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DEVELOPMENT OF RAIN-EROSION-RESISTANT COATINGS FOR HIGH-SPEED AIRCRAFT (U)

Final Report

(15 January 1970 to 14 January 1971)

March 1971

by

A. C. Tanquary
Robert E. Burks, Jr.
M. Virginia Jackson

Prepared Under Contract N00019-70-C-0330

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13. ABSTRACT

A polymer prepared as a prospective rain-erosion-resistant coating from hexafluoroacetone, propylene, and bis(dimethylamino)-dimethylsilane had a glass-transition temperature of -50°C, and it had good resistance to heat and aliphatic or aromatic hydrocarbons. However, it was not successfully cured to an elastomer. A polymer prepared from 1,4-bis(dimethylhydroxysilyl)benzene and bis(dimethylamino)dimethylsilane had a glass-transition temperature of -62°C, excellent thermal stability, but less resistance to hydrocarbons than the fluoropolymer. It was cured to a tough elastomer at room temperature. The coating obtained when this elastomer was sprayed onto air-foil test specimens was found to have much greater resistance to simulated rain erosion at ordinary temperatures than a silicone coating and slightly less than neoprene. It suffered no degradation on being heated 4 hours at 250°C, as indicated by sand-erosion tests.

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FOREWORD

This summary report pertains to research performed on a project sponsored by the Naval Air Systems Command, Department of the Navy, under Contract N00019-70-C-0330. The report includes work accomplished during the period 15 January, 1970, to 14 January, 1971. The research was monitored by Mr. A. M. Malloy, of the Naval Air Systems Command.

The authors wish to acknowledge the valuable suggestions and discussions of Mr. T. A. Johnston of the Naval Air Systems Command. The measurements of surface tension were performed by Mr. Frank Y. Johnson.

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

I. INTRODUCTION AND SUMMARY

Polymeric fluoroalkylene-siloxane polymers were investigated as candidates for coatings that will protect the leading edges of high-speed aircraft from rain erosion. Requirements for the new coating material are radar transparency; moderate cost; simplicity of application; and resistance to fuels, lubricants, paint strippers, low temperatures, high temperatures, and rain erosion. Several fluoroalkylene-siloxane polymers were prepared with progressively greater resistance to organic liquids and progressively lower glass-transition temperatures. The latest one prepared in the series contained hexafluoroacetone, propylene, and dimethylsiloxane units. It had a glass-transition temperature of -50°C, but efforts to cure it to an elastomer have not been successful.

A silphenylene-dimethylsiloxane polymer that is less resistant to organic liquids than the fluorinated polymer was sprayed onto air-foil test specimens and subjected to simulated rain in the whirling-arm device at Wright-Patterson Air Force Base. The special merits of this polymer are exceptional toughness combined with high thermal stability. Its rain-erosion resistance at 500 miles per hour at ordinary temperatures was much greater than that of a silicone elastomer and slightly less than that of neoprene, but resistance to thermal stress was not a part of the evaluation.

This report covers work done under Contract N00019-70-C-0330 in the period January 15, 1970 to January 14, 1971.

II. SUMMARY OF EARLIER WORK

A. Requirements

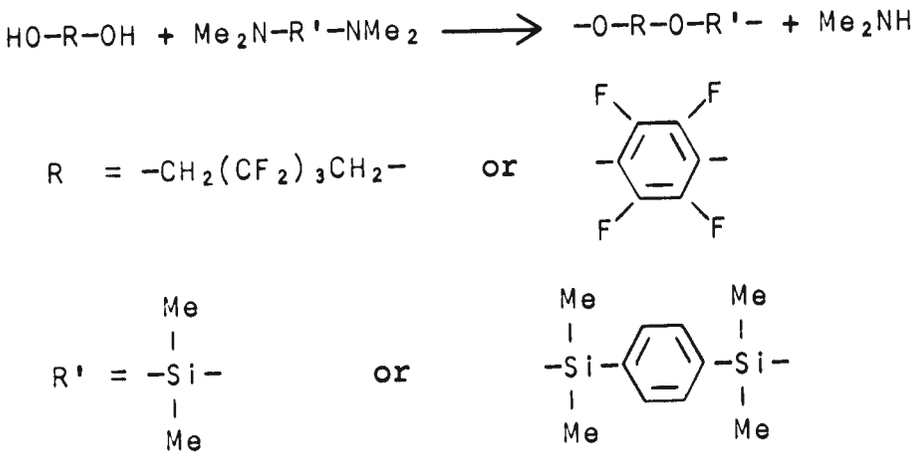
Tough, thermally stable elastomers are needed to protect the leading edges of high-speed aircraft from rain erosion. Existing high-temperature elastomers have poor erosion resistance or require curing under conditions that are impractical for shipboard use. In addition, a satisfactory coating must be radar transparent, inexpensive, and resistant to fuels, lubricants, paint strippers, sunlight, low temperatures, and salt spray. These properties suggest fluorocarbons with moieties that will facilitate curing.

B. Fluorocarbon-Thiazole Polymer

Poly[4-(m-phenylene)thiazole 2-perfluoropropylenethiazole] was prepared[1] to determine whether the fluorocarbon portion would provide the softness needed to form an elastomer from molecules consisting largely of the thermally stable 4-phenylenethiazole units. The polymer melted at 130-140°C which precluded its further consideration as a base for making elastomers.

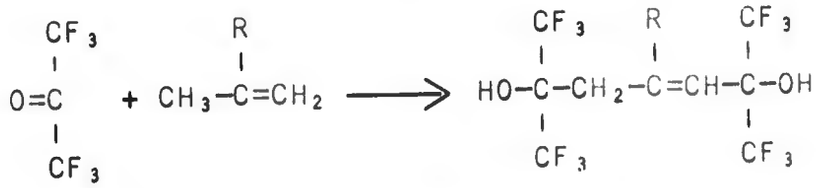
C. Polymers from Reactions of Fluorinated Diols with Diaminosilanes

Fluorinated diols were treated with diaminosilanes to form polymers. The first combinations tried formed polymers that were unstable to the moisture in laboratory air.



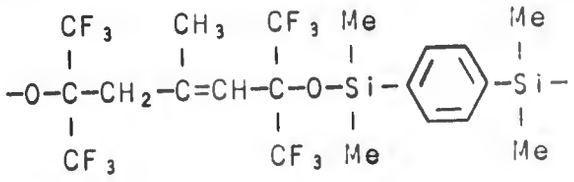
The hydrolytic sensitivity of the C-O-Si units was not eliminated by the presence of the fluorine atoms in aromatic or straight-chain aliphatic components. However, trifluoromethyl groups attached to the carbon atom of the C-O-Si unit offered a new type of polymer that was found, later, to be much more stable to hydrolysis.

Diols prepared from hexafluoroacetone and alkenes were attractive because of their potentially low cost and the possibility that the trifluoromethyl groups would inhibit the hydrolysis of C-O-Si units



R' = H, methyl, or other alkyl

The first polymer prepared had this structure:



hexafluoroacetone-isobutylene-
silphenylene polymer

The synthesis was conducted in a manner to favor termination with silanol groups, and the polymer was cured to an elastomer with ethyl silicate and dibutyltin diacetate at room temperature. The tensile strength (nominal) of an elastomer made from a polymer with an inherent viscosity of 0.14 dl/g* was 1240 psi, and the elongation at break was 265%. It was expected that increasing the molecular weight would increase the tensile strength. The resistance of the hexafluoroacetone-isobutylene-silphenylene polymer to aliphatic and aromatic solvents was better than that of a peroxide-cured silicone (Table I). However, the elastomer became stiff at 0°C, so its low-temperature properties were not desirable.

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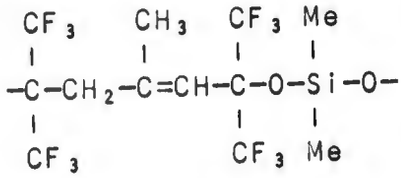
*Measured at 30°C in tetrahydrofuran at a concentration of 1.0 g/dl.

Table I. Swelling of Elastomers in Solvents

	Swelling ratio[a] in Toluene	Swelling ratio[a] in JP-4 fuel
Neoprene N-83 (Gates Rubber Co.)	1.80	1.02
Hexafluoroacetone-propylene-dimethylsiloxane, 6021-145-2	1.08	1.07
Hexafluoroacetone-propylene-silphenylene, 5514-53-12G (SRI)	1.26	1.11
Polyurethane RM115C (Air Force)	1.34	1.04
Hexafluoroacetone-isobutylene-silphenylene, 5293-11-4A (SRI)	1.41	1.26
Silphenylene-dimethylsiloxane, 4952-65-2 (SRI)	1.60	1.45
Silicone K1213 (Union Carbide) peroxide-cured	1.82	1.55

a. Ratio of swollen length to original length.

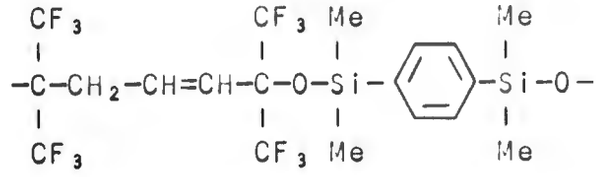
The next polymerization attempted was the reaction of the hexafluoroacetone-isobutylene diol with bis(dimethylamino)-dimethylsilane to form this structure:



hexafluoroacetone-isobutylene-dimethylsiloxane polymer

The main reaction was cyclization instead of polymerization.

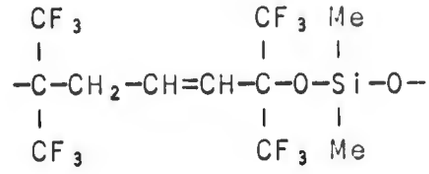
To avoid cyclization and reduce the amount of aliphatic material, we returned to the diaminosilphenylene and used it in a reaction with the diol prepared from hexafluoroacetone and propylene.



hexafluoroacetone-propylene-
silphenylene polymer

It proved difficult to obtain high molecular weight polymers, but a polymer was made and partially cured, although it was fragile.[2] The glass-transition temperature, -12°C, was lower than that of the hexafluoroacetone-isobutylene-silphenylene polymer but not low enough for utility on aircraft.

The fourth reaction of the series was that of hexafluoroacetone-propylene diol and bis(dimethylamino)dimethylsilane:



hexafluoroacetone-propylene-
dimethylsiloxane polymer

Details of the work with this polymer are given below in this report. The properties of this polymer indicate that progress has been made in the desired direction, although the polymer has not been cured successfully.

III. THE HEXAFLUOROACETONE-PROPYLENE-DIMETHYLSILOXANE POLYMER

A. Discussion

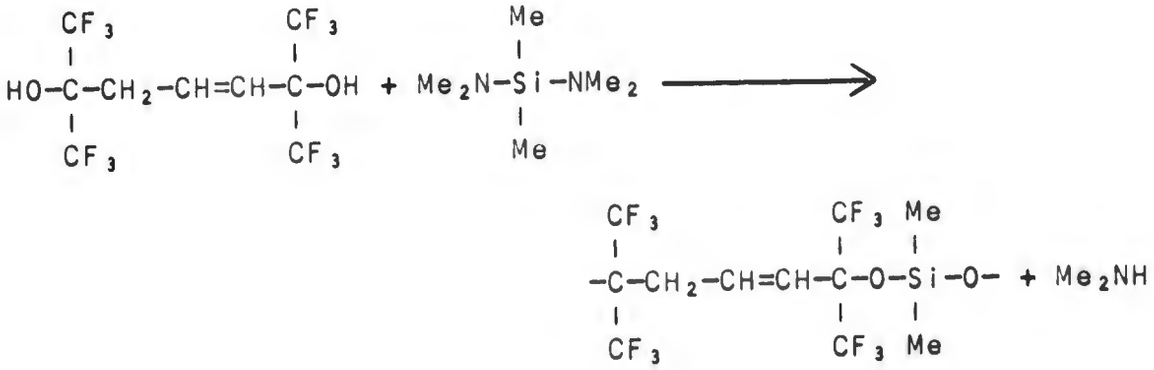
1. Purpose

The hexafluoroacetone-propylene-dimethylsiloxane polymer was prepared as a result of efforts to obtain the maximum fluorine content in a fluoroalkene-siloxane polymer. The high fluorine content (53%) was desirable for high thermal stability and resistance to organic liquids; the siloxane component was desirable for thermal stability, elasticity at low temperatures, and curability. The cost is potentially low compared with that of other fluoroorganic compounds.

2. Polymer preparation

a. Reaction of the fluorodiol with the diaminosilane

The first reaction of the hexafluoroacetone-propylene diol with bis(dimethylamino)dimethylsilane in tetrahydrofuran produced polymer of low molecular weight.

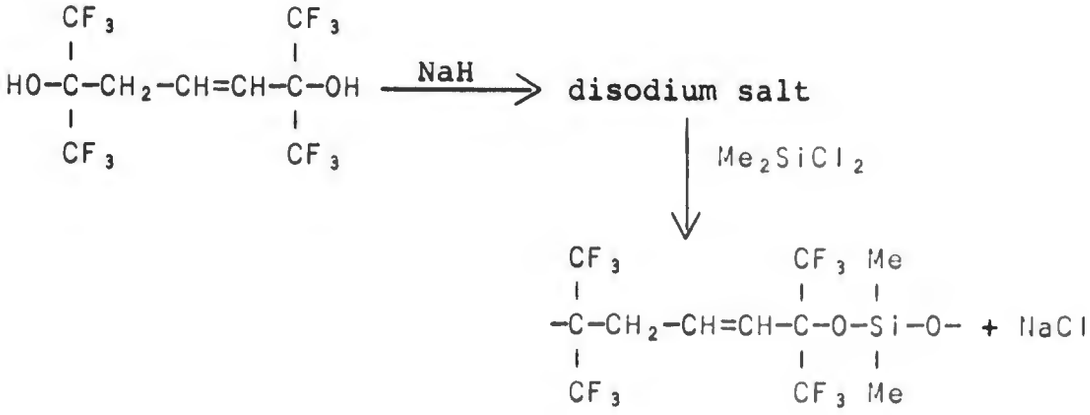


hexafluoroacetone-propylene-dimethylsiloxane polymer

The difficulty in obtaining high molecular weights was attributed to the unusually high acidity of the fluoroalcohol, which caused the amine by-product to become a chain terminator.

b. Reaction of the sodium salt of the diol with a dichlorosilane

To avoid the problem of chain termination by the amine, the sodium salt of the diol was treated with dimethyldichlorosilane in tetrahydrofuran.

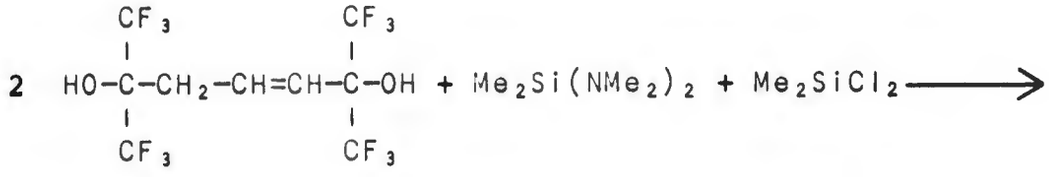


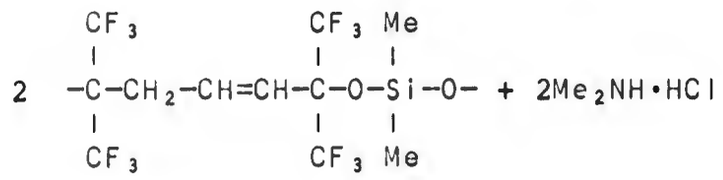
This method was expected to produce cyclic compounds along with some polymers of high molecular weight, but the only polymers produced had low molecular weights.

Purity of the disodium salt was a source of uncertainty. Because the salt reacted so rapidly with the dichlorosilane, it appeared that the reaction would be useful for polymerization. However, elemental analyses and the failure to form high polymers suggested that the disodium salt was not sufficiently pure. An investigation of its properties revealed that it formed crystalline hydrates on exposure to air and that it had a strong affinity for tetrahydrofuran, in which it was soluble. If prepared in diethyl ether, it remained in solution as the ether was evaporated until the entire mass solidified in an amorphous form. The last traces of ether were not easily removed, and the amorphous solid re-dissolved in ether with difficulty even at a lower concentration. The behavior of the salt in tetrahydrofuran was not fully explained. One batch seemed, according to elemental analysis, to have formed a solid clathrate from which the tetrahydrofuran could not be removed by prolonged heating at 85°C at 0.1 mmHg. A small sample of another batch was freed of tetrahydrofuran relatively easily; but on standing, the solution darkened. Because of the better results obtained by treating the fluorodiol with the diaminosilane and dichlorosilane simultaneously, the sodium salt was abandoned as a monomer.

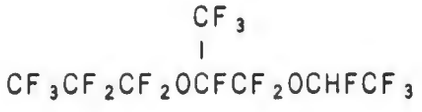
c. Reaction of the fluorodiol with the diaminosilane and the dichlorosilane

Reactions of the hexafluoroacetone-propylene diol with bis(dimethylamino)dimethylsilane and dimethyldichlorosilane in tetrahydrofuran formed polymers of low molecular weight.





Darkening of the reaction mixture suggested that the tetrahydrofuran was not inert to the chlorosilane, so other solvents were sought. The polymer was insoluble in benzene, toluene, hexane, carbon tetrachloride, chloroform, diethyl ether, methylene chloride, and dimethylformamide. Finally, a search was made for fluorinated ethers, and it was found that the polymer and the monomers were soluble in Freon E-2, and the dimethylammonium chloride by-product was not.

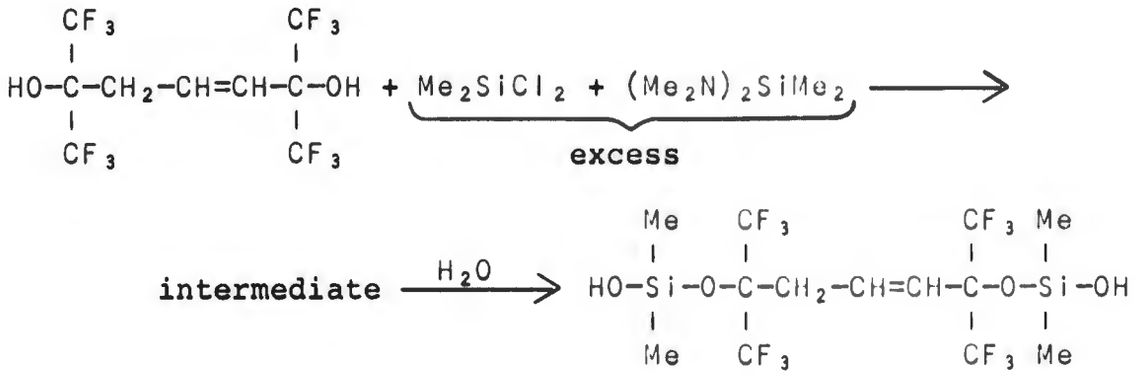


Freon E-2 (Du Pont)
b.p. 105°C

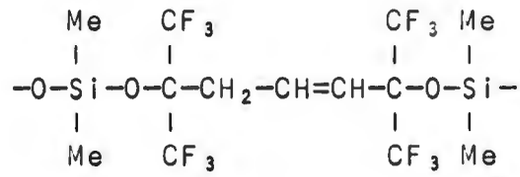
Consequently, a procedure was adopted with Freon E-2 as the reaction medium. A polymerization involves dissolving the diol in Freon E-2 and adding diaminosilane and dichlorosilane in equimolar amounts slowly until 97% of the stoichiometric amounts of the silanes have been added. Then the two silanes are added in increments of about 0.5 mole % at 10-minute intervals until the viscosity begins to increase. The procedure is given in the section on experimental details. The highest inherent viscosity obtained was 0.26 dl/g.

d. Modification of monomers

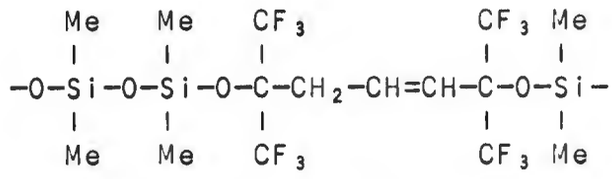
An attempt was made to prepare a new monomer that would present additional opportunities for polymerization.



It was anticipated that the silanol-terminated compound could be polymerized by treatment with strong acid, which would produce a polymer with this structure:



In addition, treatment with a diaminosilane could produce this polymer:



These two polymers are variants of the hexafluoroacetone-propylene-dimethylsiloxane polymer. They would have a higher proportion of siloxane which would impart lower glass-transition temperatures at the sacrifice of some solvent resistance. However, the pure monomer was not obtained. The crude reaction product was an oil that could not be crystallized or distilled, so it was not successfully purified.

e. Physical properties of the hexafluoroacetone-propylene-dimethylsiloxane polymer

The hexafluoroacetone-propylene-dimethylsiloxane polymer was the culmination of a series of polymers in which the glass-transition temperature became progressively lower and the resistance to organic liquids became progressively greater. The polymer having an inherent viscosity of 0.26 dl/g was a soft, tacky, colorless, transparent gum.

The glass-transition temperatures (Tg) of three polymers are shown in Table II. The Tg of the hexafluoroacetone-propylene-dimethylsiloxane polymer was -50°C, which probably would be sufficiently low for use on aircraft.

Table II. Glass-Transition Temperature of Polymers

	Tg, °C
Hexafluoroacetone-isobutylene-silphenylene	0
Hexafluoroacetone-propylene-silphenylene	-12
Hexafluoroacetone-propylene-dimethylsiloxane	-50

The resistance to organic liquids became apparent when difficulty was encountered in finding a suitable solvent for the polymerization. The resistances of the polymers to toluene and JP-4 fuel were determined by observing dimensional changes when pieces of the polymer were immersed in the liquids. The data of Table I show that the hexafluoroacetone-propylene-dimethylsiloxane polymer was much more resistant than neoprene to toluene and only slightly less resistant to JP-4 fuel.

Data on the relation between molecular weight and inherent viscosity of the polymer were obtained to facilitate the work on preparation and curing. The data are summarized in Table III and the figure.

Table III. Inherent Viscosities, Molecular Length and Molecular Weight of the Hexafluoroacetone-Propylene-Dimethylsiloxane Polymer

Polymer No. 5724-	η_{inh}[a]	Molecular length[b] $\bar{A}_n$, Å	$\bar{A}_w$, Å	MWD	Molecular weight[c] $\bar{M}_w$
85-10	0.058	73	338	4.63	--
143-2	0.21	53	994	18.8	--
105-9	0.26	197	1095	5.6	31,700

a. Inherent viscosity measured at a concentration of 1.0 g per deciliter in tetrahydrofuran at 30°C.

b. $\bar{A}_n$ is number-average molecular length, by gel-permeation chromatography.

$\bar{A}_w$ is weight-average molecular length, by gel-permeation chromatography.

MWD is ratio of $\bar{A}_w$ to $\bar{A}_n$.

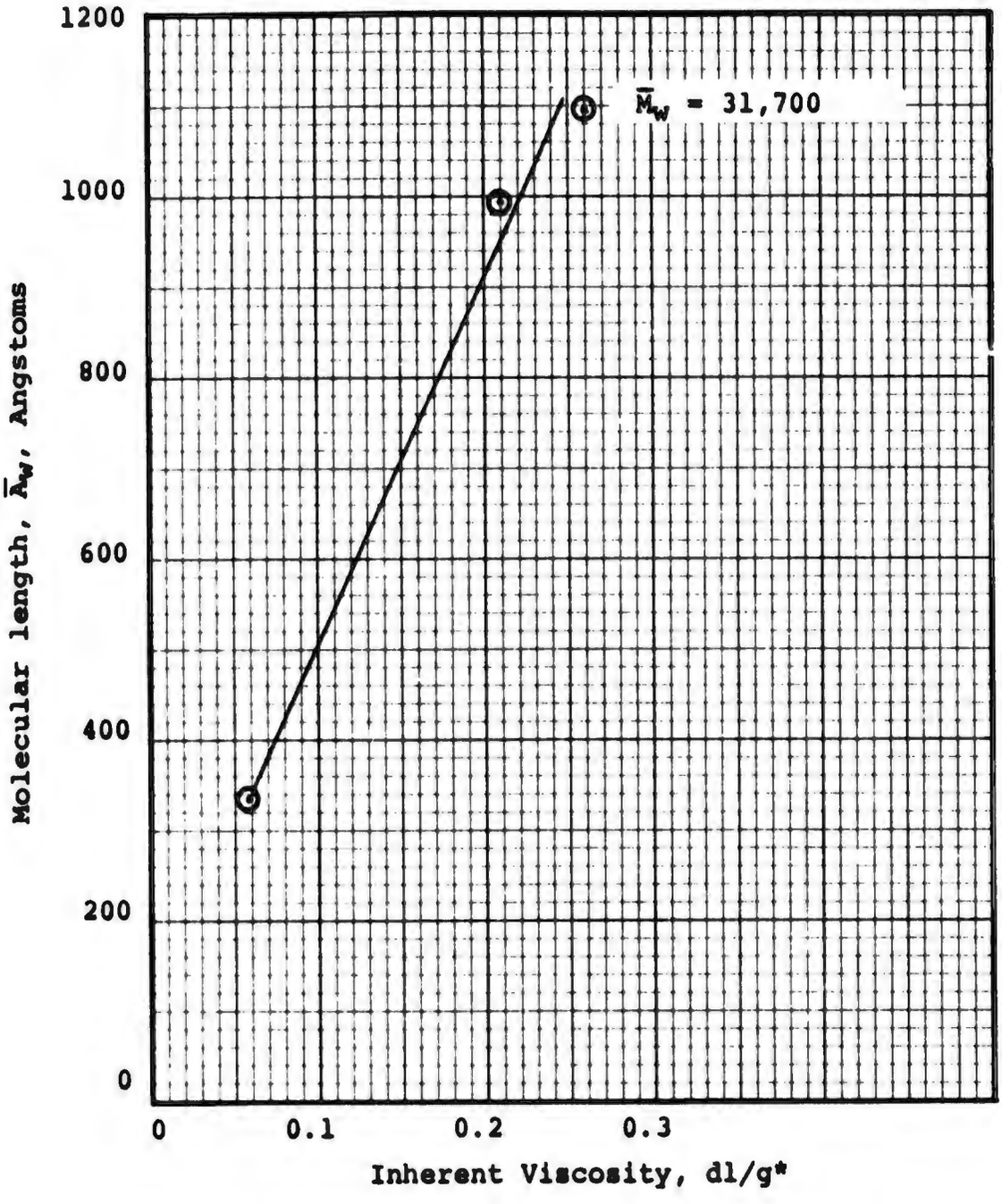
c. $\bar{M}_w$ is weight-average molecular weight by light scattering.

The formula weight of the repeating unit is 430.27.

The average molecular lengths, $\bar{A}_w$ and $\bar{A}_n$, were determined by gel permeation chromatography; and the average molecular weight, $\bar{M}_w$, of one polymer was determined by light scattering. The ratio of $\bar{M}_w$ to $\bar{A}_w$, the Q factor, for that polymer was 29. Having the Q factor and the relationship shown in the figure, it is possible to estimate molecular weight from inherent viscosity. Additional data would provide greater accuracy, but the available data provided useful approximations.

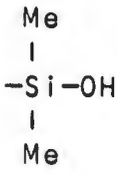
f. Attempts to cure the hexafluoroacetone-propylene-dimethylsiloxane polymer

The hexafluoroacetone-propylene-dimethylsiloxane polymer was prepared for curing studies with a slight excess of the silane reagents followed by hydrolysis to favor termination of chains with silanol groups:

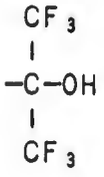


Relation Between Molecular Length, Inherent Viscosity, and Molecular Weight

*Determined in tetrahydrofuran at 30°C at a concentration of 1.0 g/deciliter.

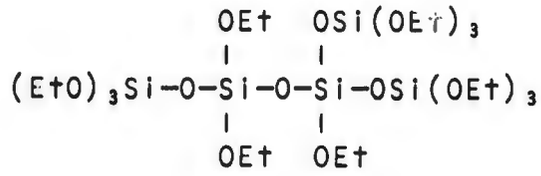


However, the difficulty encountered in attempts to cure the polymer with ethyl silicate, $Si(OC_2H_5)_4$, suggested that chains may also be terminated with bis(trifluoromethyl)carbinol groups.



Hence, we tried reagents, such as isocyanates and polyethoxyl compounds, which would be expected to react with both silanols and alcohols; and we also tried peroxides, which might crosslink the polymers through attack on the allylic hydrogens of adjacent chains.

Ethyl silicate and its derivative, "ES 40", have given the most promising results. ES 40, obtained from Union Carbide Corp., is a partially hydrolyzed form of ethyl silicate which can be represented by this formula:



ES 40, which has several reactive ethoxyl groups, is used for curing silanol-terminated silicones through elimination of ethanol in a reaction catalyzed by metal soaps.

We tried ethyl silicate and ES 40 in a variety of concentrations and with the following catalysts: dibutyltin diacetate, dibutyltin dilaurate, stannous octoate, and iron naphthenate. Mixtures were made in solution or by milling, and temperatures from 27°C to 165°C were tried. At best, the polymer was converted from a grease to a sticky gum that showed some recoverability.

Methyl triacetoxysilane, CH_3-Si$(OCOCH_3)_3$, is also used for curing silanol-terminated silicones in a reaction catalyzed by metal soaps in the presence of moisture. Attempts were made to cure the hexafluoroacetone-propylene-dimethylsiloxane polymer with methyl triacetoxysilane at different temperatures, with different metal soaps, and with mixtures made in solution or by milling, but the results were no better than those with ES 40.

Isocyanates, which usually react with both alcohols and silanols, were tried with the hexafluoroacetone-propylene-dimethylsiloxane polymer. Preliminary trials with the hexafluoroacetone-propylene diol and a silanol-terminated silicone resin (DC 805, a coating agent of Dow Corning) indicated that reactions occurred. However, no evidence of curing was obtained when the polymer was treated with the Upjohn Company's polymethylene polyphenylisocyanates, PAPI and Isonate 500. Various mixtures of dibutyltin diacetate and triethylenediamine were used as catalysts. It was difficult to keep the mixtures homogeneous after the solvent evaporated. Mixing by milling produced uniform opaque films, but curing did not occur. Avoidance of moisture or the incorporation of small amounts of glycerol was not beneficial.

Aluminum isopropoxide reacted rapidly with the polymer dissolved in tetrahydrofuran and caused gelling so rapidly that mixing could not be completed. Attempts were made to retard the reaction by the use of aluminum tertiary-butoxide or a product made by the reaction of aluminum isopropoxide with the hexafluoroacetone-propylene diol. Neither agent resulted in an appreciable amount of crosslinking. Curing was tried at a pressure of 0.1 mmHg to avoid moisture and accelerate the removal of by-product alcohol, but the results were no better.

Tetra(2-ethylhexyl) orthotitanate was tried with the hexafluoroacetone-propylene-dimethylsiloxane polymer and dibutyltin diacetate. Tetra(2-ethylhexyl) orthotitanate was tried also in mixtures with ES 40 and dibutyltin diacetate, but none of these caused crosslinking.

Peroxide catalysts were tried, because they have been successful in curing siloxanes that have unsaturated side chains. Both benzoyl peroxide and 2,4-dichlorobenzoyl peroxide were used

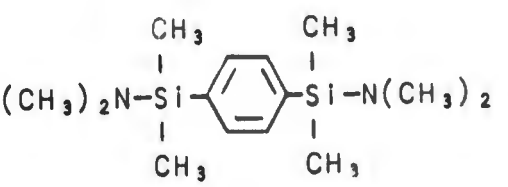
at temperatures of 145°C and 250°C, but the viscosity of the polymer did not increase appreciably. The double bond in the polymer is evidently not very reactive, for neither the polymer nor the hexafluoroacetone-propylene diol decolorized bromine in carbon tetrachloride.

Tris(methylamino)phenylsilane is a trifunctional compound that reacts quantitatively with many alcohols and silanols:

$$PhSi(NHCH_3)_3 + 3ROH \longrightarrow PhSi(OR)_3 + 3CH_3NH_2$$

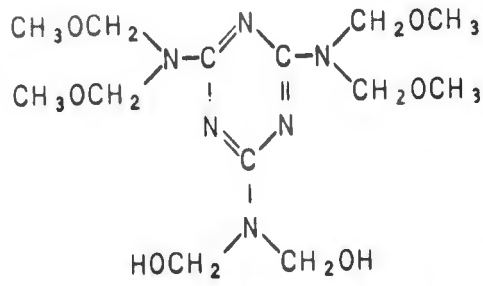
We attempted to cure the hexafluoroacetone-propylene-dimethylsiloxane polymer with the tris compound but failed to obtain an appreciable amount of reaction. Because we previously found that the hexafluoroacetone-propylene diol failed to polymerize satisfactorily with a diaminosilane unless a chlorosilane were present, we tried to cure the polymer with a mixture of tris(methylamino)phenylsilane and methyltrichlorosilane, but curing did not occur.

We treated the hexafluoroacetone-propylene-dimethylsiloxane polymer with an excess of 1,4-bis(dimethylaminodimethylsilyl)-benzene



which was expected to cap the chains with the silphenylene group. Then the product was hydrolyzed to convert the ends to silanols, $-Si(CH_3)_2OH$. The resulting hydroxysilphenylene ends were expected to react in the manner of the silphenylene-dimethylsiloxane polymer, which is easily cured with ES 40 and dibutyltin diacetate, but subsequent attempts to cure were not successful.

Aerotex 19, tetrakis(methoxymethyl)-bis(hydroxymethyl)-melamine, and Aerotex P225, hexakis(methoxymethyl)melamine (American Cyanamid Co.) were tried alone and in combination with ES 40 and dibutyltin diacetate, but curing did not occur.

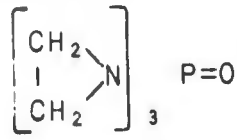


Aerotex 19

Aerotex P225 is fully methylated

The reaction desired was the elimination of methanol as a result of interaction between the methoxyl groups of the agent and the hydroxyl ends of the polymer.

Tris(aziridinyl)phosphine oxide ("APO", Dow Chemical Co.) was tried to cure the hexafluoroacetone-propylene-dimethylsiloxane polymer.



APO

Partial hardening occurred, but the products were not uniform, which indicated that APO was not miscible with the polymer.

As a final trial of the most promising curing reaction, the hexafluoroacetone-propylene-dimethylsiloxane polymer was milled with reinforcing silica, ES 40, and dibutyltin diacetate, and pressed between plates to form a film. After 24 hours the film resembled wax in texture.

The reactions discussed above were tried with polymers of high and low molecular weights. The inherent viscosities were 0.06-0.22 dl/g.* The persistent failure of the polymer to react suggests that it has an exceptional steric or electronic character.

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*Measured at 30°C in tetrahydrofuran at a concentration of 1.0 g per deciliter.

B. Experimental Details

1. Preparation of monomers

a. 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 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 the 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.

For additional purification, the crude diol was redistilled through a 300 x 15-mm column packed with thin, perforated stainless steel rectangles (4 x 6 mm) bent in the form of C's. Fractions boiling from 68-69°C at 8 mmHg were found to consist of 99+% trans isomer by gas chromatography.

Anal. Calculated for $C_9H_6F_{12}O_2$: C 28.89, H 1.62.
Found: C 28.97, H 1.69.

In recent preparations the initial heating time was reduced to 24 hours.

b. Bis(dimethylamino)dimethylsilane

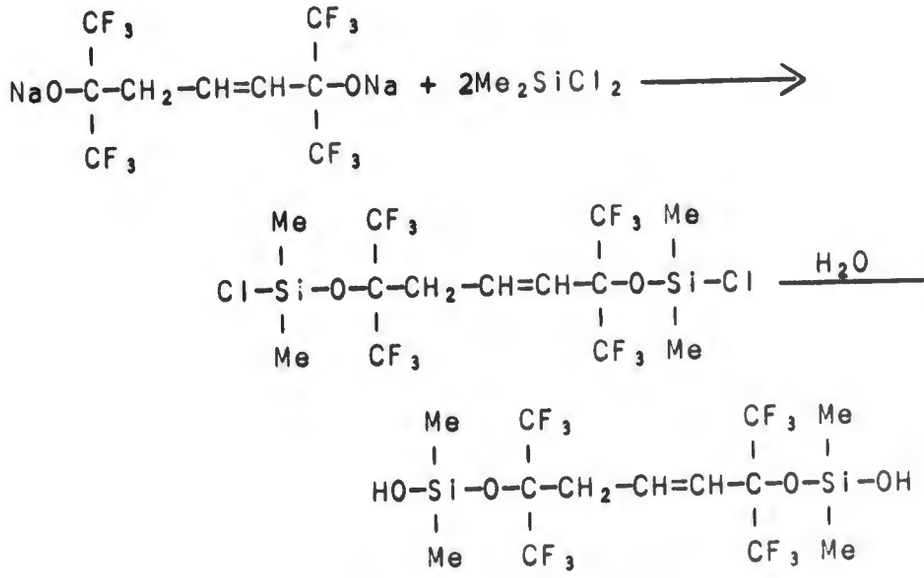
In a 3-liter, 3-neck flask fitted with a thermometer, reflux condenser, stirrer, and gas-inlet tube were placed 194 g (1.5 mole) of dimethyldichlorosilane and 1500 ml of benzene. Liquid dimethylamine, approximately 400 g (8.9 mole), was drawn from a cylinder into a flask containing a few pea-size pieces 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 at 750 mmHg pressure. Anderson[4] reported 128.4°C at 760 mmHg.

c. Disodium salt of the hexafluoroacetone-propylene adduct

The initial work on the disodium salt of the hexafluoroacetone-propylene adduct was described earlier.[2] The procedure was the same for the work under the present contract, except that the salt was not isolated but used in solution. Sodium hydride, 25.56 g (0.626 mole) of a 58.8% dispersion in mineral oil, was washed with ether in a 1-liter, 3-neck flask. The ether used for washing was decanted, and 500 ml of ether was added for the reaction. The mixture was cooled to 5°C, and the hexafluoroacetone-propylene adduct, 42.27 g (0.113 mole), was added dropwise with stirring over 45 minutes. The reaction mixture was stirred overnight at room temperature. The excess sodium hydride and other solid products were filtered off with a filter stick to avoid exposure to air. An aliquot of the liquid was evaporated, and the weight of residue indicated a 56% yield of the disodium salt. An additional 17% was obtained by extraction of the solid portion of the reaction mixture. The solutions were combined for the attempt to form the disilylated diol as described in the next paragraph.

d. Disilylated fluorinated diol

An attempt was made to attach two silanol groups to the hexafluoroacetone-propylene diol.



1,5-bis(dimethylhydroxysiloxy)-
1,1,5,5-tetrakis(trifluoromethyl)-2-pentene
or
1,1,1,7,7,7-hexafluoro-2,6-bis(trifluoromethyl)-
2,6-bis(dimethylhydroxysiloxy)-3-heptene
or
"disilylated fluorinated diol"

Freshly distilled dimethyldichlorosilane, 53.8 g (0.417 mole), was dissolved in 250 ml of diethyl ether in a 2-liter, 3-neck flask equipped with a magnetic stirring bar, thermometer, dropping funnel, and condenser. The ether solution of the disodium salt described in the preceding paragraph, 950 ml containing 34.9 g (0.0833 mole), was added dropwise with stirring over a 3-hour period. The temperature rose to 34°C, and a white solid appeared. The liquid was removed under a nitrogen atmosphere by drawing it off through a sintered-glass filter stick. The salt was rinsed twice with ether, dried, and found to weigh 13.6 g (theory, 13.2 g). The filtrate was freed of ether and excess dimethyldichlorosilane by distillation; the residue was distilled through a Vigreux column (3 in. x 1/2 in.), and collected in four fractions that boiled over the range of 62-104°C at 2.0 mmHg. The distillate, 24.1 g, was presumed to be the dichloro intermediate (73% of theory).

The dichloro intermediate, 6.27 g (0.0112 mole, Fraction 1, b.p. 62-85°C at 2.0 mmHg) was dissolved in 100 ml of ether and added dropwise with stirring to 500 ml of ice and water that contained 12.5 g (0.3 mole) of sodium hydroxide. The hydrolyzate was neutralized with hydrochloric acid to a pH of 8, the ether layer was separated, and the water layer was extracted with ether. The combined ether solutions were dried with sodium sulfate, and the ether was removed by evaporation under nitrogen and at reduced pressure. The pale, straw-colored liquid was 4.86 g (83% of theory). Similar results were obtained with the other fractions. All were combined and distilled to yield a liquid that had the boiling point of the original hexafluoroacetone-propylene diol. Evidently hydrolysis of the dichlorosilyl derivative removed the entire silicon-containing portion.

2. Preparation of the hexafluoroacetone-propylene-dimethylsiloxane polymer

a. By reaction of the fluorodiol, diaminosilane, and dichlorosilane

The preparation of Polymer 5724-105 is described as typical. The hexafluoroacetone-propylene adduct, 13.27 g (0.0354 mole), was dissolved in 25 ml of Freon E-2 (Du Pont) in a 100-ml round-bottom flask equipped with a magnetic stirrer, condenser with a Drierite tube, and two rubber septums. As the solution was being stirred, bis(dimethylamino)dimethylsilane, 1.29 g (0.0088 mole), was added, as described below, from a syringe with a stainless-steel needle through a septum; then dimethyldichlorosilane, 1.12 g (0.0086 mole), was added from a syringe through a septum. The reaction mixture, in an oil bath, was heated to reflux, 105°C. The diaminosilane and dichlorosilane were added alternately, about 0.02 to 0.03 ml each addition, at intervals of 3 minutes. The specific gravity of the diaminosilane is about 0.8 and of the dichlorosilane is about 1.2. However, actual weights were determined by weighing the syringes periodically. As the stoichiometric amounts were approached, the viscosity of the solution increased perceptibly. The final total amount of diaminosilane was 2.72 g (0.0185 mole) and of dichlorosilane was 2.45 g (0.0191 mole). The slight excess of dichlorosilane was used to avoid subsequent hydrolysis of polymer, which occurs faster in basic media. The salt accumulated in a pasty layer on top of the reaction medium. A sample of the polymer was found to have an inherent viscosity of 0.07 dl/g.

Higher molecular weight was desired. Because the point of stoichiometric equivalence had been passed, water, 2 ml, was stirred in at 100°C for 15 min. The reaction mixture was cooled, most of the water was removed with a pipette, and anhydrous sodium sulfate was added. After the mixture had stood overnight, the liquid was decanted, and the salt was rinsed with Freon E-2.

The polymerizate was returned to the reaction flask and the dropwise addition of reagents was resumed. This process of washing followed by resumption of polymerization was continued until the inherent viscosity reached 0.20 dl/g. The polymer solution was mixed with an equal volume of tetrahydrofuran, and twice the total volume of methanol was added. The polymer was removed under reduced pressure. The yield of polymer was 90% of theory, and the inherent viscosity was 0.26 dl/g.

Anal. Calculated for $C_{11}H_{10}F_{12}O_2Si$: C 30.71%, H 2.34%,
Found: C 30.90%, H 2.47%.

Data on molecular size as determined by gel permeation chromatography are given in Table II.* The molecular weight by light scattering was 31,700.*

b. Trials of other methods

Attempts were made to form a polymer by treating the hexafluoroacetone-propylene diol with dimethyldichlorosilane in pyridine according to the Schotten-Baumann reaction. The chlorosilane was added slowly to the diol dissolved in pyridine, and two layers formed. Attempts to separate polymer from each layer by washing with water resulted in recovery of the diol.

Polymerization by treating the sodium salt of the diol with dimethyldichlorosilane was prevented by the lack of a suitable solvent. Tetrahydrofuran dissolved the monomers, but it apparently reacted with the dichlorosilane. The sodium salt of the diol was prepared in tetrahydrofuran by adding the diol to an excess of sodium hydride, filtering, and assaying the salt in solution by titrating a sample. Dimethyldichlorosilane was added slowly to the solution of the sodium salt. A white precipitate formed, but it could not be completely separated by centrifuging. On standing the mixture became gelatinous. Evaporation of samples revealed no evidence of polymeric materials.

Preparation of the sodium salt in Freon E-2 was attempted, but the salt was not soluble.

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*Determined by ArRo Laboratories, Inc., Joliet, Illinois.

3. Physical properties

a. Molecular length and molecular weight

ArRo Laboratories determined the molecular length of the hexafluoroacetone-propylene-dimethylsiloxane polymer by gel permeation chromatography and the molecular weight by light scattering. The results are in Table III.

b. Glass-transition temperature

ArRo Laboratories determined the glass-transition temperature of the hexafluoroacetone-propylene-dimethylsiloxane polymer to be -50°C by differential thermal analysis.

c. Surface tension

The surface properties of the hexafluoroacetone-propylene-dimethylsiloxane polymer were of special interest, because the high fluorine content was expected to impart excellent repellency. The contact angle of a droplet of water on the polymer was greater than 90°, but it could not be measured accurately, because the droplet sank into the polymer. Accordingly, a tensiometer method was used with the Instron Tensile Tester.[5] A tensiometer ring fitted into the Instron was immersed in the polymer and withdrawn at a crosshead speed of 0.02 in./min. At such a slow speed, viscosity effects are negligible. The surface tension was found to be 16 dynes/cm. For comparison, critical surface tension values of other materials are listed in Table IV.

To confirm the tensiometer measurement, droplets of several liquids were placed on a film of the polymer to observe their tendency to spread. Droplets of liquids having higher surface tensions than the polymer remain intact; droplets of liquids having equal or lower surface tensions wet the polymer and have zero contact angles. Decane with a surface tension of 24 dynes/cm remained intact. Droplets of octane with a surface tension of 22 dynes/cm spread out so that the actual contact angle could not be determined. Thus the surface energy of the polymer was less than 24 dynes/cm, but the actual value could not be determined by this method.

Table IV. Critical Surface Tensions of Polymers[a]

	Critical surface tension, dynes/cm
Poly(6-aminocaproic acid), nylon 6	42
Poly(11-aminoundecanoic acid), nylon 11	33
Polyethylene	31
Poly(dimethylsiloxane)	24
Poly(trifluoroethylene)	22
Poly(tetrafluoroethylene)	18.5

a. See Reference 6.

4. Attempts to cure the polymer

a. Ethyl silicate

Methods involving ethyl silicate produced the closest approach to curing. The reagent used with most effect was ES 40, a partially hydrolyzed form of ethyl silicate produced by Union Carbide Corp.

Prior experience with curing silanol-terminated silphenylene-dimethylsiloxane polymers showed that an amount of ethyl silicate equal to 10% of the weight of the polymer resulted in the best cure. Consequently, we started at that level but found that amounts in the range of 1% to 5% were better. Even so, the best cured film obtained was tack-free on the surface but sticky underneath. This sample, 5724-143-2, was made by mixing the polymer (inherent viscosity, 0.21 dl/g) in tetrahydrofuran with 5% of its weight of ES 40 and 0.9% of its weight of dibutyltin diacetate. The solution was poured into a flat dish at room temperature, and the resulting film was tack free on the surface in 1 hour, but it remained somewhat leathery and sticky when torn.

Many different curing conditions were tried in solution with ethyl silicate and ES 40. The catalysts tried were dibutyltin diacetate, dibutyltin dilaurate, stannous octoate, iron napthenate, and cobalt naphthenate. Temperatures up to 250°C were tried, also, but the results were no better.

In other trials, the polymer was mixed with curing agents, by curing them together on a glass plate with a small stainless-steel roller. A polymer with an inherent viscosity of 0.21 dl/g was milled with 7.3% by weight of ES 40 and 1.7% of dibutyltin diacetate. The latter caused it to become milky. After 3 hours the sample was essentially tack free on the surface. After 3 days the sample was peeled from the plate, but it had very little strength and recovered sluggishly on being stretched.

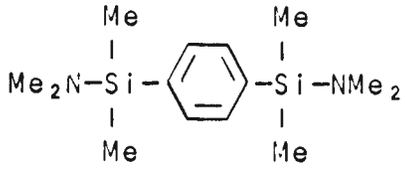
Another trial was made by milling the polymer with reinforcing silica on a paint mill with stainless-steel rollers. A polymer with an inherent viscosity of 0.16 dl/g was milled with 20% of Cab-O-Sil H-5 (Cabot Corp.), 11% of ES 40, and 3% of dibutyltin diacetate (all percentages on the weight of polymer). Half of the milled product, which had the consistency of a gum, was removed and pressed between two plates. After 3 days, the mass was appreciably stiffer and it yielded when drawn, but it had almost no recoverability and very little tensile strength. The other half was milled with APO (4% by weight of the polymer) and triethanolamine (2.7%) and pressed between two plates. After 3 days, the portion with APO was harder and friable.

b. Isocyanates

Isocyanates were tried as curing agents, because they react with both the silanol and fluorochemical alcohol end groups that may be present. Attempts to cure films cast from solvents were not successful with isocyanates; the problem appeared to be partially that the isocyanates were not soluble in the polymer. The mixtures dissolved in tetrahydrofuran (THF) were usually homogeneous, but they separated into two phases as the solvent evaporated, and small grainy spots appeared in the films. These were thought possibly to have resulted from reaction with moisture in the air, but the graininess appeared, also, when mixtures were milled in a bag filled with dry nitrogen. The agents used in attempts to prepare films were Isonate 500 and PAPI, which are polymethylene polyphenyl isocyanates made by the Upjohn Company. Both of these isocyanates have functionalities greater than 2, so they are capable of crosslinking. NIAX (tolylene diisocyanate, Union Carbide Corp.) was used in preliminary trials to establish that a reaction occurred with the representative compounds, 1,4-bis(dimethylhydroxysilyl)benzene and the hexafluoroacetone-propylene adduct. The catalysts used were dibutyltin diacetate and dibutyltin dilaurate. The accelerators were triethylamine and triethylenediamine.

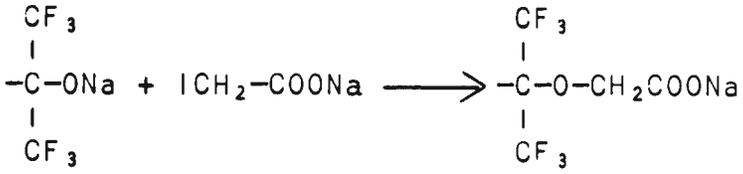
The lack of reactivity of the polymer suggested that it might be beneficial to termina'e the chains with a more reactive and versatile functional group. In an attempt to make isocyanate-terminated chains, a polymer dissolved in Freon E-2 was stirred at 105°C for 2 hours with an excess of tolylene diisocyanate. The solution did not become homogeneous, so the excess isocyanate was removed mechanically, and portions of the polymer solution were treated with the prospective curing agents dissolved in tetrahydrofuran, which made the mixtures homogeneous. The reagents tried in a variety of different combinations were glycerol, triethylenediamine, dibutyltin diacetate, dibutyltin dilaurate, and Aerotex P225. No evidence of curing was seen.

The silphenylenediamine, 1,4-bis(dimethylaminodimethylsilyl)-



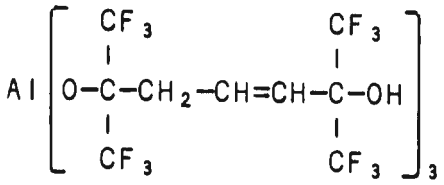
benzene was used, also, in an attempt to terminate the chains with more reactive groups. The polymer was treated in Freon E-2 with a slight excess of the diamine and dimethyldichlorosilane. It was assumed that any aminosilane ends would be converted to silanols by the moisture in the air. Aluminum isopropoxide and ES 40 with dibutyltin diacetate were tried as curing agents, and some loss of tack was observed, but none of the films was strong enough to be peeled.

An attempt was made to cap the chains with oxyacetic acid groups by treating an aqueous suspension of the polymer in mild alkali with sodium iodoacetate.



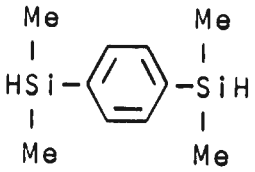
If termination by unhindered carboxyls could be achieved, isocyanate curing agents would probably be effective. However, the alkalinity required to form the sodium salt of the polymer, and the heat required to promote the Williamson Reaction destroyed the polymer.

Non-uniform gelation occurred rapidly when the polymer was mixed with solutions of aluminum isopropoxide, so attempts were made to retard the reaction. Aluminum t-butoxide apparently did not react. Aluminum isopropoxide was treated with an excess of the fluorodiol in tetrahydrofuran in an attempt to form a reagent with this structure:



No precipitate formed in the tetrahydrofuran, so the solution was used to treat a polymer in tetrahydrofuran. No gelation occurred either in solution or later in a thin cast film after the solvent evaporated.

The olefinic bonds in the polymer are relatively inert as shown by their failure to decolorize solutions of bromine. Even so, an attempt was made to cure with a silyl-hydrogen compound in a reaction catalyzed by a trace of platinic chloride.



This reaction is widely used for room-temperature curing of silicones with vinyl side-chains. No evidence of curing was obtained with our polymer even at temperatures up to 205°C.

Hexamethylenediamine carbamate, a compound used to cure Viton rubbers, was tried in an effort to cure through the fluorocarbon groups. No curing was obtained at temperatures up to 300°C.

"APO", tris(aziridinyl)phosphine oxide, with and without triethanolamine and zinc trifluoborate was mixed with the polymer in solution and by milling. No reaction was observed at room temperature, and on heating for 24 to 48 hours at 105°C, the films separated into solid and liquid portions.

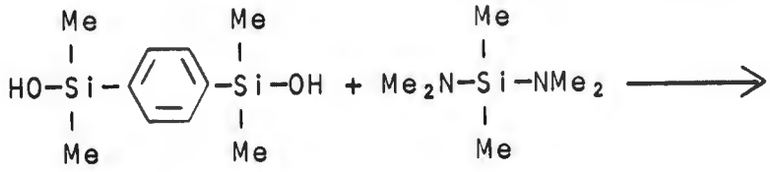
No reaction was obtained in mixtures of the polymer with Epon 828 up to 135°C.

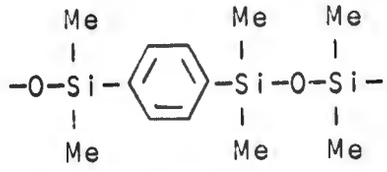
Other reagents tried without promising results were sulfur, methyltriacetoxysilane, tetra(2-ethylhexyl)orthotitanate, benzoyl peroxide, 2,4-dichlorobenzoyl peroxide, and tris(methylamino)-phenylsilane.

IV. EROSION RESISTANCE OF THE SILPHENYLENE-DIMETHYLSILOXANE POLYMER

A. Discussion

An alternating copolymer of 1,4-bis(dimethylhydroxysilyl)-benzene and dimethylsiloxane was prepared for evaluation as a rain-erosion-resistant coating. The method of preparation was developed in an earlier program on high-temperature elastomers.[7]





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

"silphenylene-dimethylsiloxane polymer"

The silphenylene-dimethylsiloxane polymer is cured to an elastomer with ES 40 and dibutyltin diacetate at room temperature. For evaluation as a rain-erosion coating it was milled with silica and ES 40 and then dispersed in toluene. The dispersion was mixed with dibutyltin diacetate and sprayed immediately onto airfoil test specimens, which were laminates of epoxy and glass fiber. Five applications, 2 mils each, were made with 3-5 minutes between applications. The laminates had been primed with

General Electric primer SS-4044. The coated specimens were exposed to simulated rain in the whirling-arm rain-erosion simulator at Wright-Patterson Air Force Base. The table prepared at the Air Force Base (Table V) includes data on several other elastomers for comparison. The silphenylene-dimethylsiloxane coating had far better erosion resistance than the silicone or epoxy coating. Neither the neoprene nor the polyurethane is classed as a high-temperature elastomer, while the silphenylene-dimethylsiloxane has exceptional thermal stability. It suffered no loss of resistance to sand erosion after being heated for 4 hours in air at 250°C.[2]

Table V. Rain Erosion Data
500 MPH, 1 inch/hour simulated rainfall

AFML No.	Coating	Thickness (mils)	Substrate	Time to failure(min)	Comments
2661	5724-23 Silphenylene-dimethylsiloxane	12-15	Glass-epoxy	24.5	Erosion and tearing
2662	5724-23 Silphenylene-dimethylsiloxane	12-15	Glass-epoxy	23.7	Erosion and tearing
2663	5724-23 Silphenylene-dimethylsiloxane	12-15	Glass-epoxy	13.8	Erosion and tearing
1273-74	DC-92-009 Silicone	15	Glass-epoxy	1.0	Erosion and adhesion loss
--	MIL-C-7439B Neoprene	12	Glass-epoxy	40.0	Erosion failure
--	MIL-C-83231 Polyurethane (Olin)	12	Glass-epoxy	160.0	Erosion failure
--	Epoxy, polyester or acrylic	12	Glass-epoxy	<5	Erosion failure

Table prepared by Elastomers and Coatings Branch, Nonmetallic Materials Division, Air Force Materials Laboratory, Wright-Patterson Air Force Base.

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