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DEVELOPMENT OF RAIN-EROSION-RESISTANT COATINGS FOR HIGH-SPEED AIRCRAFT

Final Report

(15 April 1968 to 14 April 1969)

June 1969

by

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for

Naval Air Systems Command
Department of the Navy

by

Southern Research Institute
Birmingham, Alabama

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39

FOREWORD

This summary report pertains to research performed on a project sponsored by the Naval Air Systems Command, Department of the Navy, under Contract N00019-68-C-0138. The report includes work accomplished during the period 15 April, 1968, to 14 April, 1969. The research was monitored by Mr. A. Malloy, of the Naval Air Systems Command.

The authors wish to acknowledge the valuable suggestions and discussions of Dr. S. N. Glarum and Dr. C. E. Feazel.

TABLE OF CONTENTS

TABLE OF CONTENTS
(continued)

LIST OF TABLES

LIST OF ILLUSTRATIONS

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DEVELOPMENT OF RAIN-EROSION-RESISTANT COATINGS FOR HIGH-SPEED AIRCRAFT

I. INTRODUCTION AND SUMMARY

New high-temperature elastomers are needed for rain-erosion-resistant coatings on radomes and leading edges of high-speed aircraft. Neoprene and polyurethanes, which are the best available erosion-resistant flexible materials, do not withstand the aerodynamic heating that occurs on the high-speed aircraft. Silicone elastomers, which cure at room temperature and have adequate thermal stability, have poor erosion resistance. Other high-temperature elastomers that are available lack erosion resistance or require curing under conditions too severe for application aboard ship. A successful rain-erosion coating must be resistant to weathering and attack by fuels and organic solvents.

Our investigation of new rain-erosion-resistant elastomers included several different types of polymers containing fluorine and silicon. A polymer made by the reaction of 1,4-bis(dimethylaminodimethylsilyl)benzene with the adduct of hexafluoroacetone and isobutylene was cured at room temperature by the action of ethyl silicate and dibutyltin diacetate. Another polymer made by the reaction of 1,4-bis(dimethylhydroxysilyl)benzene with bis(dimethylamino)dimethylsilane was cured by the same system. The former elastomer, the "hexafluoroacetone-isobutylene-silphenylene" had better solvent resistance, but the latter, the "silphenylene-siloxane" had better tensile properties. Neither of these elastomers has been tested in a whirling-arm, rain-erosion simulator. The silphenylene-siloxane was found superior in erosion resistance to an RTV silicone when the elastomers were compared in a sand-blast apparatus that has been used for screening. When compared by the sand blast method, the silphenylene-siloxane had almost as much erosion resistance as neoprene N-83 initially but more than neoprene N-83 after both had been held at 150°C (302°F) or more for 4 hours.

Several fluorocarbon-siloxane polymers were prepared and found to be sensitive to moisture. Poly(perfluoropropylene-3-phenylenethiazole) was prepared, but it melted at 130-140°C. Since concurrent findings in other laboratories suggested it would not have good thermal stability, it was not pursued further.

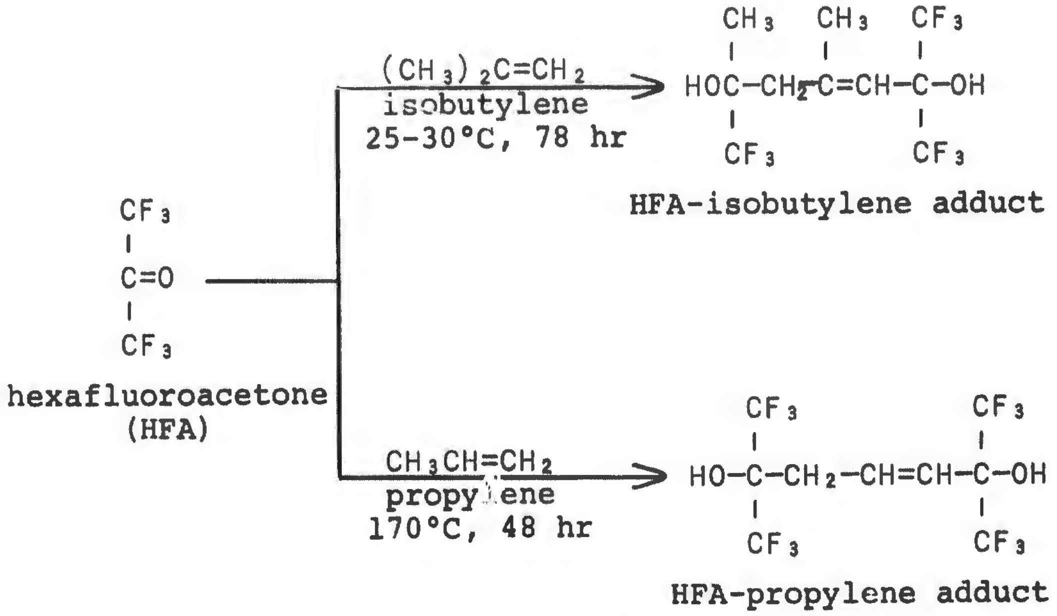
In further work on rain-erosion-resistant coatings under Contract N00019-68-0138 we are attempting to improve the hexafluoroacetone-alkylene-siloxane and silphenylene-siloxane elastomers and find satisfactory methods of applying them.

This report covers the work done under Contract N00019-68-0138 in the period April 15, 1968, to April 15, 1969.

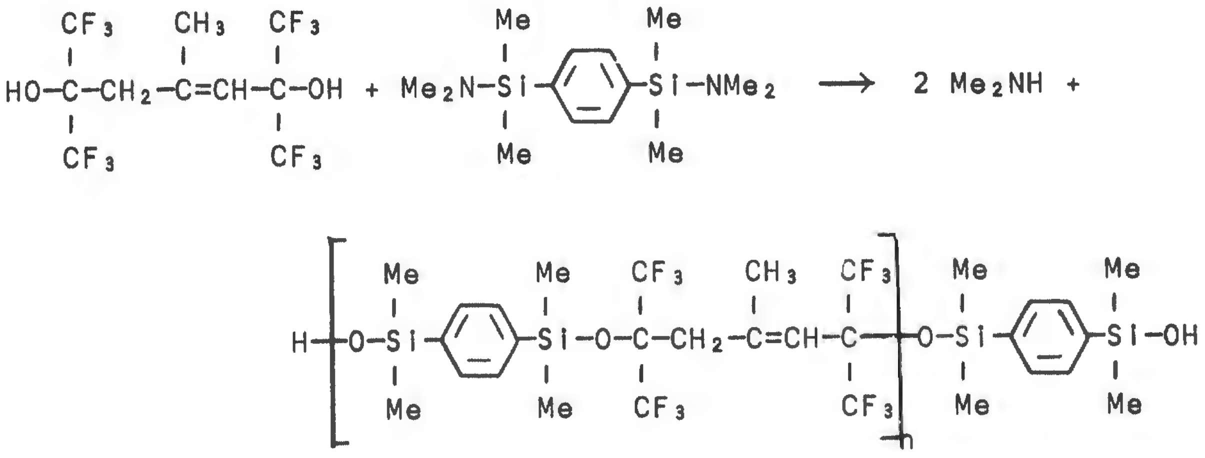
II. ELASTOMERS PREPARED FROM A SILPHENYLENE DIAMINE AND HEXAFLUOROACETONE-ALKYLENE ADDUCTS

A. Discussion

The availability of hexafluoroacetone-alkylene adducts and their potential contributions to thermal stability and fuel resistance suggested that they should be tried as monomers to form elastomers for rain-erosion coatings.



The HFA-isobutylene adduct was made into a polymer by treating it with a silphenylene diamine by the diol-diaminosilane reaction.[1]



hexafluoroacetone-isobutylene-silphenylene polymer

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[1] See References, page 29.

This polymer, as a cast film, was cured at room temperature to an elastomer with a tensile strength (nominal) of 1240 psi and an elongation at break of 265%. Although the tensile product of this film, 330,000, was low compared with that of filled elastomers being considered for rain-erosion coatings, it is rather high for an unreinforced film made from a polymer of such a low molecular weight. It is likely that further investigation would result in finding better methods of preparation, particularly for obtaining narrow-molecular weight distribution, and in finding better formulations for curing and reinforcing with inorganic fillers.

The diols made by adding hexafluoroacetone to isobutylene or propylene exist as cis and trans isomers, and the isobutylene adduct also exists in two forms having the double bond in the chain or between the middle carbon and the side methylene group. A research sample of the isobutylene adduct was obtained from Allied Chemical Corporation, but the propylene adduct has been prepared at the Institute. The method of preparing the isobutylene and propylene adducts by uncatalyzed addition under pressure at 25-30°C and 170°C, respectively, was described by Litt and Schmitt[2] and by Urry, Niu, and Lundsted[3].

The potential price of hexafluoroacetone (HFA) is attractive in comparison with the prices of other fluorinated monomers. HFA now sells for about $6.00 per lb, but it is expected to reach $0.65 per lb in large commercial quantities. The additions to isobutylene and propylene would reduce the costs of materials even further.

Polymerization with the HFA-isobutylene adduct was tried first and studied more extensively. A thermogravimetric analysis of the HFA-isobutylene-silphenylene polymer, Figure 1, showed that only 10%, by weight, of the polymer had been lost by the time the temperature reached 400°C at a heating rate of 10°C per minute in nitrogen. The thermal stability indicated by TGA places the HFA-isobutylene-silphenylene among the most stable elastomers.

Because of the hydrolytic instability of many polymers that contain SiOC units, it was interesting to find that this polymer, dissolved in xylene, was not degraded by 2 hours of refluxing with water. A cured film, which was still flexible after 3 hours at 305°C in air, was not visibly changed during 1 hour in boiling water.

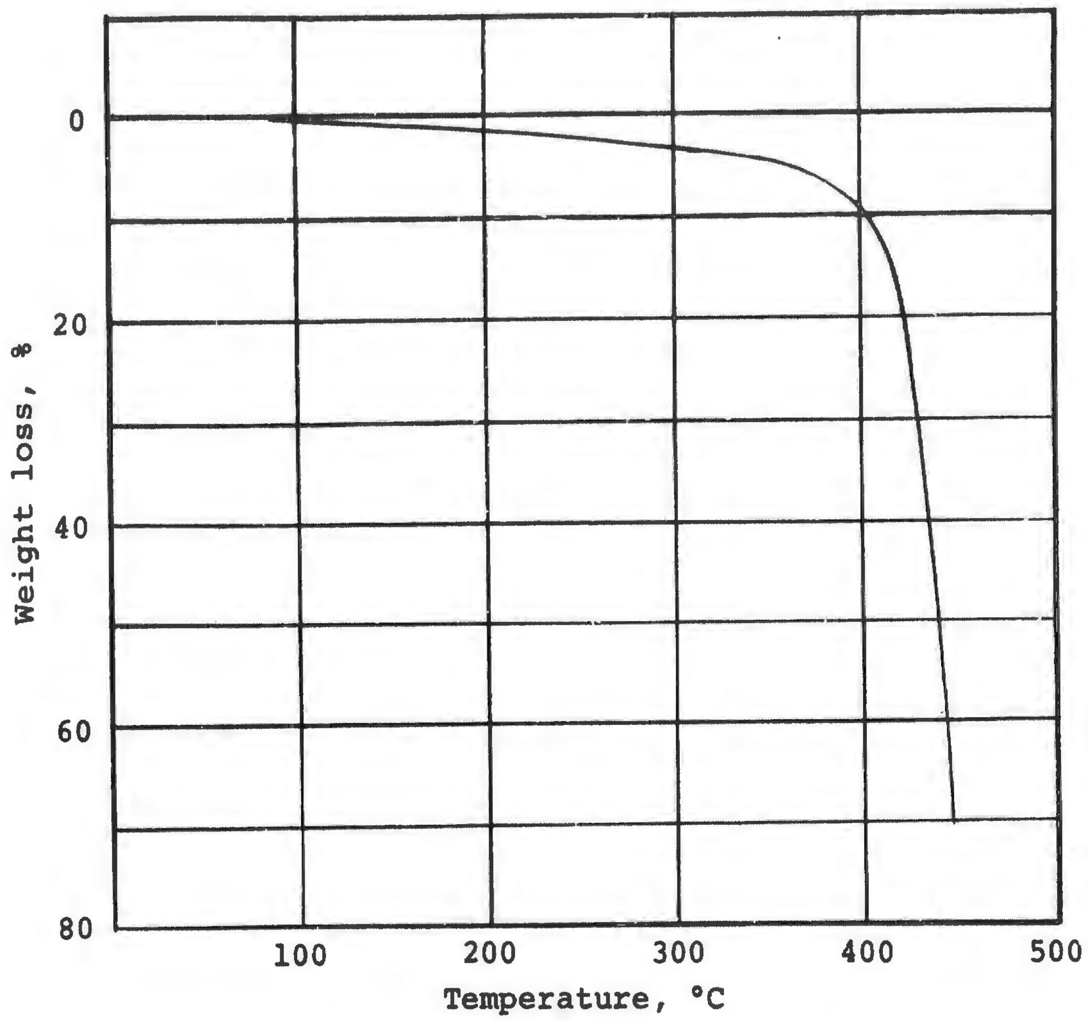
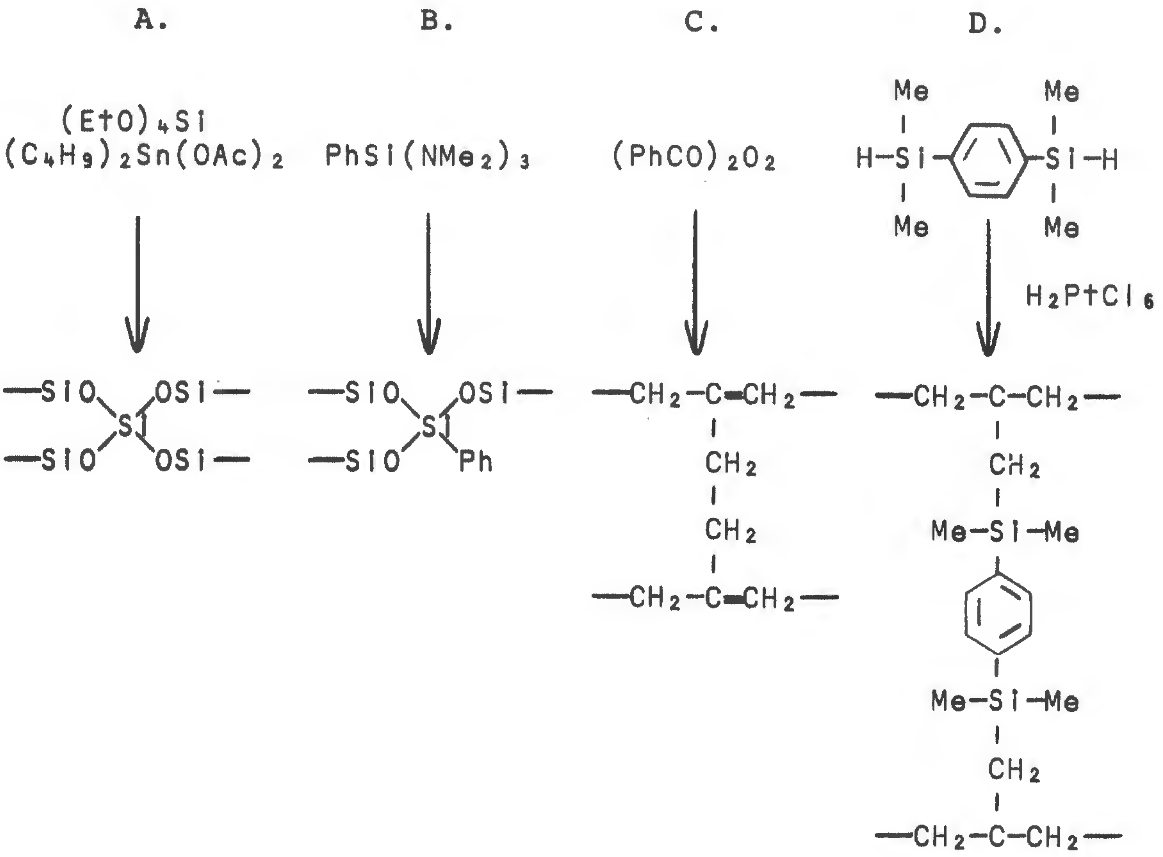


Figure 1. Thermogravimetric Analysis of
Hexafluoroacetone-Isobutylene-Silphenylene Elastomer (5293-11-17A)
(In nitrogen; 10°C/min)

The HFA-isobutylene-silphenylene polymer has been crosslinked by four methods according to the reactions shown below. Method A produced a strong elastomer, the one mentioned above. We expect to be able to increase the strength further by increasing the molecular weight and narrowing the molecular-weight distribution.



Silanol end groups, which are needed for curing with ethyl silicate by the method in use with RTV silicones (Method A, above),[4] are obtained by adding a slight excess of the silphenylene amine after polymerization is largely complete and by hydrolyzing the aminosilane end groups with water as the final step of polymer preparation.

By gel permeation chromatography, we estimated the average molecular weight of one HFA-isobutylene-silphenylene polymer to be: $\overline{M}_n = 11{,}000$; $\overline{M}_w = 29{,}000$. This polymer had an inherent viscosity of 0.12 dl/g measured in tetrahydrofuran at 30°C at a concentration of 1.0 g/dl. The swelling ratios of several elastomers in toluene and in JP-4 fuel are given in Table I.

Table I. Swelling of Elastomers in Solvents

	Swelling ratio[a] in	
	Toluene	JP-4 fuel
Neoprene N-83 (Gates Rubber Co.)	1.80	1.02
Hexafluoroacetone-isobutylene-silphenylene, 5293-11-4A	1.41	1.26
Silphenylene-siloxane, 4952-65-2	1.60	1.45
Silicone K1213 (Union Carbide), peroxide-cured	1.82	1.55

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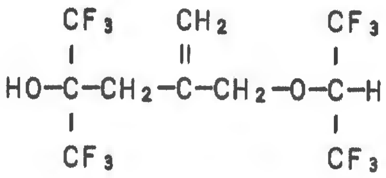
[a] Ratio of swollen length to original length.

The hexafluoroacetone polymer was more resistant to toluene than the silphenylene-siloxane discussed in Section III, neoprene N-83, or a peroxide-cured silicone, in that order. In JP-4 fuel the order of resistance was generally the same, except the neoprene N-83 was the most resistant.

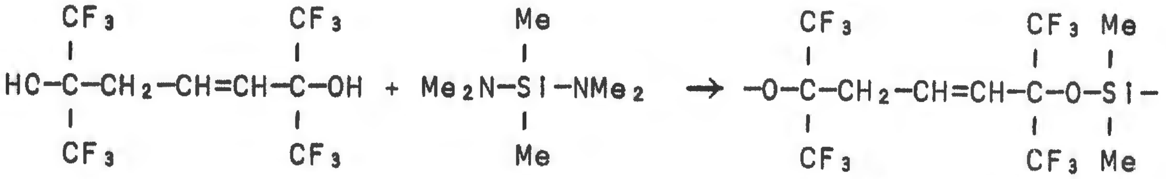
The HFA-propylene-silphenylene adduct was prepared without difficulty, but we have not succeeded in making polymers with molecular weights as high as those prepared with the HFA-isobutylene adduct. The only two isomers of the propylene adduct that are known are the cis and trans forms, whereas the isobutylene adduct exists in three isomers, cis and trans of the form having the double bond in the chain and the form having the double bond on the side. Because of the smaller number of isomers and the higher fluorine content, it appeared that the propylene adduct would be more desirable. However, for reasons not yet understood, we have had more trouble obtaining adequate molecular weights with the propylene adduct. The problem may be a result of impurities in the adduct. However, examination of molecular models suggests that one of the hydroxyl groups in the cis adducts has a higher level of steric hindrance. Actually, all of the hydroxyl groups are crowded by the trifluoropropyl groups, but the cis compound appears to have less freedom. There is also the possibility, not mentioned in the literature, that another isomeric form, an alcohol-ether, exists as a result of a different mode of addition:



$$\mathrm{HO{-}C(CF_3)_2{-}CH_2{-}C({=}CH_2){-}CH_2{-}O{-}C(CF_3)_2{-}H}$$

Such an alcohol-ether would act as a chain terminator in polymerizations. It would be easier to remove this isomer from the isobutylene adduct, which is crystalline, than from the <u>trans</u> propylene adduct, which is a liquid.

An attempt to prepare a polymer by a diol-diaminosilane reaction between the HFA-isobutylene adduct and bis(dimethylamino) dimethylsilane resulted mainly in cyclization. This reaction continues to be interesting, however, because a linear polymer of equivalent structure would contain an exceptional amount of fluorine and have excellent fuel resistance. A similar polymer made with the propylene adduct would have still higher fluorine content.



$$\mathrm{HC{-}C(CF_3)_2{-}CH_2{-}CH{=}CH{-}C(CF_3)_2{-}OH + Me_2N{-}SiMe_2{-}NMe_2 \rightarrow {-}O{-}C(CF_3)_2{-}CH_2{-}CH{=}CH{-}C(CF_3)_2{-}O{-}SiMe_2{-}}$$

53% fluorine

B. <u>Experimental Details</u>

1. <u>Preparation of compounds</u>

a. <u>Bis(dimethylamino)dimethylsilane</u>

In a 3-liter, 3-neck flask fitted with a thermometer, reflux condenser, stirrer, and gas-inlet tube were placed 194 g (1.5 mole) of dimethyldichlorosilane and 1500 ml of benzene. Liquid dimethylamine, approximately 400 g (8.9 mole), was drawn from a cylinder into a flask containing a few pea-size pieces of sodium and distilled slowly through a rubber tube into the reaction flask over a period of about 5 hours as the chlorosilane and benzene were stirred. The salt formed was filtered off and washed with benzene, and the combined benzene solutions were found to give a positive Beilstein test for halogens. Consequently, introduction of methylamine was resumed as before with the formation of additional salt. The reaction mixture was filtered, and the filtrate was distilled through a 15-inch Widmer column to yield 90 g

(41% of theory) of bis(dimethylamino)dimethylsilane, b.p. 126.5-127.5°C at 750 mmHg pressure. Anderson[5] reported 128.4°C at 760 mmHg.

b. 1,4-Bis(dimethylchlorosilyl)benzene

The method of Sveda[6] was used to prepare 1,4-bis(dimethylchlorosilyl)benzene in a 5-liter, 3-neck flask fitted with a stirrer and an extraction device. The extraction device consisted of a still with a partial take-off head that was arranged to return the distilled solvent to the reaction flask through a reservoir of p-dibromobenzene (400 g, 1.69 moles), which also contained 200 ml of ether. In the flask were placed 124.0 g (5.09 moles) of magnesium turnings, 800 ml of dry diethyl ether, and 656 g (5.09 moles) of dimethyldichlorosilane. The system was swept with dry nitrogen, and the reaction was started by gentle heating after adding about 50 ml of the ether solution of p-dibromobenzene. The flask was warmed slightly to reflux the ether which extracted the p-dibromobenzene from the reservoir. As the dibromobenzene returned to the flask, the exothermic reaction kept the ether distilling. After reaction was complete (1.5 hours), the mixture was refluxed for 30 minutes. The mixture was filtered with a filter stick, the cake was washed with ether, and the ether solutions were combined and distilled. When most of the ether was gone, 400 ml of dry toluene was added and distilled at atmospheric pressure to ensure removal of the dichlorosilane. The product remaining in the flask was then distilled at reduced pressure, and the portion that distilled at 110-111°C at 1.5 mmHg pressure was retained as product. The product weighed 202 g, 46% of theory. It was a white crystalline solid.

c. 1,4-Bis(dimethylhydroxysilyl)benzene

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

d. 1,4-Bis(dimethylaminodimethylsilyl)benzene

1,4-Bis(dimethylaminodimethylsilyl)benzene was prepared in the manner described for bis(dimethylamino)dimethylsilane. The reaction mixture was distilled twice through a 12-in. jacketed Vigreux column to give a fraction boiling at 100-101°C at 0.50 mmHg (30% of theory).

e. Hexafluoroacetone-isobutylene adduct

The hexafluoroacetone-isobutylene adduct was obtained from Allied Chemical Corporation. The white crystalline material (10 g) was recrystallized from 400 ml of carbon tetrachloride. The main crop of the product, 5.9 g, melted at 145-146°C.

Anal. Calculated for $C_{10}H_8F_{12}O_2$: C 30.94, H 2.08.

Found: C 30.60, H 2.17.

f. Hexafluoroacetone-propylene adduct

Hexafluoroacetone (Pierce Chemical Co.), 106 g (0.64 mole) was mixed with 10.5 g (0.25 mole) of propylene (Matheson Chemical Co.) in a 300-ml stainless-steel reaction vessel. Since both reactants are gases at room temperature, they were weighed and introduced into the reaction vessel as follows: (1) the gases were condensed and collected in test tubes cooled in dry ice, (2) the test tubes were placed in insulated containers for weighing, (3) the liquid reactants were poured into the reaction vessel that had been cooled in dry ice, and (4) the reaction vessel was quickly sealed.

The hexafluoroacetone and propylene were heated at 170°C for 48 hours. The vessel was cooled to room temperature, and the clear yellow reaction mixture was poured out. A gas presumed to be excess hexafluoroacetone bubbled out of the reaction mixture. The *cis* isomer, 4.2 g, was filtered off, and the filtrate was distilled through a 12-in. Vigreux column to yield 89.7 g of liquid, b.p. 178-179.5°C. There was about 5 g of a brown liquid residue, possibly a tri-adduct. Since the theoretical yield of di-adduct was 93.5 g, the yield was essentially quantitative, based on propylene. The excessive weight of product is attributed to the difficulty of weighing the original propylene as a liquid at -47.7°C. The error in weighing was much less than 1 g, since the di-adduct is only 11% propylene, and the tri-adduct is 8% propylene. The boiling point of the product agrees with that reported by Urry, Niu, and Lundsted,[3] but we encountered variability in the carbon-hydrogen analyses depending on combustion time. Gas chromatography indicated that the liquid product contained mono-adduct and *cis* and *trans* isomers of the di-adduct.

2. Preparation of polymers

a. Hexafluoroacetone-isobutylene-silphenylene polymer

The reaction of the hexafluoroacetone-isobutylene adduct and the silphenylene diamine was conducted by several different procedures. Reaction 5293-17 is described as typical. The hexafluoroacetone-isobutylene adduct, 3.03 g (0.00780 mole), was placed in a 50-ml, 3-neck, round-bottom flask with 5.0 ml of reagent-grade xylene (Baker and Adamson). The reaction flask was fitted with a reflux condenser, thermometer, magnetic stirring bar, and a rubber serum cap. 1,4-Bis(dimethylaminodimethylsilyl)-benzene, 1.79 g (0.00638 mole), was placed in the flask in a single addition while dry nitrogen was being blown gently into the flask to provide an inert blanket. The reaction flask was immersed in an oil bath at 155°C, and the xylene was refluxed for 1 hour while the initial gas evolution took place. Then an additional 0.018-g portion of diaminosilane were added every 20 minutes from a hypodermic syringe through the serum cap until the total added was 0.41 g (0.00146 mole). The solution was then refluxed overnight. The inherent viscosity of the polymer, measured in tetrahydrofuran at a concentration of 1.0 g/dl at 30°C, was 0.05 dl/g. The addition of diamine was resumed until 0.21 g (0.00074 mole) had been added, and the mixture was, again, refluxed overnight. The inherent viscosity was then 0.129 dl/g. Since the diamine was in excess and the viscosity apparently would go no higher, the reaction was terminated by adding 2.0 ml of water and continuing to reflux for 2 hours. After cooling, the excess water and a trace of brown insoluble material were removed by centrifugation. The inherent viscosity was measured again and found to be 0.125 dl/g.

Anal. Calculated for $C_{20}H_{22}F_{12}O_2Si_2$: C 41.52, H 3.83.

Found: C 41.54, H 3.92.

The molecular length by gel permeation chromatography* was found to be

$$\bar{A}_n = 278\ \text{Å}$$
$$\bar{A}_w = 738\ \text{Å}$$
$$\bar{A}_w/\bar{A}_n = 2.65$$

If a value of 40 is assumed for the number of molecular weight units per Ångstrom of length, the molecular weight values become

$$\bar{M}_n = 11{,}000$$
$$\bar{M}_w = 30{,}000$$

---

*ArRo Laboratories, Joliet, Illinois.

Since higher molecular weights were needed to determine the most desirable range for the highest tensile properties, a number of attempts were made to purify reactants and improve reaction conditions. These are summarized as follows: The diol was purified by additional crystallizations, and the diamine was purified by additional fractional distillations; the polymerization was conducted without solvent and under reduced pressure at temperatures up to 220°C; the xylene was purified by refluxing with sodium; additional diamine was added in refluxing xylene after the hydrolysis step; and attempts were made to reduce steric hindrance and to extend the chains by adding bis(dimethylamino)dimethylsilane as the diamine in the latter portion of the polymerization. None of these attempts resulted in significant improvements in the molecular weights. The highest inherent viscosity obtained was 0.19 dl/g in Polymer 5293-41, which was prepared by treating the polymer after the hydrolysis with additional silphenylenediamine.

Precipitation of the polymer from solution by adding a non-solvent was tried as a means of refining the polymer and removing components of low molecular weight. A 30% solution in benzene of Polymer 5293-55-3 (inherent viscosity, 0.13 dl/g) was shaken vigorously with a 10-fold volume of methanol. After the polymer precipitated, it was redissolved in benzene and reprecipitated. The inherent viscosity of the product (5293-55-4) was 0.16 dl/g, and the recovery was about 75%.

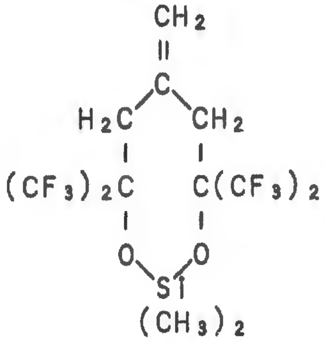
b. Hexafluoroacetone-propylene-silphenylene polymer

The hexafluoroacetone-propylene-silphenylene polymer was prepared essentially by the method described above for the isobutylene polymer. The best results were obtained when the hexafluoroacetone-propylene adduct was added incrementally to the refluxing solution of the silphenylenediamine in xylene. The inherent viscosity was 0.14 dl/g. An attempt was made to refine this polymer by precipitating it from the xylene solution by adding methanol. However, satisfactory separation did not occur and time did not permit additional work. We intend to repeat this experiment after making some intermediate attempts to separate the cis and trans isomers of the diol.

c. Attempted polymerization of hexafluoroacetone-isobutylene adduct with bis(dimethylamino)dimethylsilane

The method of preparing the silphenylene-dimethylsiloxane polymer was used with a slight modification in an attempt to prepare a fluorinated siloxane polymer from the hexafluoroacetone-isobutylene adduct and bis(dimethylamino)dimethylsilane. A 35%

solution of the diaminosilane in dioxane was added slowly to a refluxing dioxane solution of the adduct. A small amount of low-molecular-weight polymer was produced, but the principal product was a cyclic ether,



<u>Anal</u>. Calculated for $C_{12}H_{12}F_{12}O_2Si$: C 32.45, H 2.75, N 0.00.
Found: C 33.26, H 2.75, N <0.3.

This compound was not hydrolyzed after being in solution with water in dioxane for an hour. Polymerization of the diol and the diaminosilane was attempted under different conditions in an effort to discourage cyclization. A longer period was allowed for the diaminosilane to react with the excess diol at a lower temperature to encourage attachment of silicon to only one end of each diol molecule. Then the stoichiometric amount of diaminosilane was reached gradually. However, cyclization was still the dominant reaction.

3. <u>Curing of polymers</u>

Polymers and curing agents were mixed in solution and cast as films in aluminum dishes. This method required less than a gram of polymer for each experiment and provided samples for measurement of tensile properties. The strongest film prepared by this method was made as follows: Polymer 5293-41-5 (inherent viscosity, 0.14 dl/g; precipitated from methanol), 4.65 g, as a 15% solution in xylene was mixed with 0.72 g of Ethyl Silicate 40 (a partially hydrolyzed version of ethyl silicate, Union Carbide Corp.) in a 20% solution in benzene and 0.19 g of dibutyltin diacetate (Eastman Organic Chemicals) in a 10% solution in benzene. The resulting elastomer thus contained 20% of Ethyl Silicate 40 and 2.6% of dibutyltin diacetate based on the weight of the polymer. The resulting mixture was stirred thoroughly and poured into a flat-bottom aluminum dish.

The film gelled in a few hours but did not reach maximum strength for several days. Forty-three days after being cast, the tensile strength (nominal) of the film was 1240 psi and its elongation at break was 265% giving a tensile product of 330,000. The film was rubbery at room temperature, but it became stiff at about 0°C.

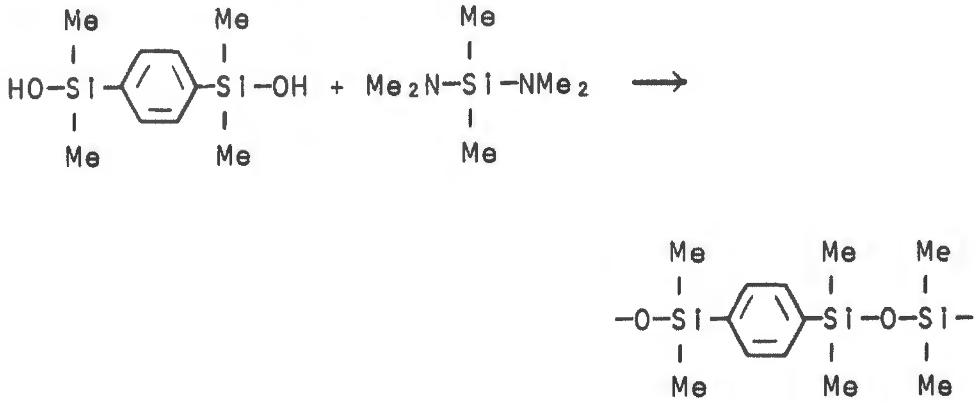
4. Solvent resistance

A small piece of polymer measuring 0.15 to 0.20 in. was placed on a glass cover slide over a scale with divisions of 0.01 in. The initial overall length was measured under a binocular microscope, and a small steel cylinder, with open ends, was placed on the glass to enclose the sample. Solvent was poured into the cylinder, and the sample was observed until the length became constant. The ratio of the swollen to the unswollen length is reported as the swelling ratio. The data are in Table I.

III. ELASTOMERS PREPARED FROM A SILPHENYLENEDIOL AND A DIAMINOSILANE

A. Discussion

A silphenylene-dimethylsiloxane elastomer was prepared for evaluation as a rain-erosion resistant coating. The method of preparation was developed in our earlier work on high-temperature elastomers.[7]



poly[1,4-bis(oxydimethylsilyl)benzene dimethylsilane]

"silphenylene-dimethylsiloxane polymer"

The silphenylene-siloxane elastomers are not in commercial production, but they can be cured at room temperature, and they are superior to room-temperature-vulcanizing silicone elastomers in tensile properties. Apparently, both the RTV silicones and the silphenylene-siloxanes are adequately stable to heat and radiation. Preliminary evaluations of abrasion resistance by sand-blasting indicated the silphenylene-siloxane had greater resistance to abrasion than Neoprene N-83 after both were heated at 150°C or above for 4 hours. The silphenylene-siloxane had greater sand-blast abrasion resistance than RTV 587 both before and after heating. The glass-transition temperature of the silphenylene-dimethylsiloxane is -60°C, which is acceptable. However, its fuel and solvent resistance, which are comparable with those of the RTV silicones, are less than desirable. Obtaining better fuel resistance was one purpose of the investigation of the polymers made from hexafluoroacetone as described in Section II.

The silphenylene-dimethylsiloxane polymer is readily cured to an elastomer by ethyl silicate and dibutyltin diacetate. Unreinforced elastomers have been made from this polymer with tensile products as high as 480,000 (900 psi nominal tensile strength and 530% elongation at break). An elastomer reinforced with silica and iron oxide had a tensile product of 890,000 (2540 psi and 350%). An unreinforced elastomer cured with iron naphthenate instead of dibutyltin diacetate had a tensile product of 1,200,000, but the iron salt reduced the thermal stability. The silphenylene-dimethylsiloxane elastomers examined by sand-blast erosion were cured films that varied in tensile products from 515,000 to 850,000. These elastomers were compared with Neoprene N-83 and a silicone elastomer, RTV 587, by sand-blast abrasion, and the results are summarized in Table II and Figure 2. The compositions of the silphenylene-dimethylsiloxane elastomers are in Table III. The resistance of the silphenylene-dimethylsiloxane elastomer to JP-4 fuel and toluene are compared with those of Neoprene N-83, the hexafluoroacetone-isobutylene-silphenylene elastomer, and a peroxide-cured silicone in Table I. The silphenylene-dimethylsiloxane had greater resistance than the silicone and less resistance than the hexafluoroacetone elastomer. It had greater resistance than Neoprene N-83 to toluene and less than Neoprene N-83 to JP-4 fuel.

The thermal stability of the silphenylene-dimethylsiloxane is known to be exceptionally high among elastomers, and it showed no degradation in abrasion resistance after being heated at 250°C (482°F) for 4 hours (Figure 2). A thermogravimetric analysis, Figure 3, showed that only 10% by weight of the polymer, either with or without filler, had been lost by the time the temperature reached 450°C at a heating rate of 10°C per minute in nitrogen.

In the continuing work under Contract N00019-C-69-0258 we intend to investigate methods of applying the silphenylene-dimethylsiloxane elastomer to the surfaces of laminates of the types used in radomes. We expect the problems to be similar to those with silicones, which normally adhere poorly unless primers are used.

Table II. Sand-Erosion Resistance of Elastomers after Being Heated for 4 Hours at Temperatures up to 250°C

Elastomer	Tensile product	Penetration time, sec/mil, after 4 hours heating at 25°C	100°C	150°C	200°C	250°C
5119-109-1	580,000	5.2	6.0	5.1	5.3	7.1
-2	620,000	5.0	7.0	5.2	5.6	8.3
-111-1	630,000	8.5	9.5	8.2	9.3	10.5
-2	555,000	6.3	8.9	7.2	5.7	7.3
-3	565,000	7.7	7.5	7.4	6.5	5.4
-4	515,000	6.5	5.8	7.5	5.2	6.8
-5	630,000	4.5	4.1	5.6	6.8	6.6
5293- 35-1	790,000	6.2	8.2	-	5.5	4.7
-2	610,000	5.2	7.9	5.8	5.3	5.8
-3	670,000	4.1	5.6	-	4.2	4.7
-4	810,000	4.6	5.9	5.7	4.4	3.6
-5	790,000	4.4	4.6	5.4	5.2	4.5
-6	850,000	4.6	5.3	4.3	4.7	4.8
Neoprene, N-83	2,510,000	10.6	14.8	7.2	0	0
Dow Corning RTV 587	112,000	3.6	3.3	2.6	3.1	2.1

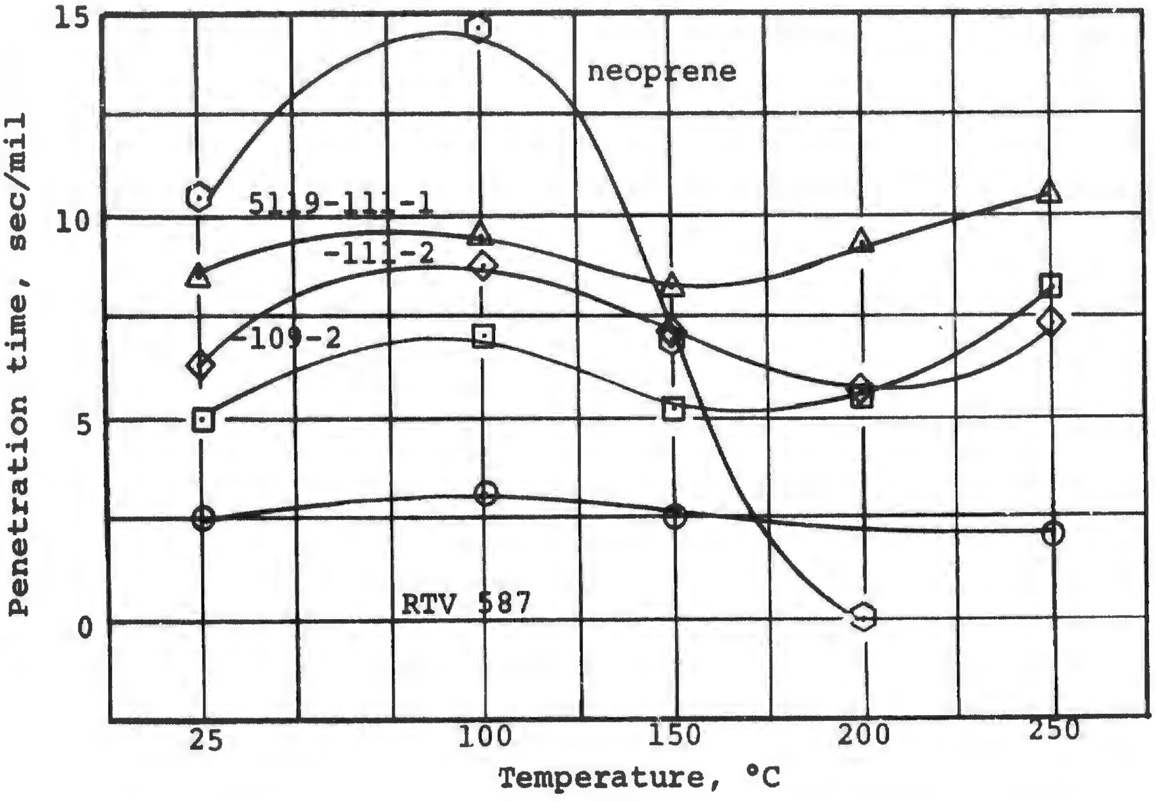


Figure 2. Sand-Erosion Resistance of Elastomers after Being Heated for 4 Hours at Temperatures up to 250°C

Table III. Formulations of Silphenylene-Dimethylsiloxane Elastomers

Elastomer	Components, % (based on weight of polymer)							Tensile strength (nominal), psi	Elongation at break, %	Tensile product
	Cab-O-Sil H-5[a]	ZnO[b]	TiO_2[c]	Carbon[d]	"Ethyl silicate 40"[e]	Dibutyltin diacetate[f]	OMCTS[g]			
5119-109-1	15	-	-	15.3	15.7	2.0	-	1000	575	575,000
-2	30	-	-	-	15.3	1.9	-	1240	500	620,000
-111-1	30	-	-	-	15.7	2.7	-	1575	400	630,000
-2	30	-	3.0	-	17.1	1.9	-	1480	375	555,000
-3	30	3.0	-	-	14.7	1.9	-	1620	350	565,000
-4	30[h]	-	-	-	15.9	2.0	-	1080	475	515,000
-5	30[h]	-	-	-	15.2	2.0	-	1265	500	630,000
5293- 35-1	30	-	-		15.0	2.8	-	1765	450	790,000
-2	25	-	-		13.0	2.7	-	1430	425	610,000
-3	35	-	-		16.0	2.4	-	1680	400	670,000
-4	30	3.0	-		15.0	2.7	-	1800	450	810,000
-5	30	-	3.0		14.0	2.1	-	1660	475	790,000
-6	30	-	-		15.0	2.4	5.1	1900	450	850,000

---

a. Silica, Cabot Corporation.

b. Zinc oxide, XX78, New Jersey Zinc Co.

c. Titanium dioxide, R-722, New Jersey Zinc Co.

d. Sterling R, Cabot Corp.

e. Partially hydrolyzed ethyl silicate, Union Carbide Corp.

f. Eastman Organic Chemicals.

g. Octamethylcyclotetrasiloxane, Chemicals Procurement Labs, Inc.

h. Silica, Aerosil 380, Degussa, Inc.

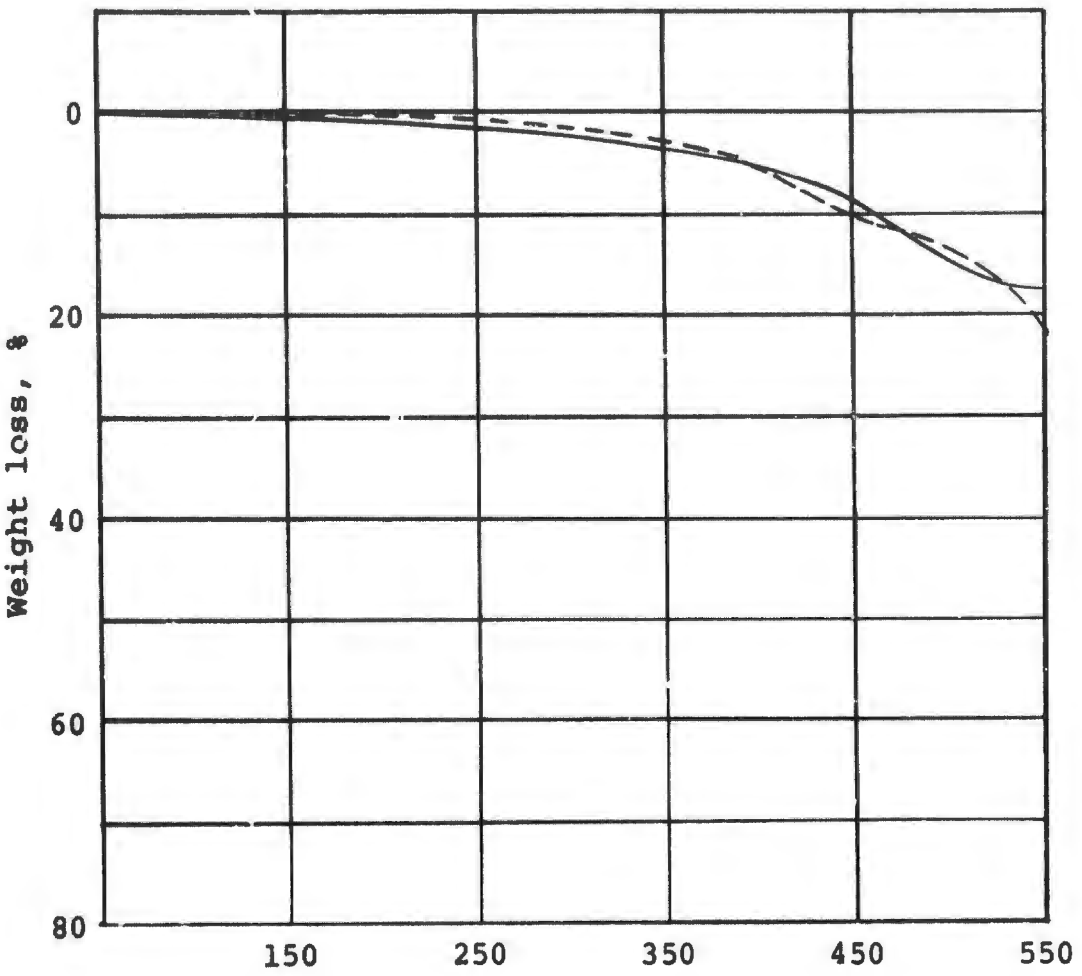


Figure 3. Thermogravimetric Analysis of Silphenylene-Dimethylsiloxane Elastomer in nitrogen; 10°C/min

—5219-111-1 (reinforced with silica)
--4758-145-5B (no inorganic filler)

B. Experimental Details

1. Preparation of monomers

The methods of preparing 1,4-bis(dimethylhydroxysilyl)-benzene and bis(dimethylamino)dimethylsilane were described in Section II.B.

2. Preparation of polymer

1,4-Bis(dimethylhydroxysilyl)benzene, 12.71 g (0.0561 mole), was placed in a dry 100-ml, 3-neck flask, equipped with a thermometer, magnetic stirrer, and a reflux condenser protected with a Drierite tube. Bis(dimethylamino)dimethylsilane, 8.02 g (0.0548 mole), and 20 ml of toluene were added while dry nitrogen was being swept slowly through the flask. The nitrogen flow was stopped, and the open neck was closed with a rubber serum cap. The flask was warmed in an oil bath in 1 hour to the reflux temperature. During this time the reaction had evolved dimethylamine and then had subsided. Additional bis(dimethylamino)-dimethylsilane was added through the serum cap with a hypodermic syringe in five increments of 0.05 ml (0.04 g, 0.00027 mole) at 10 minute intervals. A slight increase in viscosity was observed after the fourth addition, and the fifth brought it almost to the point judged to be desired. Thus the total amount of diamine was 8.21 g (0.0561 mole). The bubbles that rose in the flask were about 0.5 cm in diameter, and they remained unbroken about 1 second. Heating at reflux was continued for 1 hour with a slight increase in viscosity. Water, 5 ml, and 20.0 ml of toluene were added, and the mixture was refluxed for 2 hours. The water was removed by azeotropic distillation with a Dean-Stark trap. The polymer solution was pale yellow and slightly cloudy. Its inherent viscosity was 0.38 dl/g measured at 30°C in tetrahydrofuran at a concentration of 1.0 g per deciliter.

3. Milling of polymer and curing to elastomers

Elastomer formulations were milled in 3- to 5-g batches on a paint mill with stainless-steel rolls. The materials being milled were scraped from the rolls with polypropylene spatulas used as doctor blades. All of the components, except the promoter, were mixed in 20 to 30 minutes. Then the promoter was milled in for about 5 minutes. The milled raw polymers, which varied from viscous, sticky greases to soft, slightly tacky ribbons, were then pressed between two stainless-steel plates that were held apart by spacers. Samples were removed from the press after 1 hour and from the plates after 1 day.

The fillers used were silica (Cab-O-Sil H-5, Cabot Corporation), iron oxide (Mapico 297, Columbian Carbon Company), zinc oxide (XX78, The New Jersey Zinc Company), and titanium dioxide (R722B2, The New Jersey Zinc Company).

4. Screening by sand-blast erosion

A device for producing a small, high-speed, air-borne stream of an abrasive has been used as a preliminary method of evaluating the abrasion resistance of experimental polymers. The device was built ("Airdent", Model H, S.S. White Dental Mfg. Co.) as a dental drill, and it can be used to compare the abrasion resistance of films whether or not they are attached to a rigid substrate. Thus, it has been possible to compare experimental cast films before methods of application by spraying or brushing have been developed.

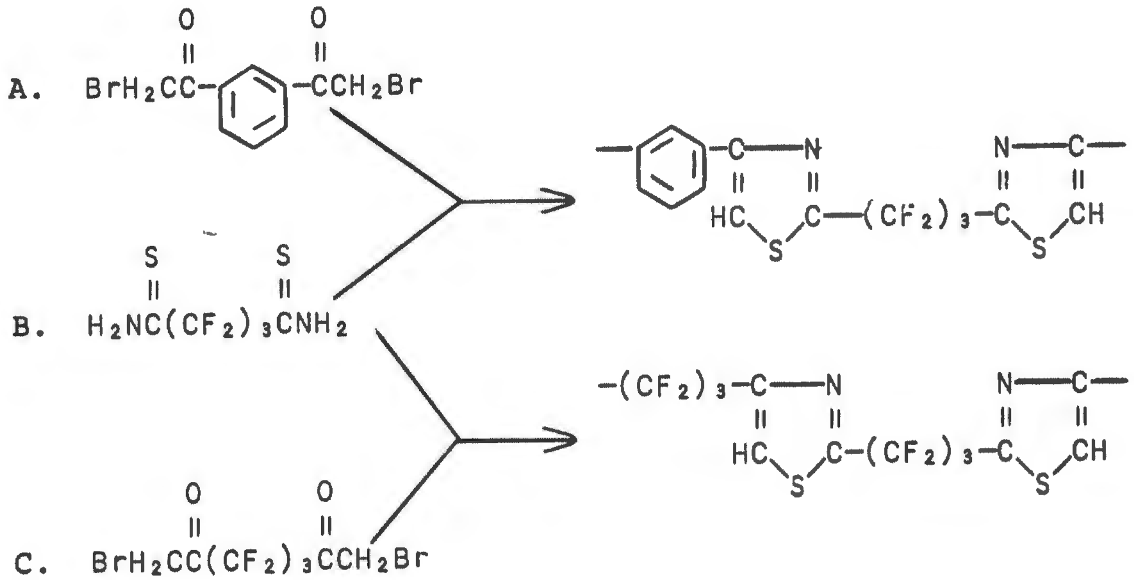
The pressure and abrasive feed rate of the "Airdent" are adjusted so as to penetrate a film of electrical tape in 30±2 seconds. Then the penetration times of the experimental films are measured alternately with those of the electrical tape. Three measurements of the experimental films are averaged to obtain penetration times in seconds per mil of thickness. The results are given in Table II and Figure 2.

IV. POLY (PERFLUOROALKYLENE THIAZOLES) AND POLY-(PERFLUOROALKYLENEPHENYLENE THIAZOLES

A. Discussion

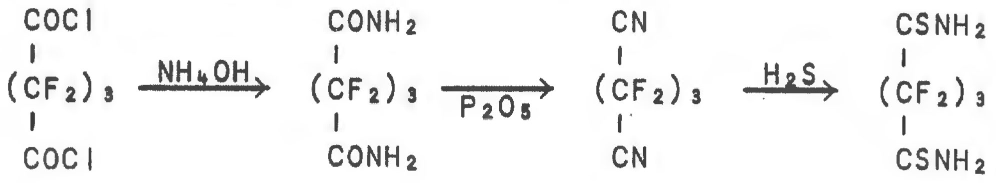
The preparation of polymers containing thiazole and fluorocarbon units was investigated because the thiazole ring has exceptional thermal stability and the fluorocarbons have exceptional fuel resistance and flexibility. From structural considerations, it appeared that the fluorocarbon and thiazole units should be capable of being combined in elastomers that would have the desired toughness and stability. Poly(perfluoropropylene-3-phenylene thiazole) was prepared after considerable difficulty. The molecular weight of the polymer was only 1275 and it melted at 130-140°C, which suggested that it was not a promising source of elastomers. A report by Wrasidlo[8] showed that a variety of fluoroalkylene-heterocyclic polymers lacked thermal stability because of interaction between the fluorocarbon and heterocyclic units. Accordingly, further work on the fluorocarbon-thiazole polymers was discontinued after the work described below was completed.

According to the following scheme, two polymers of the above types could be prepared from three monomers:



Monomer A, bis(bromoacetyl)benzene, was prepared without difficulty. Monomer B was prepared with considerable difficulty as described in Section IV.B., and Monomer C was not prepared.

To prepare Monomer B, or a homolog of it, the glutaric derivatives were chosen in preference to the adipic derivatives because of their potentially lower cost. However, the 5-carbon compounds form cyclic by-products during the second and third reactions of the following sequence:

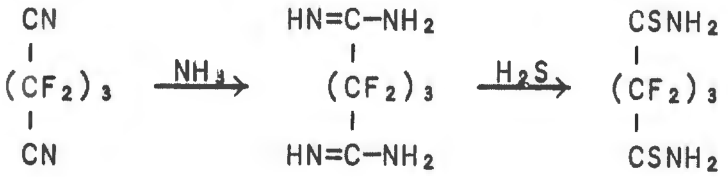


$$\begin{matrix} COCl \\ | \\ (CF_2)_3 \\ | \\ COCl \end{matrix} \xrightarrow{NH_4OH} \begin{matrix} CONH_2 \\ | \\ (CF_2)_3 \\ | \\ CONH_2 \end{matrix} \xrightarrow[P_2O_5]{} \begin{matrix} CN \\ | \\ (CF_2)_3 \\ | \\ CN \end{matrix} \xrightarrow{H_2S} \begin{matrix} CSNH_2 \\ | \\ (CF_2)_3 \\ | \\ CSNH_2 \end{matrix}$$

D E F G

Perfluoroglutaramide (E) was prepared easily in good yield, but was dehydrated by phosphorus pentoxide to the dinitrile (F) (b.p. 38°C) only in a low yield. Thionyl chloride, phosphorus oxychloride, and benzotrichloride were ineffective dehydrating agents. By the preferred dehydration method, the powdered amide was mixed with an excess of P_2O_5 and placed in one flask of a system consisting of an inverted U with a round-bottom flask attached to each leg. The system was evacuated and closed off from the pump. Then the reaction flask was heated to 230-240°C while the receiver was cooled in dry ice. When the reaction was complete, the receiver contained both the desired liquid product and a solid, which may have been perfluoroglutarimide. Redistillation in the same apparatus produced the clear liquid dinitrile (F).

Treatment of the perfluoroglutaronitrile with hydrogen sulfide in pyridine produced only sulfur and a tarry material from which no dithioamide could be isolated. However, the conversion was accomplished successfully by forming the amidine (H) first, according to the method of Dorfman and Bean.[9]



$$\begin{matrix} CN \\ | \\ (CF_2)_3 \\ | \\ CN \end{matrix} \xrightarrow{NH_3} \begin{matrix} HN{=}C{-}NH_2 \\ | \\ (CF_2)_3 \\ | \\ HN{=}C{-}NH_2 \end{matrix} \xrightarrow{H_2S} \begin{matrix} CSNH_2 \\ | \\ (CF_2)_3 \\ | \\ CSNH_2 \end{matrix}$$

F H G

Poly(perfluoropropylene-3-phenylene thiazole) was prepared by heating perfluoroglutarodithioamide (G) with bis(bromoacetyl)-benzene in dimethylformamide.

B. Experimental Details

1. Preparation of monomers and intermediates

a. p-Bis(bromoacetyl)benzene

The method described by Ruggli and Gassenmeier[10] was used to prepare p-bis(bromoacetyl)benzene. p-Diacetylbenzene, 25.0 g (0.154 moles), was added to 110 ml chloroform in a 3-liter, 3-neck flask equipped with a thermometer, stirrer, reflux condenser, and a dropping funnel. The chloroform was heated to reflux with a reflector ("Photoflood") lamp, and a solution of bromine, 54.0 g (0.338 moles) in 250 ml of chloroform was added dropwise. The addition of the bromine required 4.5 hours; heating and refluxing were continued for another hour. The cream-colored precipitate was separated by filtering the cooled reaction mixture. The product, after recrystallization from hot acetone and carbon black, was 34.5 g (70% of theory) of a fine white powder, m.p. 175-76.5°C. Ruggli and Gassenmeier reported 173°C.[10]

b. Hexafluoroglutarodiamide

In a 1-liter, 3-neck flask fitted with a thermometer, stirrer, and a dropping funnel was placed 700 ml ammonium hydroxide (10.5 moles). The ammonium hydroxide was cooled to 3-7°C, and 73.8 g (0.266 moles) of hexafluoroglutaryl chloride (Columbia Organic Chemicals) was added slowly to the cold solution with stirring. The product, hexafluoroglutarodiamide, was removed by filtering; after washing five times with water and drying, it weighed 43.56 g (68.8% of theory), m.p. 208-12°C. After reprecipitation from ethanol by addition of benzene, the m.p. was 212.5-4.0°C. Remy[11] reports m.p. 214-14.5°C.

Anal. Calculated for $C_5H_4F_6N_2O_2$: C 25.22, H 1.69, N 11.77.

Found: C 25.00, H 1.71, N 11.82.

c. Hexafluoroglutaronitrile

Hexafluoroglutaronitrile was prepared by the method of McBee, Wiseman, and Bachman.[12] Hexafluoroglutarodiamide, 10.0 g (0.042 moles), was mixed with 45 g of phosphorus pentoxide in a 200-ml flask equipped with a Claisen head and condenser. Ice water was circulated through the condenser and the collection flask was cooled in dry ice. The reaction flask was heated in an oil bath whose maximum temperature reached 270°C. The distillate, b.p. 35-6°C, weighed 4.10 g (48% of theory). Remy[11] reports b.p. 38.5°C. The dinitrile contained a small amount of solid material, so it was redistilled by volatilization at room temperature and 0.1 mm pressure and recondensation at dry ice temperature.

Attempts to prepare perfluoroglutaronitrile from the amide by dehydration with thionylchloride, $POCl_3$, and benzotrichloride were unsuccessful.

d. Hexafluoroglutarodiamidine

The method of Reilly and Brown[13] for the preparation of perfluoroamidines was used to prepare hexafluoroglutarodiamidine. The distilled hexafluoroglutaronitrile, 0.51 g (0.0025 mole), was cooled to -33°C, and a large excess of anhydrous ammonia was added. The nitrile and ammonia were mixed by gentle swirling. A dry ice condenser was attached to the reaction flask, and the ammonia was allowed to reflux for 3 hours. After the excess ammonia was allowed to evaporate, the crude product, 0.39 g (0.0016 mole) (64% of theory), was recrystallized from benzene to yield 0.29 g (0.0012 mole) of a white crystalline product (48% of theory).

e. Hexafluoroglutarodithioamide

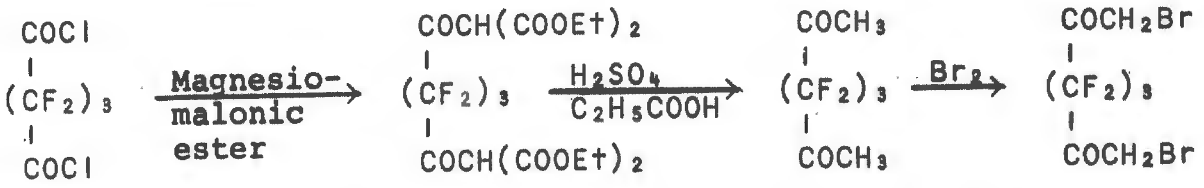
The method described by Dorfman and Bean[9] was used to prepare hexafluoroglutarodithioamide. The recrystallized hexafluoroglutarodiamidine, 0.29 g (0.0012 mole), was dissolved in ether and transferred to a 3-neck flask equipped with a stirring bar, thermometer, and gas inlet tube above the surface of the ether solution. Hydrogen sulfide was passed over the surface of the stirred solution at 0°C for 4 hours. The ether was distilled from the reaction product, which was then dissolved in methanol and filtered to remove the trace of free sulfur. After the methanol was removed, the crude product was recrystallized from hot chloroform. The yellow product amounted to 0.17 g (0.00063 mole, 53% of theory), m.p. 125°C (with decomposition).

Anal. Calculated for $C_5H_4F_6N_2S_2$: C 22.22, H 1.49, N 10.37.

Found: C 22.29, H 1.50, N 10.40.

f. 1,7-Dibromo-3,3,4,4,5,5-hexafluoro-2,6-heptanedione

Several attempts were made to prepare 1,7-dibromo-3,3,4,4,5,5-hexafluoro-2,6-heptanedione by the malonic ester synthesis. R. E. Bowman[14] reported the preparation of β-keto-esters *via* the decarboxylation of malonic esters prepared from acylchlorides.



$$\underset{COCl}{\overset{COCl}{(CF_2)_3}} \xrightarrow[\text{malonic ester}]{\text{Magnesio-}} \underset{COCH(COOEt)_2}{\overset{COCH(COOEt)_2}{(CF_2)_3}} \xrightarrow[C_2H_5COOH]{H_2SO_4} \underset{COCH_3}{\overset{COCH_3}{(CF_2)_3}} \xrightarrow{Br_2} \underset{COCH_2Br}{\overset{COCH_2Br}{(CF_2)_3}}$$

The tetraester was formed without difficulty, but the decarboxylation resulted in extensive formation of tars. We obtained only a low yield of a liquid with about the desired elemental analysis.

Anal. Calculated for $C_7H_6F_2O_2$: C 35.61, H 2.56.

Found: C 39.14, H 2.65.

2. Preparation of polymer: poly(perfluoropropylene-3-phenylene)-thiazole

In a 100-ml 3-neck flask equipped with a stirring bar, thermometer, and condenser were placed 0.703 g (0.0026 mole) of hexafluoroglutarodithioamide and 0.833 g (0.0026 mole) of p-bis-(bromoacetyl)benzene. Dimethylformamide, 35 ml, was used as solvent. The reaction mixture was heated for 4 hours at 75°C, 16 hours at 90°C, 144 hours at 100°C, 48 hours at 110°C, and 24 hours at 120°C. Aliquots (1.25 ml) were removed at intervals and diluted to 5.0 ml with dimethylformamide. The inherent viscosity of the solution was measured at 30°C, and a maximum inherent viscosity of 0.06 dl/g was measured at the end of 24 hours at 110°C. The reaction mixture was added with stirring to twice its volume of water. A cream-colored solid precipitated; after drying, it weighed 0.56 g, m.p. 130-40°C. Considering the amounts removed for viscosity measurements, the yield was 76%.

Anal. Calculated for $C_{15}H_6F_6N_2S_2$: C 45.92, H 1.54, N 7.14.

Found: C 45.69, H 2.08, N 7.16.

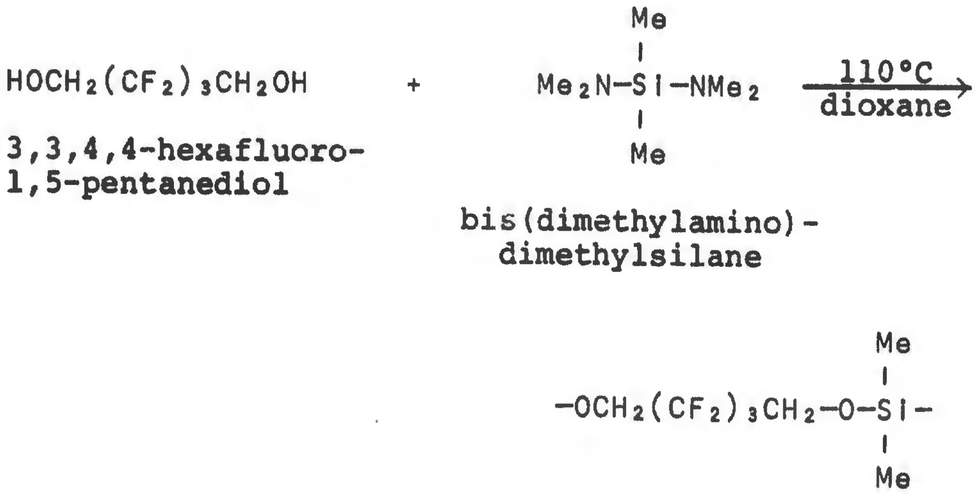
Molecular weight (vapor osmometry): 1276.

V. FLUOROALKYLENE- AND FLUOROARYLENE-SILOXANE POLYMERS

A. Discussion

Polymers containing fluoroalkylene and fluoroarylene units alternating with siloxane were investigated to determine whether they would have desirable properties as rain-erosion-resistant coatings. It is well known that Si-O-C units are sensitive to moisture and that moisture sensitivity is increased by attaching fluorine atoms to the carbons attached to the silicon. However, it was thought that moisture sensitivity might be less when the carbons attached to oxygen were attached to fluorinated units. Relatively little effort was required to prepare polymers of this type since fluorinated diols could be purchased and diaminosilanes could be prepared easily.

The first fluoroalkylene siloxane polymer was prepared by this reaction:



$$HOCH_2(CF_2)_3CH_2OH + Me_2N-\overset{Me}{\underset{Me}{Si}}-NMe_2 \xrightarrow[\text{dioxane}]{110°C} -OCH_2(CF_2)_3CH_2-O-\overset{Me}{\underset{Me}{Si}}-$$

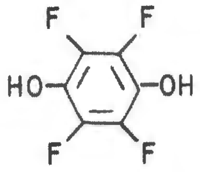
2,2,3,3,4,4-hexafluoro-1,5-pentanediol

bis(dimethylamino)-dimethylsilane

poly(1,5-dioxy-2,2,3,3,4,4-hexafluoropentane dimethylsilane)

This polymer was a viscous oil, but its viscosity decreased visibly on exposure to laboratory air. When the polymer was exposed to laboratory air for several days, crystals formed in the oil, and these were shown to be the original diol. The polymer apparently started to cure when mixed with ethyl silicate and dibutyltin diacetate according to the method used for curing RTV silicones; but after gelling, it became friable.

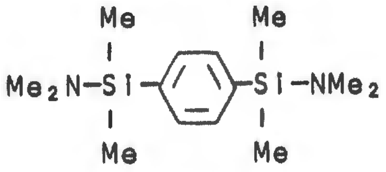
A diol-diaminosilane reaction was conducted with tetrafluorohydroquinone as the diol.



The reaction mixture darkened, and a granular precipitate appeared, perhaps the tetrafluoroquinone.

A second attempt was made with oxygen rigorously excluded, and a polymer was obtained. It was a dark brown, sticky grease when the solvent was first removed from it, but it changed rapidly to a friable mass on exposure to laboratory air. Evidently the Si-O-C bond in this polymer was sensitive to moisture, also.

An attempt was made to prepare a polymer from tetrafluorohydroquinone and 1,4-bis(dimethylaminodimethylsilyl)benzene.



1,4-bis(dimethylaminodimethylsilyl)benzene

The product was also a dark brown, friable mass.

Because of the moisture sensitivity, work on this type of polymer was discontinued.

B. Experimental Details

1. Fluoroalkylene-siloxane polymer

Poly(1,5-dioxy-2,2,3,3,4,4-hexafluoropentane dimethylsilane) was prepared in the same manner as the silphenylene-dimethylsiloxane polymer, Section III.B.2. Spectro grade dioxane was the solvent. The bis(dimethylamino)dimethylsilane was added to the refluxing dioxane solution of 2,2,3,3,4,4-hexafluoro-1,5-pentanediol at the rate of 0.05 ml per 5 minutes. Refluxing was continued for 3.5 hours after the calculated stoichiometric amount of diaminosilane had been added. This preparation resulted in a polymer with an inherent visocsity of 0.29 dl/g measured at 30°C in tetrahydrofuran at a concentration of 1.00 g/dl.

Anal. Calculated for $C_7H_{10}F_6O_2Si$: C 31.34, H 3.76.

Found: C 31.36, H 3.87.

A second batch of polymer was prepared by a modified reaction method. A dioxane solution of the bis(dimethylamino)dimethylsilane was added slowly to the refluxing diol solution. The viscosity of the resulting polymer solution was higher, as judged visually, but it became fluid rapidly in air.

2. Polymerization of tetrafluorohydroquinone and bis(dimethylamino)dimethylsilane

Another diol-diaminosilane reaction was conducted with tetrahydroquinone as the diol in the manner described in the preceding section for hexafluoropentanediol. The reaction mixture darkened, and a granular precipitate appeared. In a second attempt, the tetrafluorohydroquinone was recrystallized under nitrogen, and oxygen was excluded rigorously from the reaction. The polymer obtained was a dark brown, sticky grease when the solvent was first removed from it, but it changed rapidly to a friable mass on exposure to laboratory air.

3. Attempted polymerization of tetrafluorohydroquinone and 1,4-bis(dimethylaminodimethylsilyl)benzene

The same procedure described above for the polymerization of tetrafluorohydroquinone and bis(dimethylamino)dimethylsilane, was tried with 1,4-bis(dimethylaminodimethylsilyl)benzene as the silane. The polymeric product changed rapidly to a dark brown, friable mass on exposure to the atmosphere.

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13. ABSTRACT

This search for new, thermally stable, rain-erosion resistant coatings for the radomes and leading edges of high-speed aircraft was concerned mainly with developing tough elastomers that cure at room temperature and that resist heat, solvents, and weather. We have prepared two new types of elastomers that are promising: silphenylene-siloxanes, and hexafluoroacetone-alkylene-silphenylenes. Both cure at room temperature, and both have good thermal stability. In their present states of development, the silphenylene-siloxanes have better tensile properties, and the hexafluoroacetone-alkylene-silphenylenes have greater fuel resistance. Both require further development of the polymerization processes to achieve higher molecular weights and of the the curing methods to improve tensile properties.

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Rain-erosion-resistant coatings						
Hexafluoroacetone-alkylene adduct						
Elastomers						
Thermally stable elastomers						
Fluorinated elastomers						
Silphenylene-siloxanes						
Silphenylene elastomers						
Fluoroalkylene thiazoles						