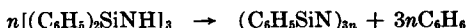


## Conversion of Hexaphenylcyclotrisilazane and Related Materials to Infusible Polymers and Coatings

ROBERT E. BURKS, JR., ROBERT E. LACEY, JAMES C. LACEY, JR., and THOMAS W. RAY, *Southern Research Institute, Birmingham, Alabama*

### Synopsis

When hexaphenylcyclotrisilazane was heated above 450°C. at atmospheric pressure, it formed an infusible polymer of exceptional thermal and chemical stability. The polymerization, which was accompanied by elimination of benzene, is represented approximately by the equation:



The infusible polymer was a foamed, vitreous, pale yellow solid with a high degree of stability to heat, acids, alkali, and organic solvents. A similar reaction occurred with a resin that was obtained as a by-product in the preparation of hexaphenylcyclotrisilazane and with a mixture of silylamines that was obtained from the reaction of methylphenyl-dichlorosilane with ammonia. Coatings on aluminum and steel prepared by heating the silylamine polymers had good thermal stability and adhesion. Inclusion of a polymeric dimethylsilyl derivative of ethylenediamine improved the flexibility of the coatings.

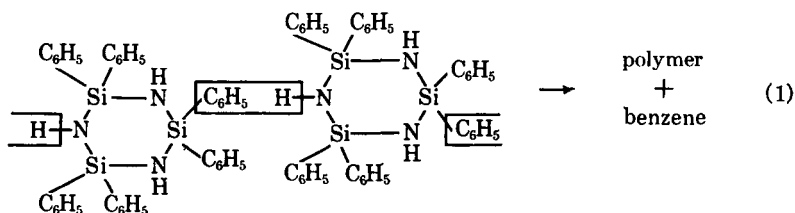
This investigation of silicon-nitrogen compounds was undertaken to develop new polymers with high thermal stability. In the past, the moisture sensitivity of silylamines has been the principal obstacle to their utilization. It has been found that certain types of silicon-nitrogen compounds not only have high thermal and chemical stability but also have the useful property of adhering to metals and glass. This is a report of the conversion of hexaphenylcyclotrisilazane and other silylamines to infusible polymers of high thermal and chemical stability. These materials have been applied to metals to form protective coatings.

When hexaphenylcyclotrisilazane was heated above 450°C. in bulk, it evolved benzene slowly and became progressively more viscous. As polymerization proceeded to form the infusible solid, the elemental composition changed from  $(C_6H_5)_2SiNH$  to approximately  $C_6H_5SiN$ . The final product was pale yellow, foamed, transparent, and brittle. It had a high degree of resistance to heat, moisture, and acids.

Prolonged heating at 550°C. or above caused further loss of weight, with carbon, hydrogen, and nitrogen being lost at a faster rate than silicon. Thermogravimetric analysis (Fig. 1) showed that the weight loss on heating the infusible polymer to 850°C. in nitrogen was 25%.

The volatile material was almost entirely benzene with traces of diphenyl, ammonia, and hydrogen. No methane or acetylene were detected in the volatile products.

These results indicate that the polymerization of hexaphenylcyclotrisilazane involves primarily an intermolecular condensation of the phenyl groups attached to silicon and hydrogen atoms attached to nitrogen. No evidence for fragmentation of the hexaphenylcyclotrisilazane rings was found. According to its formula, hexaphenylcyclotrisilazane is trifunctional with respect to N-H and hexafunctional with respect to Si-phenyl groups. However, it is not likely that all of the functionalities can be utilized because of steric factors. Probably polymerization proceeds by more than one route, and the product remains soluble and fusible through the trimer stage. Thereafter, the reaction rate is reduced by immobility of the molecules and steric shielding of the reactive centers. Crosslinking ultimately leads to infusibility and insolubility. One possible mechanism of polymerization is the formation of chains of trisilazane rings as shown in eq. (1), followed by crosslinking. Another possibility is opening of the rings with rearrangement into linear silazanes, followed by crosslinking. However, ring opening would probably be followed by further scission that would result in the formation of small silylamine fragments, which would be volatile at the reaction temperature. The presence of volatile materials other than benzene was not detected except in minute quantities.



Polymerizations carried out by heating hexaphenylcyclotrisilazane in air on aluminum or steel produced transparent coatings that had good adhesion with a high degree of thermal and chemical stability. Elemental analysis of the coating showed that partial replacement of nitrogen by oxygen occurred.

In the preparation of hexaphenylcyclotrisilazane, a resin was obtained as a by-product. This resin underwent the same type of polymerization, but coatings made from the resin were more flexible and more easily cured than those made from hexaphenylcyclotrisilazane. The resin had a higher average molecular weight than hexaphenylcyclotrisilazane, and it probably contained amine endgroups which condensed with each other to facilitate polymerization. Coatings of still better flexibility were obtained when a silylamine made from dimethyldichlorosilane and ethylenediamine was used with the hexaphenylcyclotrisilazane by-product resin.

2,4,6-Trimethyl-2,4,6-triphenylcyclotrisilazane, which boiled at approximately 405°C., polymerized relatively slowly at that temperature. However, a mixture of methylphenyl silazanes, which was obtained as a by-product in the preparation of 2,4,6-trimethyl-2,4,6-triphenylcyclotrisilazane, polymerized in the manner described for hexaphenylcyclotrisilazane. Analysis of the vitreous polymer indicated that the condensation involved loss of both methyl and phenyl groups.

Groszos and Hall<sup>1</sup> converted hexaphenylcyclotrisilazane to thermoplastic materials by heating at temperatures in the range of 450–700°C. in sealed tubes. Their products were viscous liquids or solids that were fusible, moisture-sensitive, and soluble in organic solvents. Presumably the pressure resulting from the use of sealed tubes was critical in determining the character of their product. The thermal polymerization of 2,4,6-trimethyl-2,4,6-triphenylcyclotrisilazane catalyzed by potassium hydroxide has also been reported.<sup>2</sup> Benzene was evolved, and low-melting solids were formed.

### Polymerization of Hexaphenylcyclotrisilazane

Hexaphenylcyclotrisilazane ( $C_{12}H_{11}SiN$ )<sub>3</sub> was prepared by the reaction of diphenyldichlorosilane with ammonia.<sup>3</sup> It is a solid melting at 215°C. that is soluble in organic solvents and is slowly attacked by atmospheric moisture. When it was heated in a test tube over an open flame, the melt began evolving vapors at 510°C. After 5 min. of heating, the temperature of the clear melt was 560°C., and the cooled vitreous material was soluble in benzene. Its elemental analysis was C, 65.36%; H, 4.84%; Si, 19.70%; N, 8.90%; this corresponds to a formula of  $C_{7.8}H_{5.9}Si_{1.0}N_{0.9}$ . The molecular weight was 1400 as determined by vapor osmometry. When heating was resumed, solid began to appear in the melt, and the mass became solid and infusible in an additional 10 minutes. When cool, the foamed, vitreous solid was insoluble in benzene and inert to aqueous acids.

The elemental analysis was C, 61.24%; H, 4.29%; Si, 23.10%; N, 9.41%; corresponding to  $C_{6.2}H_{5.2}Si_{1.0}N_{0.8}$ . Further heating for 1 hr. at 560°C. produced no visible change. The final elemental analysis was C, 58.63%; H, 4.64%; Si, 30.24%; N, 8.22%; this corresponds to  $C_{4.5}H_{4.3}Si_{1.0}N_{0.5}$ .

Further experiments showed that the time required for complete solidification of the melt decreased from 570 min. in an oven at 450°C. to 23 min. in an oven at 550°C.

### Thermogravimetric Analysis of the Condensation Polymer

The thermal stability of the infusible polymer formed by heating hexaphenylcyclotrisilazane was demonstrated by thermogravimetric analysis. The data, obtained at a heating rate of 6°C./min. in a nitrogen atmosphere, are shown in Figure 1. The total weight loss on heating to 850°C. was 25%. The most rapid weight loss, 15%, occurred between 550 and 650°C. Above 650°C. the loss was only 2%.

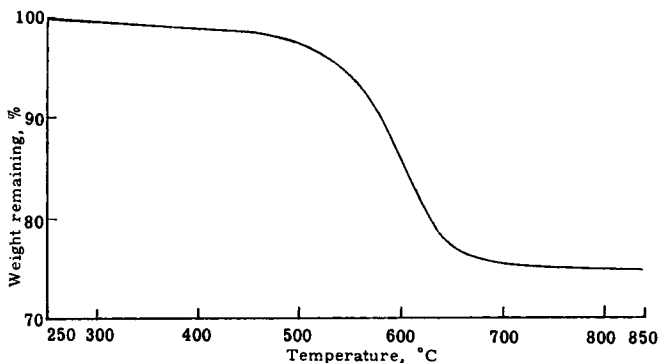


Fig. 1. Thermogravimetric analysis of hexaphenylcyclotrisilazane condensation polymer in a nitrogen atmosphere. Rate of temperature rise 6°C./min.

### Volatile Products of the Condensation Polymerization of Hexaphenylcyclotrisilazane

Hexaphenylcyclotrisilazane, 1.883 g., was placed in a small tared distilling apparatus that had been swept with nitrogen. The receiver was cooled in a Dry Ice-acetone bath. The hexaphenylcyclotrisilazane was heated until it solidified; then heating was stopped, and dry nitrogen was passed through the apparatus slowly to sweep the volatile products into the receiver. The weight of the foamed, pale yellow, solid residue was 1.121 g., which was 59.5% of the starting material or 98% of theory for production of  $(C_6H_5SiN)_n$  from  $(C_{12}H_{11}SiN)_n$ . The weight of the distillate was 0.746 g. (39.6% of the starting material). Hence, 0.9% of the starting material was not recovered. The distillate contained a small droplet of water that was no more than 0.01 ml. or 0.5% of the weight of starting material. The organic portion of the distillate was analyzed by gas chromatography and found to be 99.1% benzene and 0.7% diphenyl, with traces of higher boiling compounds.

The pyrolysis described was one of a series, the others being designed specifically to trap particular volatile products. In one, the volatile products were swept into a measured amount of standard sulfuric acid which was then titrated to reveal the amount of volatile base evolved. Calculated as ammonia, the amount was less than 0.4 mg. which was obtained from 2.2627 g. of hexaphenylcyclotrisilazane. This quantity was less than 0.02% of the weight of the sample or less than 0.3% of the total nitrogen in the sample. Another pyrolysis was conducted in a gas chromatographic apparatus, and 0.2% by weight of hydrogen was detected. This quantity was 3.5% of the total hydrogen in the starting material. A trace (less than 0.01%) of hydrocarbons and no acetylene was detected. Consequently, the volatile matter produced during condensation polymerization of hexaphenylcyclotrisilazane, including the amount lost, was at least 96% benzene.

### Resinous By-Product of Hexaphenylcyclotrisilazane

Larsson and Bjellerup<sup>3</sup> obtained 62% of the theoretical yield of hexaphenylcyclotrisilazane from the reaction of diphenyldichlorosilane with ammonia. The method used in this laboratory was slightly different from theirs, and it is reported here in detail to describe the resinous by-product obtained by evaporation of the mother liquor. The procedure was as follows:

In a 5-liter, three-necked flask fitted with a stirrer, reflux condenser, and gas inlet tube were placed 3 liters of benzene and 310 ml. (378 g., 1.49 mole) of diphenyldichlorosilane. The chlorosilane solution was stirred under an atmosphere of dry ammonia for 4 hr. The mixture was refluxed for 4 hr., the ammonium chloride was filtered off, and the occluded hexaphenylcyclotrisilazane was extracted from it by stirring and filtering four times with 200 ml. portions of hot benzene. The benzene solutions were combined and distilled until the pot temperature reached 95°C. The undistilled liquid was repeatedly cooled and filtered to obtain crystalline hexaphenylcyclotrisilazane, 166.0 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 crude hexaphenylcyclotrisilazane, 50.3 g. (0.084 mole, 17.0% of theory). The resin was obtained from the mother liquor by evaporation, finally at 0.05 mm. pressure. The yield of resin, a pale yellow sticky gum, was 55.5 g. (0.28 mole), 18.8% of theory if the formula is assumed to be  $[(C_6H_5)_2SiNH]_n$ . Thus the yield of the combined products was 92.3%. The molecular weight of the resinous by-product as determined by vapor osmometry was 980 (hexaphenylcyclotrisilazane, 592).

ANAL. Calcd. for  $(C_{12}H_{11}SiN)_n$ : C, 73.02%; H, 5.63%; N, 7.11%; Si, 14.24%. Found: C, 72.74%; H, 5.60%; N, 5.64%; Si, 12.80%; O, 2.64% (by activation analysis).

### Dimethylsilyl Derivative of Ethylenediamine

The method used in this laboratory to prepare the dimethylsilyl derivative of ethylenediamine differed slightly from the method of Minné and Rochow.<sup>4</sup> Ethylenediamine, 300.5 g. (5.0 mole), was dissolved in 1500 ml. of benzene, and dimethyldichlorosilane, 129.0 g. (1.0 mole), was added dropwise with stirring over a period of 2 hr. The mixture was refluxed for 4 hr., and, after being cooled, the two layers were separated in a separatory funnel. The upper layer was freed of benzene by evaporation at reduced pressure. The product, 83 g., was a brown viscous liquid. The molecular weight, as determined cryoscopically in cyclohexane, was 1200.

### 2,4,6-Trimethyl-2,4,6-triphenylcyclotrisilazane and a Mixture of Methylphenyl Silazanes

Methylphenyldichlorosilane, 191.1 g. (1.0 mole), was dissolved in 1600 ml. of benzene and stirred under an atmosphere of ammonia for about 2 hr.

until no further reaction was apparent. The reaction mixture was then refluxed for 4 hr., while a slow stream of ammonia was passed through the reaction vessel. The ammonium chloride was removed from the product by filtration, and the benzene was removed by evaporation at reduced pressure. The product, 114 g., was a cloudy, colorless, viscous liquid that did not crystallize in several days at 0°C. The yield of mixed methylphenyl silazanes was 85% of theory assuming  $(\text{SiCH}_3\text{C}_6\text{H}_5\text{NH})_n$  to be the formula. A portion of the product, 67 g., was distilled to yield 57.6 g. of a viscous liquid (b.p. 180–205°C./0.3 mm. pressure) and 9.0 g. of residue. After the distillate had stood for 2 days at 0°C., crystals appeared. They were recrystallized from *n*-hexane to yield 3.5 g. of 2,4,6-trimethyl-2,4,6-triphenylcyclotrisilazane, m.p. 113.5–115.5°C.

ANAL. Calcd. for  $\text{C}_{21}\text{H}_{27}\text{Si}_3\text{N}_3$ ; C, 62.16%; H, 6.70%; Si, 20.77%; N, 10.37%; mol. wt. 405.72; neutral equivalent after hydrolysis 135.24. Found: C, 62.02%; H, 6.68%; Si, 20.76%; N, 9.76%; mol. wt. (camphor) 410, (cyclohexane) 403; neutral equivalent after hydrolysis 146.

The initial reaction product, a mixture of methylphenyl silazanes, polymerized to a foamed brittle solid when it was heated at 450–480°C. for about 30 min. The elemental analysis of the polymer was C, 53.81%; H, 5.52%; N, 11.59%. If the remainder is assumed to be silicon, the analysis corresponds to  $\text{C}_{4.3}\text{H}_{5.3}\text{Si}_{1.00}\text{N}_{0.8}$ . By contrast, pure 2,4,6-trimethyl-2,4,6-triphenylcyclotrisilazane was heated in an open flask at approximately 400°C. without visible change. After about 30 min. of boiling, the rate of heat input was increased to boil the sample away, and only a trace of friable solid polymer remained.

### Coatings

Hexaphenylcyclotrisilazane was partially polymerized by heating in an open test tube until the melt temperature reached 550°C. The product was dissolved in benzene to form a 2.5% solution. Coatings on aluminum panels were prepared by evaporation of the benzene in air, and then the panels were heated in an oven at 520°C. for 5 min. The resulting coatings were smooth, adherent, colorless, and transparent, but brittle. They were not visibly affected by benzene, acetone, alcohol, aqueous 8% sodium hydroxide, or aqueous 10% hydrochloric acid when exposed for an hour. Coatings that were thicker than 0.3 mil. bubbled while being cured, or they cracked when the panels were cooled. Films on aluminum or stainless steel remained essentially unchanged in appearance when heated for an hour at 550°C. in air. After that time crazing was apparent, but adhesion remained good. Elemental analyses of the coatings indicated that partial replacement of nitrogen by oxygen had occurred. A coating heated in air at 450°C. for 15 min. had the composition, C, 64.45%; H, 4.70%; N, 6.65% (calculated for  $\text{C}_6\text{H}_6\text{SiN}$ , C, 60.46%; H, 4.23%; N, 11.75%).

Coatings made by heating the hexaphenylcyclotrisilazane by-product resin were similar but less brittle, and coatings made from a mixture of

90% of this resin and 10% of the dimethylsilyl derivative of ethylenediamine had similar resistance to chemicals and heat (1 hr. at 500°C. without apparent change), and they were even more flexible.

The research reported herein was sponsored by the George C. Marshall Space Flight Center, National Aeronautics and Space Administration, Huntsville, Alabama.

The authors wish to express their appreciation for the advice and assistance of Mr. Harold Perkins, Mr. James D. Byrd, and Mr. James E. Curry of the National Aeronautics and Space Administration.

Molecular weights by vapor osmometry were determined by Galbraith Laboratories, Inc., Knoxville, Tennessee. Radioactivation analysis for oxygen was done by the General Atomic Division of General Dynamics Corporation, San Diego, California.

### References

1. Groszos, S. J., and J. A. Hall (to American Cyanamid Company), U. S. Pat. 2,885,370 (May 5, 1959).
2. Andrianov, K. A., and G. V. Kotrelev, *Vysokomolekul. Soedin.*, **6**, 691 (1964).
3. Larsson, E., and L. Bjellerup, *J. Am. Chem. Soc.*, **75**, 995 (1953).
4. Minné, R., and E. G. Rochow, *J. Am. Chem. Soc.*, **82**, 5625, 5628 (1960).

### Résumé

Lorsqu'on chauffe de l'hexaphénylcyclotrisilazane au dessus de 450°C à pression atmosphérique, il se forme un polymère infusible possédant une stabilité thermique et chimique exceptionnelle. La polymérisation qui s'accompagne de l'élimination de benzène, est représentée approximativement par l'équation présenté dans le résumé anglais. Le polymère infusible est un solide spongieux, vitreux, jaune-pâle, possédant une stabilité élevée vis-à-vis de la chaleur, des acides, des alcalis et des solvants organiques. Une réaction semblable a été effectuée avec une résine obtenue comme produit secondaire dans la préparation de l'hexaphénylcyclotrisilazane et avec un mélange de silylamines obtenu à partir de la réaction du méthylphényldichlorosilane avec l'ammoniaque. Des revêtements sur aluminium et acier, préparés en chauffant les polymères de silylamine, possèdent une bonne stabilité thermique et une bonne adhésion. L'introduction d'un dérivé polymérique diméthylsilyle de l'éthylènediamine, améliore la flexibilité des revêtements.

### Zusammenfassung

Hexaphénylcyclotrisilazan bildete bei der Erhitzung über 450°C bei Atmosphärendruck ein unschmelzbares Polymeres von aussergewöhnlicher thermischer und chemischer Stabilität. Die Polymerisation, welche unter Abspaltung von Benzol verläuft, lässt sich angenähert durch die in der englischen Zusammenfassung gezeigten Gleichung darstellen. Das unschmelzbare Polymere bildet einen schaumigen, glasartigen, schwach gelben Festkörper mit hochgradiger Beständigkeit gegen Hitze, Säuren, Alkali und organische Lösungsmittel. Eine ähnliche Reaktion trat bei einem als Nebenprodukt bei der Darstellung von Hexaphénylcyclotrisilazan erhaltenen Harz und bei einer durch Reaktion von Methylphenyldichlorsilan mit Ammoniak erhaltenen Mischung von Silylaminen auf. Durch Erhitzung der Silylaminpolymeren dargestellte Überzüge auf Aluminium und Stahl besaßen gute thermische Stabilität und Adhäsionseigenschaften. Einbau eine polymeren Dimethylsilylderivats von Äthylendiamin verbesserte die Flexibilität der Überzüge.

Received December 15, 1964

Revised March 29, 1965