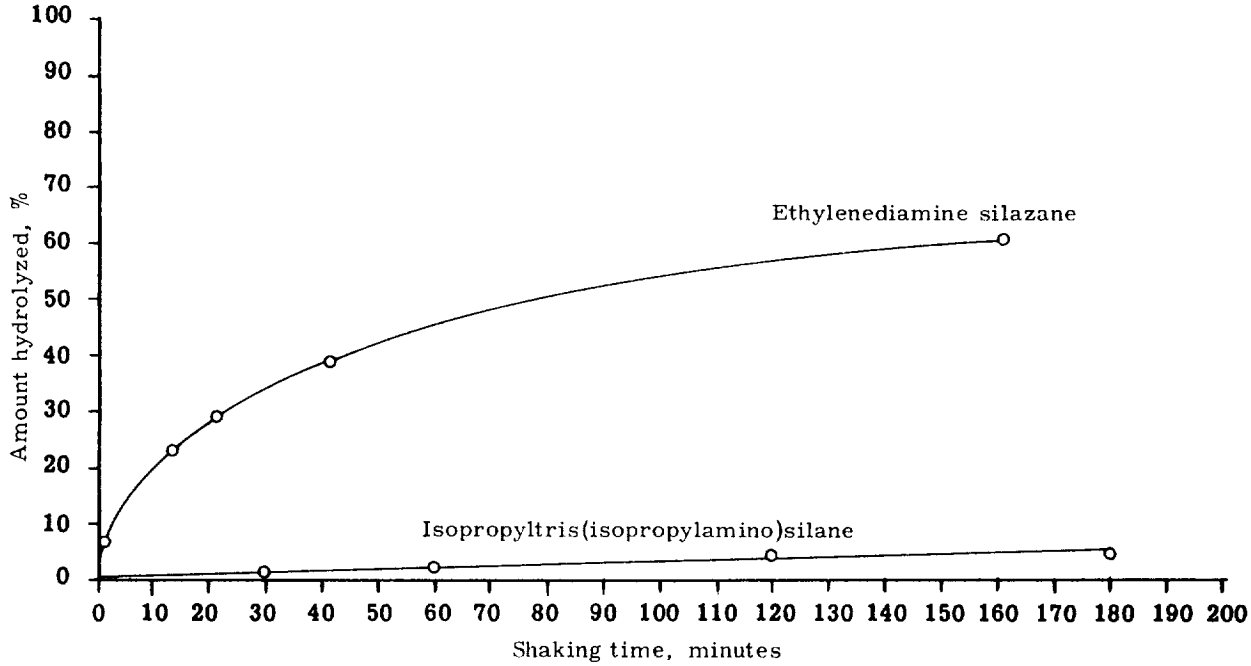


Figure 6. Hydrolysis in Carbon Tetrachloride and Water

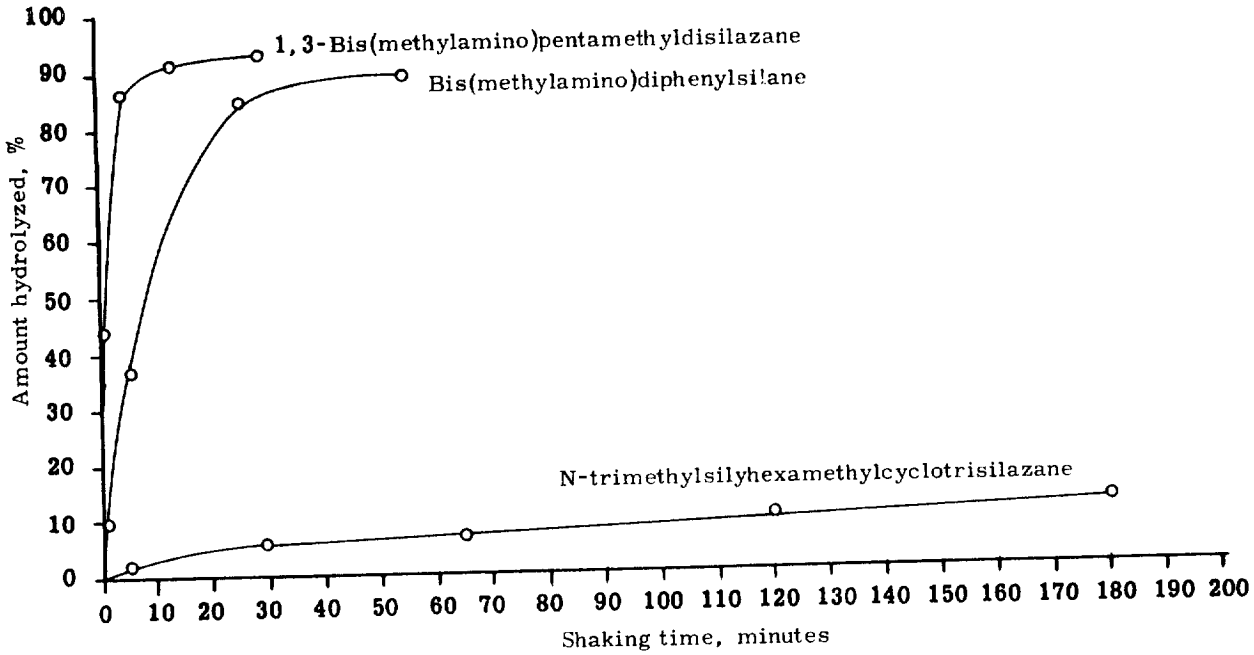


Figure 7. Hydrolysis in Carbon Tetrachloride and Water

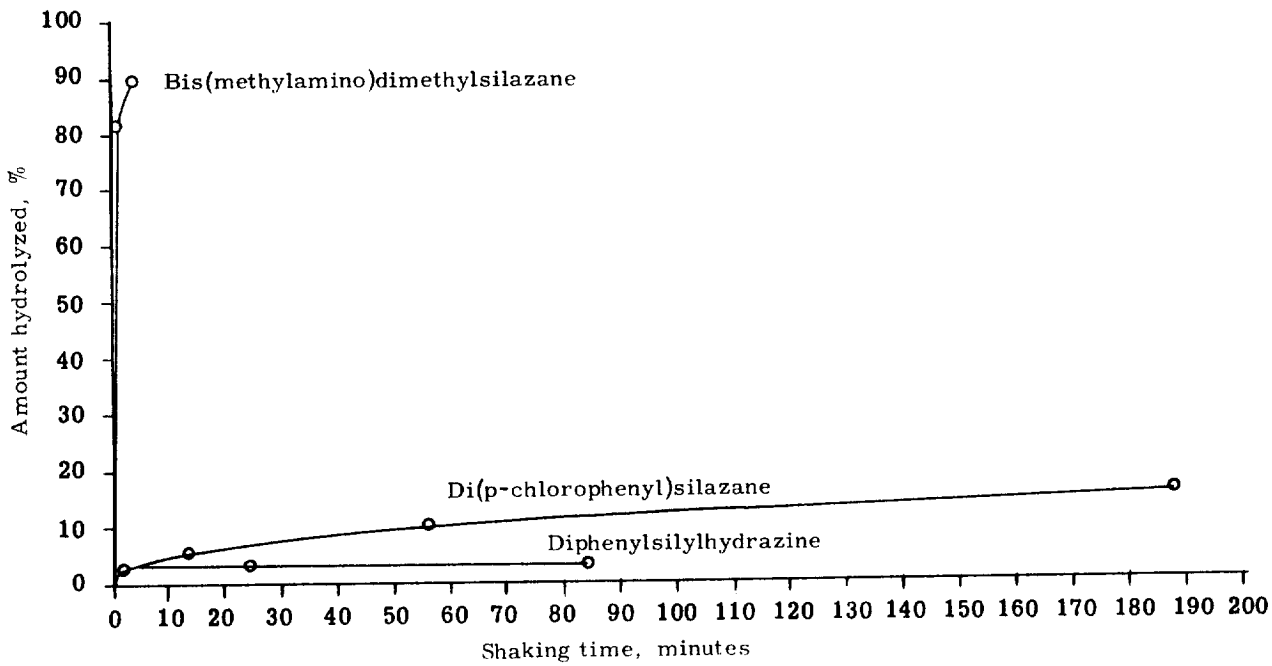


Figure 8. Hydrolysis in Carbon Tetrachloride and Water

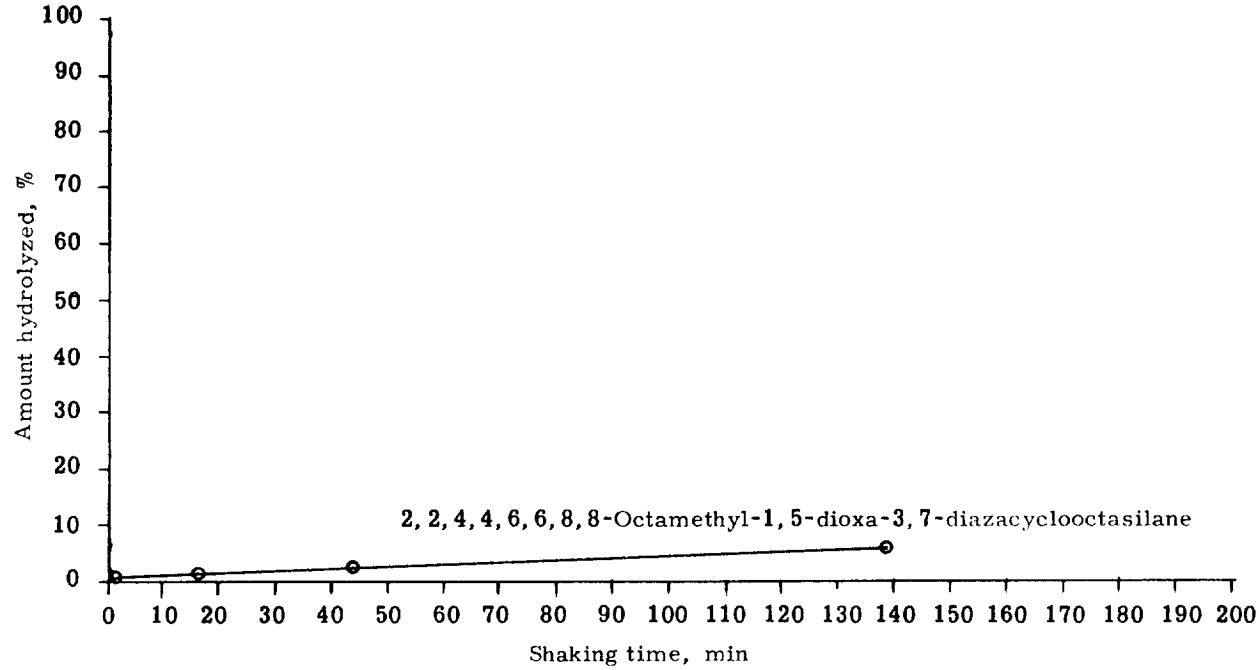


Figure 9. Hydrolysis in Carbon Tetrachloride and Water

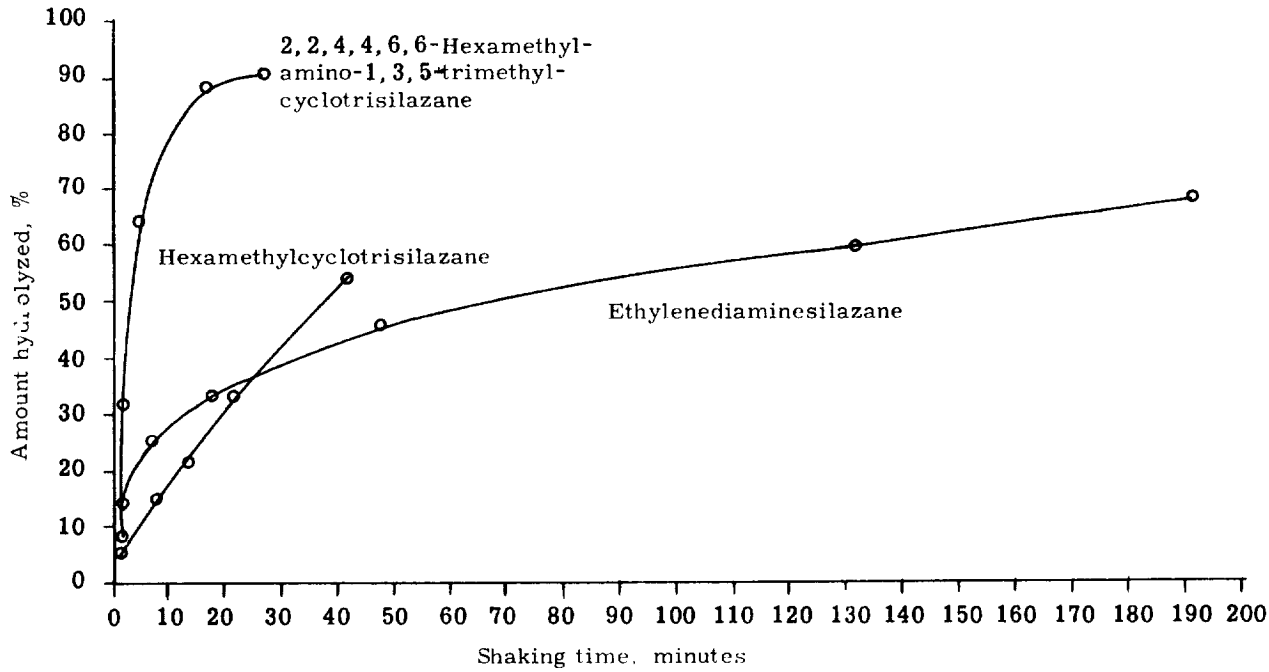


Figure10. Hydrolysis in Benzene and Water

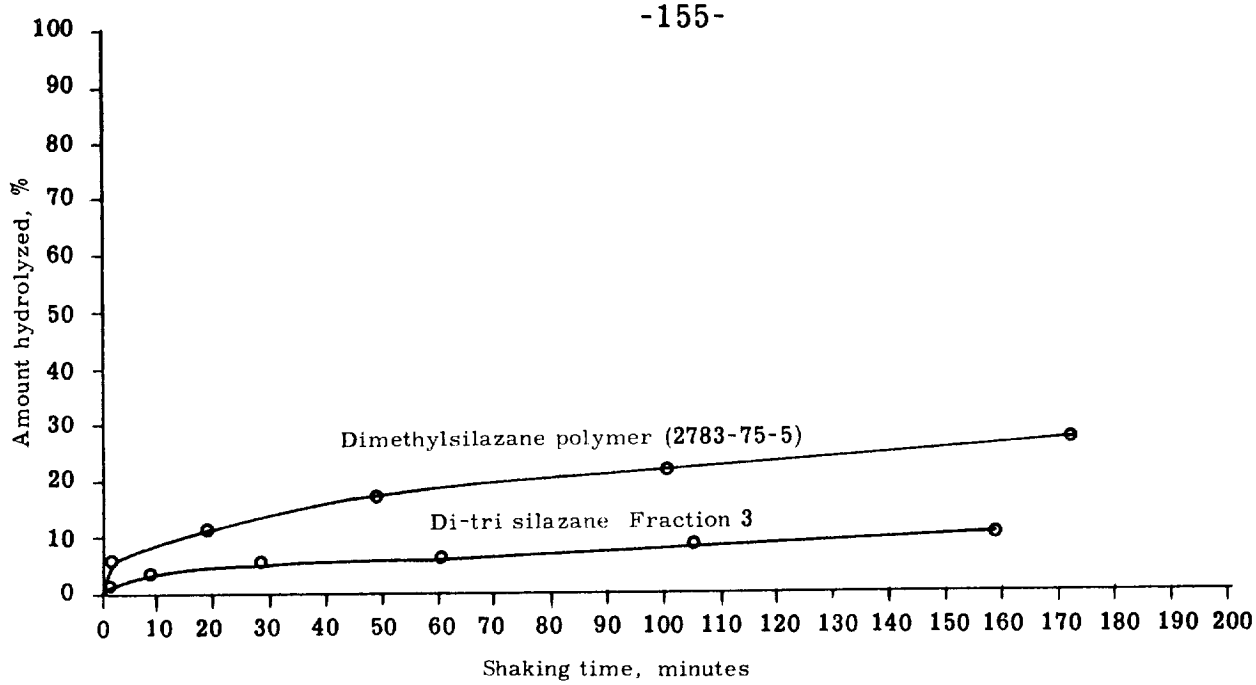


Figure 11. Hydrolysis in Carbon Tetrachloride and Water

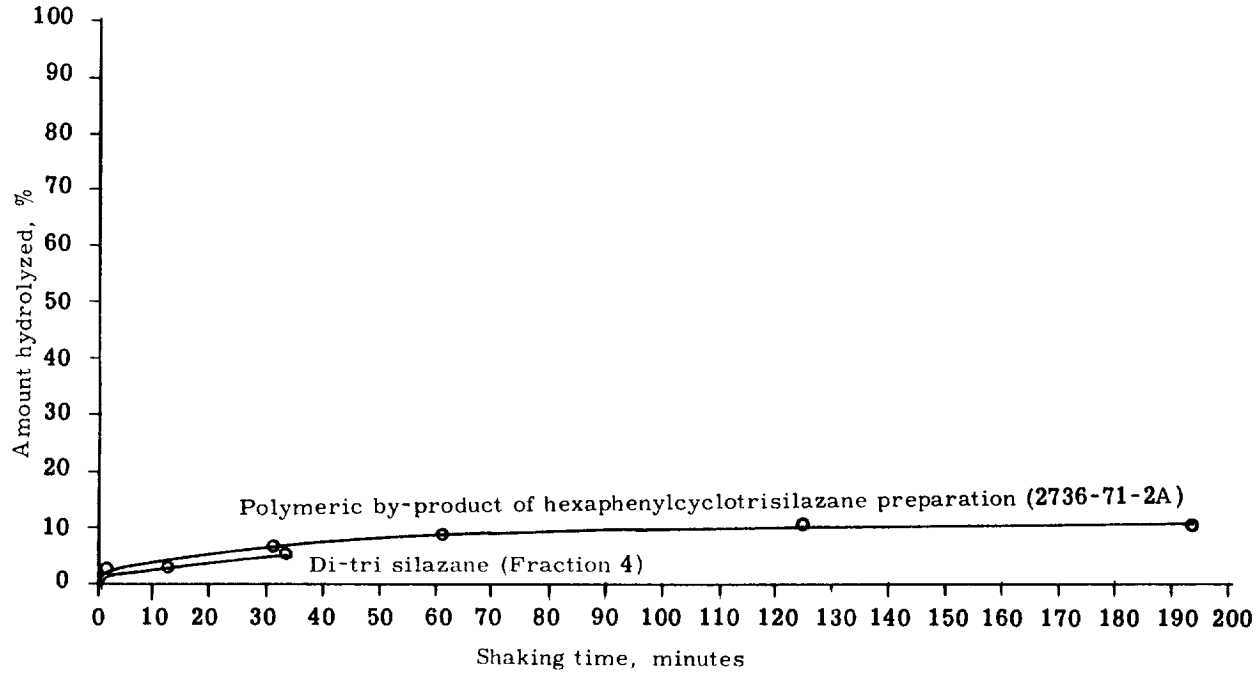


Figure 12. Hydrolysis in Carbon Tetrachloride and Water

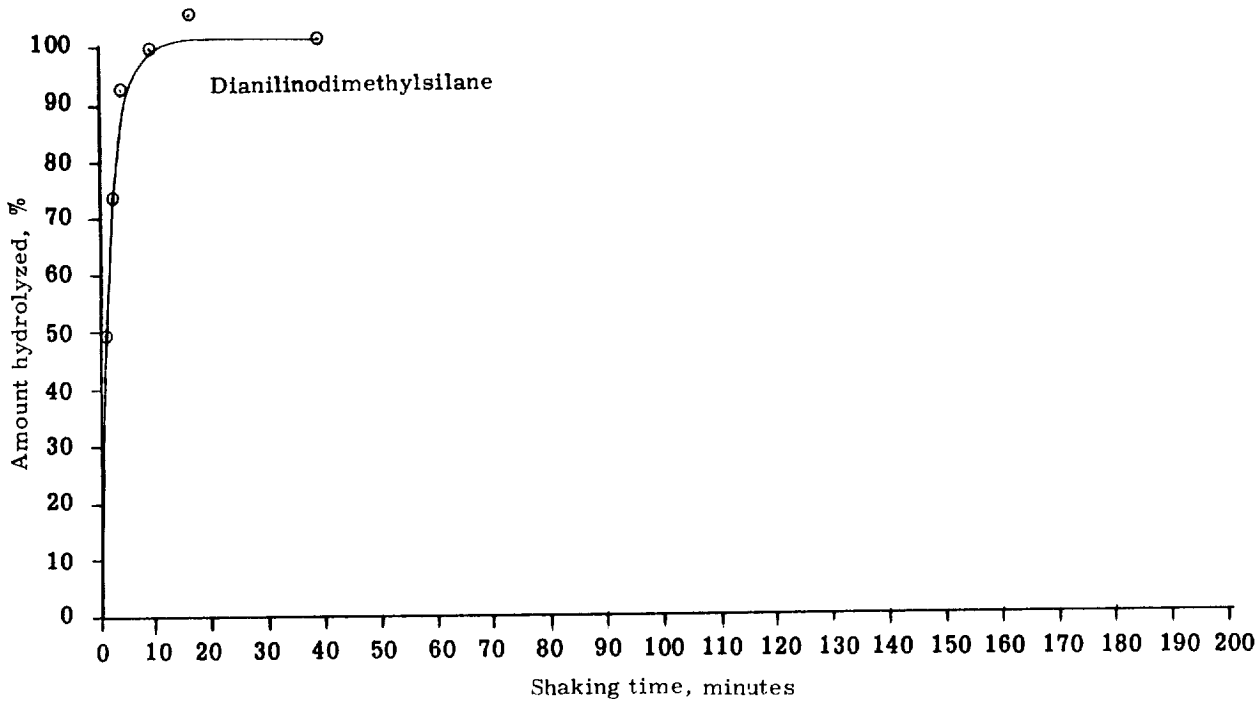


Figure 13. Hydrolysis in Carbon Tetrachloride and Hydrochloric Acid

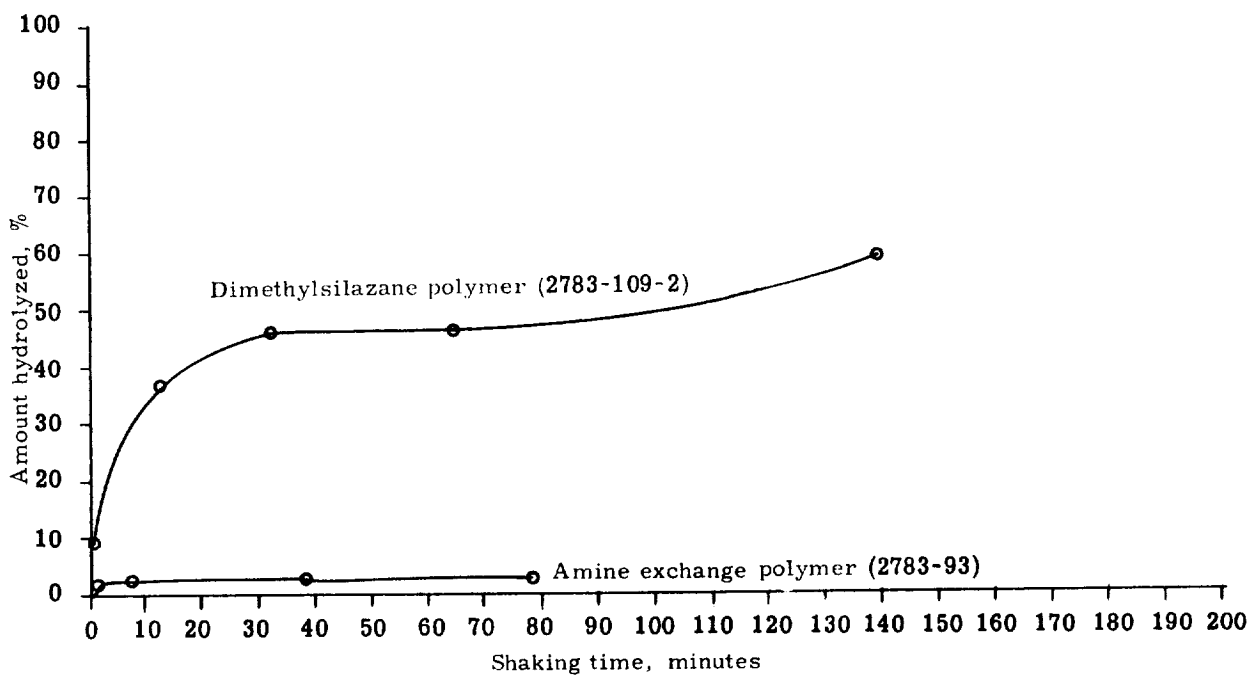


Figure 14. Hydrolysis in Carbon Tetrachloride and Water