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10059-2258-V

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

Final Report

(15 April 1969 to 14 January 1970)

March 1970

by

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Prepared Under Contract N00019-69-C-0258

for

Naval Air Systems Command
Department of the Navy

by

Southern Research Institute
Birmingham, Alabama

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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 N00019-69-C-0258. The report includes work accomplished during the period 15 April, 1969, to 14 January, 1970. 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.

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

I. INTRODUCTION AND SUMMARY

Tough, heat-resistant elastomers are needed to protect radomes and leading edges of high-speed aircraft from rain erosion. To be successful, a new coating must be radar transparent and resistant to degradation on exposure to sunlight, low temperatures, salt spray, fuels, lubricants, and paint strippers. In addition it must be inexpensive enough for use in large quantities and easily applied and cured. Several polymeric fluorochemical silyl ethers and a silphenylene-dimethylsiloxane appear to be promising candidates for this application.

The polymeric fluorochemical silyl ethers were prepared from diaminosilanes or diaminosilphenylenes by reactions with diols prepared from hexafluoroacetone and either propylene or isobutylene. The fluorochemical components impart solvent resistance and thermal stability while the organosilane components impart thermal stability, flexibility, and curability at moderate temperatures. Some difficulty has been encountered in obtaining high molecular weights with the diol-diaminosilane reaction because the acidic fluorocarbon diol forms salts with the amine by-products. Because the molecular weights were below the desired level, the strength of the cured elastomers was low. However, there are several alternative methods of preparing the polymer that should overcome this difficulty. One such method, the reaction of the disodium salt of the diol with a dichlorosilane, appeared to be promising in a preliminary trial.

The silphenylene-dimethylsiloxane elastomer was more resistant to sand abrasion than any other high-temperature elastomer that could be cured at room temperature. Its sand-abrasion resistance was similar to that of neoprene at ordinary temperatures and better than that of neoprene when both had been heated above 150°C for 4 hours. Its sand-abrasion resistance was better than that of a new polyurethane that is being proposed for use as a rain-erosion-resistant coating after both were heated at 250°C for 4 hours, but the polyurethane was better after being heated 4 hours at 200°C or less. The silphenylene-dimethylsiloxane can be applied in the desired thickness by multiple sprayings. We have submitted samples of the silphenylene-dimethylsiloxane for simulated rain-erosion tests.

This report covers work done under Contract N00019-C-69-0258 in the period April 15, 1969 to January 14, 1970.

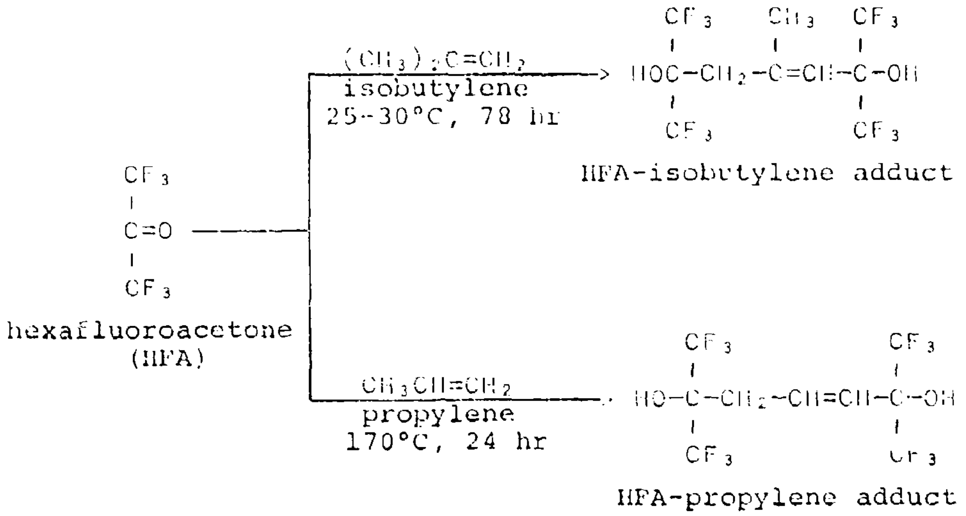
II. POLYMERS DERIVED FROM HEXAFLUOROACETONE AND ALKENES

A. Discussion

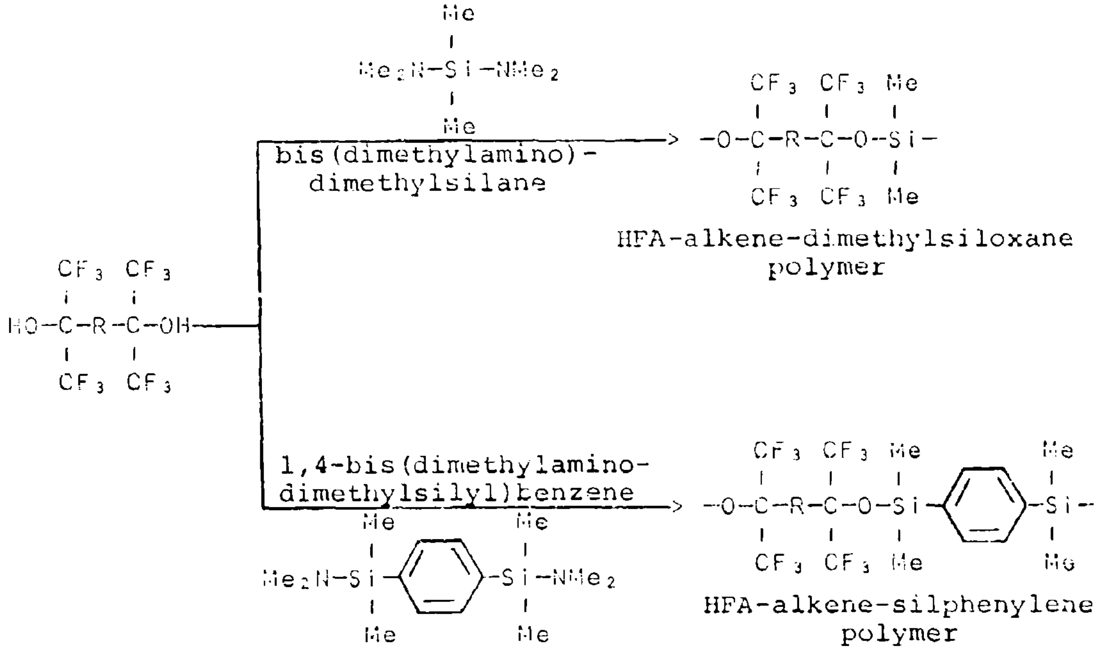
1. Overview and summary of previous work

A new type of polymer is needed to meet the requirements for thermally stable rain-erosion-resistant coatings for radomes and leading edges of high-speed aircraft. In addition to rain-erosion resistance, a coating must be flexible, radar transparent, and inexpensive. It must also be capable of application under shipboard conditions and resist degradation on exposure to aerodynamic heating, sunlight, low temperatures, salt spray, fuels, lubricants, and paint strippers. The need for such properties suggests elastomers that combine some of the best properties of fluorocarbons and siloxanes. Known fluorocarbon elastomers have excellent resistance to solvents and good thermal stability, but they are expensive and do not cure at moderate temperatures. Some of the known siloxane elastomers cure at room temperature and have adequate resistance to heat, but they have poor erosion resistance and only moderate solvent resistance. We are attempting to combine the desirable qualities of the fluorocarbons and siloxanes into a single polymer that will have better erosion resistance than any known high-temperature elastomer that cures at moderate temperatures.

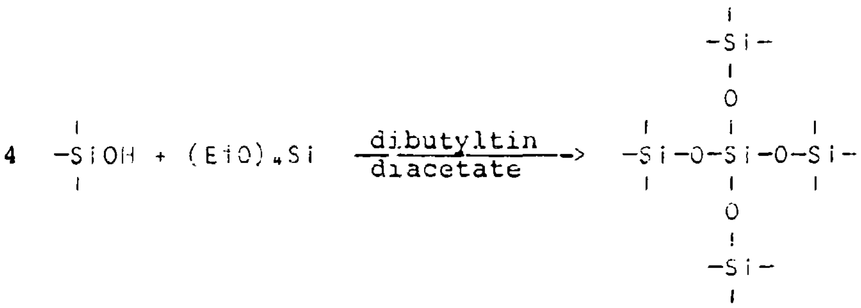
For several reasons, hexafluoroacetone (HFA) derivatives are attractive starting materials for polymers. First, HFA, itself, is relatively inexpensive for a fluorocarbon. The price, which is presently about $6.00 per pound, is likely to fall below $2.00 per pound if large-scale uses are developed. Second, HFA reacts with many unsaturated hydrocarbons to form diols in high yields. We have worked with the diols prepared from isobutylene and propylene:



And third, the HFA-alkene adducts form stable polymers through reactions with diaminosilanes:



The C-O-Si bond is normally easily hydrolyzed, but the pendant trifluoromethyl groups protect the structure against hydrolysis. When the polymerization reactions are completed in the presence of a slight excess of the silicon compounds, the polymers are terminated with $Si(NMe_2)$ units, which are readily hydrolyzed to silanol, SiOH. These silanol end groups make it possible to cure the polymers to elastomers by the method used to cure RTV silicones, which is an ester-exchange reaction catalyzed by metal soaps:



$$4\ -\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{OH} + (\mathrm{EtO})_4\mathrm{Si} \xrightarrow[\text{diacetate}]{\text{dibutyltin}} \begin{array}{ccccc} & & | & & \\ & & -\mathrm{Si}- & & \\ & & | & & \\ & & \mathrm{O} & & \\ | & & | & & | \\ -\mathrm{Si} & -\mathrm{O}- & \mathrm{Si} & -\mathrm{O}- & \mathrm{Si}- \\ | & & | & & | \\ & & \mathrm{O} & & \\ & & | & & \\ & & -\mathrm{Si}- & & \\ & & | & & \end{array}$$

The reaction between the HFA-alkene adduct and bis(dimethylamino)dimethylsilane produces mainly a cyclic compound rather than a polymer, but we expect to be able to make polymers satisfactorily by modifying the reaction conditions. The preceding report[1] discussed the preparation and curing of a polymer that was made by treating the HFA-isobutylene adduct with 1,4-bis(dimethylaminodimethylsilyl)benzene, which falls in the general class of diaminosilphenylene compounds, but which, because of steric factors, minimizes formation of cyclic compounds. The resulting polymer, designated the hexafluoroacetone-isobutylene-silphenylene polymer, was cured to an elastomer with a tensile strength (nominal) of 1240 psi and an elongation at break of 265%, a tensile product of 330,000. Although this tensile product was less than the 1,000,000 preferred, it was rather high for an unreinforced film made from a polymer with a relatively low molecular weight. A cured film of the polymer was still flexible after 3 hours at 305°C in air, and it was not visibly changed during 1 hour in boiling water. However, this polymer lost its flexibility on being cooled to 0°C. We have since shifted attention to other polymers of the same type that were expected to have lower glass-transition temperatures. Subsequent work is described below.

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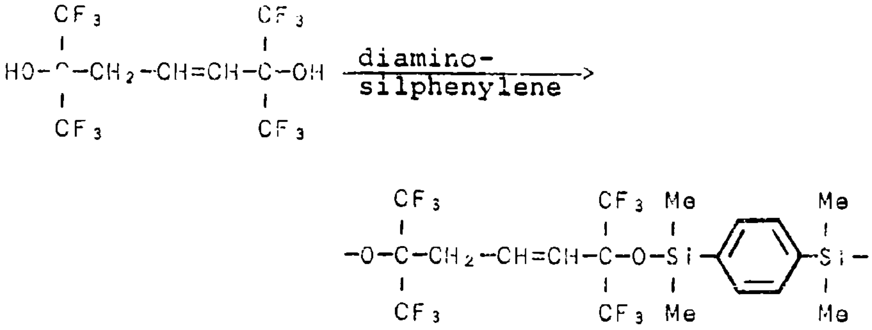
[1] See References, page 22.

2. Hexafluoroacetone-propylene-silphenylene polymer

The hexafluoroacetone-propylene-silphenylene polymer has been made by the reaction of 1,4-bis(dimethylaminodimethylsilyl)-benzene with the adduct of HFA and propylene:



Although considerable difficulty was experienced with obtaining high molecular weights, we prepared 34 g of the polymer for a study of physical properties. The glass-transition temperature of the polymer was -12°C, which places it on the borderline of acceptability as a rain-erosion-resistant coating for aircraft. Its fuel resistance was the best of the polymers prepared, so far, in this program, as shown 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-propylene-silphenylene, 5514-53-12G	1.26	1.11
Polyurethane RM115C	1.34	1.04
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

---

a. Ratio of swollen length to original length.

The solubility parameter of the hexafluoroacetone-propylene-silphenylene polymer was calculated to be 9.2 $cal^{1/2}/cc^{1/2}$. Solvents with similar parameters are tetrahydrofuran (9.1), trichloroethylene (9.2), toluene (8.9), and benzene (9.2). Therefore, these are the solvents that will cause the most swelling of the cured elastomer. Straight-chain aliphatic hydrocarbons, which have solubility parameters of 7.3 to 7.6, will cause much less swelling.

By gel permeation chromatography, a polymer having an inherent viscosity of 0.20 dl/g* was found to have a number-average chain length, $\bar{A}_n$, of 604 Å, and a weight-average chain length, $\bar{A}_w$, of 1031 Å. Thus the ratio of $\bar{A}_w/\bar{A}_n$ was 1.71, which indicates an unusually narrow chain-length distribution. The narrow distribution is desirable for good tensile properties. Molecular weights can be calculated from the A values if the factor Q is known:

$$\frac{\bar{M}_n}{\bar{A}_n} = \frac{\bar{M}_w}{\bar{A}_w} = Q$$

where Q is the molecular weight per angstrom of chain length. An attempt was made to determine Q by measuring the molecular weight, $\bar{M}_w$, by light scattering. The value obtained for $\bar{M}_w$ was 220,000, which indicates the value of Q to be 213, an unusually high value. (Dimethyl siloxane polymers, for example, have a Q value of about 30.) If the light-scattering measurement is correct, then the chains must be coiled to an exceptional degree. We will resume studies of molecular weights when samples of the hexafluoroacetone-propylene-dimethylsiloxane polymer are prepared as discussed below.

Curing of the hexafluoroacetone-propylene-dimethylsiloxane polymer was slow and incomplete with ethyl silicate and dibutyltin diacetate, but it was much better with ethyl silicate and stannous octoate. The highest tensile strength (nominal) obtained was 330 psi with 250% elongation, a tensile product of 82,500,** which is too low for rain-erosion-resistant coatings.

It was found, also, that the polymer could be cured to an elastomer with aluminum isopropoxide. However, curing occurred so rapidly that mixing could not be completed, and we did not find a satisfactory method of retarding the curing.

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

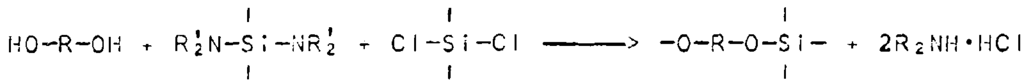
** Tensile product = tensile strength (nominal) x percent elongation.

Difficulties in achieving higher molecular weights are believed to stem from the acidity of the diol, which results in retention of dimethylamine and subsequent inhibition of polymerization. The fluorochemical moiety of the diol, $-C(CF_3)_2OH$, is more acidic than ordinary alcohols or phenols; and salts can be formed with dimethylamine, which is a product of the diol-diaminosilane reaction. Chains thus terminated would resist curing with ethyl silicate and dibutyltin diacetate, which cure through reactions with silanol groups (-SiOH). Attempts were made to polymerize the monomers in bulk (without solvent), so the amine reaction product could be removed by heat and low pressure, but these attempts were unsuccessful.

The difficulties encountered with polymerizing by the diol-diaminosilane reaction suggest at least three alternatives. One of these, the reaction of the disodium salt of the diol with a dichlorosilane, has been tried as described below for the hexafluoroacetone-propylene-dimethylsiloxane polymer.

$$NaO-R-ONa + Cl-\underset{|}{\overset{|}{Si}}-Cl \longrightarrow -O-R-O-\underset{|}{\overset{|}{Si}}- + 2NaCl$$

A second, the treatment of 1 mole of the diol with a mixture containing 0.5 mole of diaminosilane and 0.5 mole of dichlorosilane has not yet been tried.



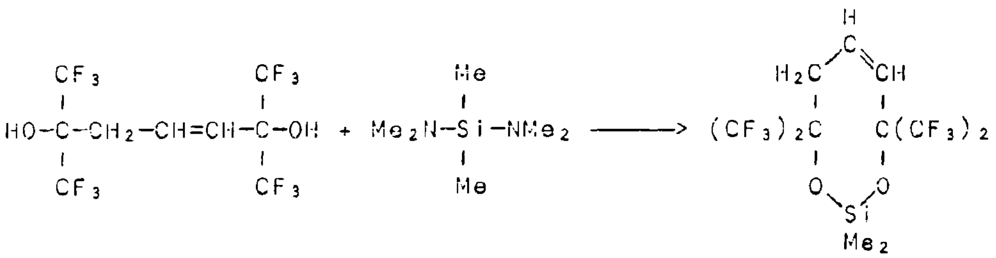
$$HO-R-OH + R'_2N-\underset{|}{\overset{|}{Si}}-NR'_2 + Cl-\underset{|}{\overset{|}{Si}}-Cl \longrightarrow -O-R-O-\underset{|}{\overset{|}{Si}}- + 2R_2NH\cdot HCl$$

A third, also not yet tried, is the reaction of the diol and a diacyloxysilane.

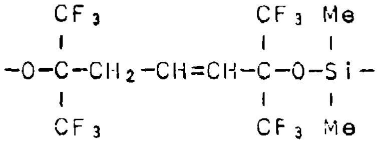
$$HO-R-OH + R'COO-\underset{|}{\overset{|}{Si}}-OOCR' \longrightarrow -O-R-O-\underset{|}{\overset{|}{Si}}- + R'COOH$$

3. Hexafluoroacetone-propylene-dimethylsiloxane polymer

The preparation of copolymers of dimethylsiloxane and the hexafluoroacetone-alkene adducts is complicated by cyclization:



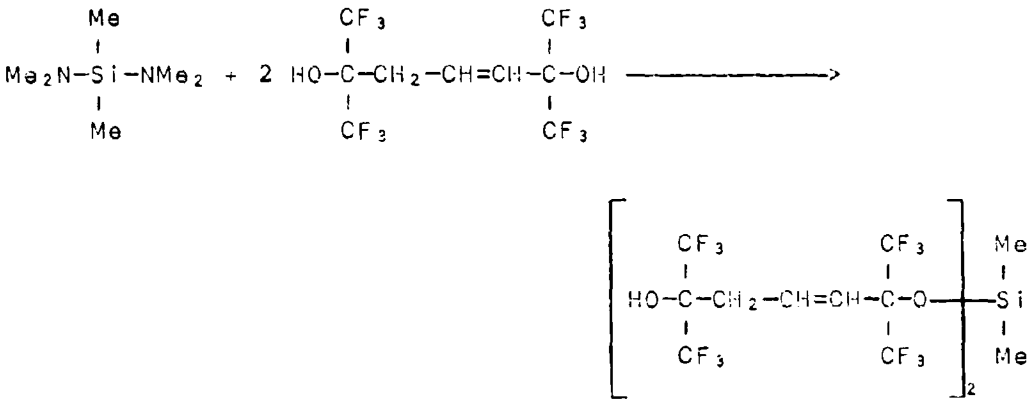
This type of cyclic compound was first identified as a result of attempts to make a hexafluoroacetone-isobutylene-dimethylsiloxane polymer.[1] If the polymer related to the above cyclic compound,



$$-\mathrm{O}-\underset{\mathrm{CF_3}}{\overset{\mathrm{CF_3}}{\mathrm{C}}}-\mathrm{CH_2}-\mathrm{CH}=\mathrm{CH}-\underset{\mathrm{CF_3}}{\overset{\mathrm{CF_3}}{\mathrm{C}}}-\mathrm{O}-\underset{\mathrm{Me}}{\overset{\mathrm{Me}}{\mathrm{Si}}}-$$

could be prepared, it would be expected to have a lower glass-transition temperature and be more resistant to solvents than the hexafluoroacetone-propylene-silphenylene polymer.

To avoid problems with cyclization, we prepared an intermediate diol by adding the diaminosilane in small increments to an excess of the hexafluoroacetone-propylene diol.



$$\mathrm{Me_2N}-\underset{\mathrm{Me}}{\overset{\mathrm{Me}}{\mathrm{Si}}}-\mathrm{NMe_2} + 2\ \mathrm{HO}-\underset{\mathrm{CF_3}}{\overset{\mathrm{CF_3}}{\mathrm{C}}}-\mathrm{CH_2}-\mathrm{CH}=\mathrm{CH}-\underset{\mathrm{CF_3}}{\overset{\mathrm{CF_3}}{\mathrm{C}}}-\mathrm{OH} \longrightarrow \left[\mathrm{HO}-\underset{\mathrm{CF_3}}{\overset{\mathrm{CF_3}}{\mathrm{C}}}-\mathrm{CH_2}-\mathrm{CH}=\mathrm{CH}-\underset{\mathrm{CF_3}}{\overset{\mathrm{CF_3}}{\mathrm{C}}}-\mathrm{O}-\right]_2 \underset{\mathrm{Me}}{\overset{\mathrm{Me}}{\mathrm{Si}}}$$

silylated adduct

The new silicon-containing diol was isolated by distillation at 92.5-94.0°C at 0.03 mmHg. Although treatment of the new diol with bis(dimethylamino)dimethylsilane resulted in polymerization, the crude polymer had an inherent viscosity of only 0.08 deciliters per gram measured at 30°C in tetrahydrofuran at a concentration of 1.0 g per deciliter. Evidently, polymerization was inhibited by salt formation between the acidic diol and the liberated amine as described above in Section II.A.2.

A second polymerization was attempted by the reaction of dimethyldichlorosilane with the disodium salt of the HFA-propylene adduct. The possibility of cyclization existed, but we expected some polymer to be formed along with the cyclic compound. A small amount of polymer with a very low inherent viscosity was formed. We will pursue this reaction further and will carry out the polymerization with the disodium salt of the silylated diol shown above.

4. Hydrolytic stability

The hydrolytic stability of C-O-Si bonds in the hexafluoroacetone-alkene-silphenylene or -dimethylsiloxane polymers has been a matter of continuing attention. The first polymer, made with isobutylene as the alkene moiety, withstood boiling in water without difficulty, but the polymer made with propylene was found to be unexpectedly sensitive to hot basic water on some occasions. According to viscosity measurements, neither the hexafluoroacetone-isobutylene-silphenylene nor the hexafluoroacetone-propylene-silphenylene polymer was hydrolyzed by boiling in 1% aqueous hydrochloric acid, and neither polymer was affected by standing for 6 days at room temperature in a solution of 1% sodium hydroxide (pH 13.4). The propylene polymer was degraded by boiling for 1 hour in 1% aqueous sodium hydroxide, but this treatment did not affect the isobutylene polymer. Preliminary experiments have indicated that the polymers containing the dimethylsiloxane units are more sensitive to hydrolysis than those containing silphenylene units. Fortunately, rain-erosion resistant coatings will not be used under conditions approaching the severity of boiling in 1% alkali, and the cured coatings should be much more resistant to hydrolysis than the uncured samples subjected to these tests.

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 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;[2] 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 has been reduced to 24 hours.

b. Disodium salt of the hexafluoroacetone-propylene adduct

The disodium salt of the hexafluoroacetone-propylene adduct was prepared by a method originated by Allied Chemical Corporation to make the sodium salt of perfluoro-*t*-butanol.[3] Sodium hydride, 6.72 g (0.140 mole) of a 50% suspension in mineral oil, was placed in a 200-ml, 3-neck, round-bottom flask equipped with a stirring bar, reflux condenser, dropping funnel, and thermometer. The sodium hydride was rinsed twice with 80-ml portions of anhydrous diethyl ether to remove the mineral oil. After the second rinse and decantation, 80 ml of ether was added to the reaction flask. The mixture was cooled to 0°C in an ice-salt bath. Hexafluoroacetone-propylene adduct, 26.18 g (0.070 mole), was added dropwise to the rapidly stirred suspension while the reaction temperature was maintained at 0-5°C. Evolution of hydrogen gas began immediately. The reaction mixture was heated

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[2] See References, page 22.

[3] See References, page 22.

at reflux for 30 minutes after the addition of adduct was complete. Part of the disodium salt was dissolved in the ether, and part remained as a pale gray solid, which was extracted with ether in a Soxhlett extractor. The original solution and the extract were combined and evaporated to dryness. The product, 5724-17, was a white powder, which weighed 17.8 g (61% yield) and melted with decomposition at 219-222°C. Undoubtedly, additional amounts of product could have been extracted with more effort.

Anal. Calculated for $C_9H_4F_{12}O_2Na_2$: C 25.86, H 0.96, F 54.53
Found: C 25.78, H 1.66, F 51.11

c. The silylated hexafluoroacetone-propylene adduct

Hexafluoroacetone-propylene adduct, 94.04 g (0.251 mole), was added to a 200-ml, round-bottom, 3-neck flask equipped with a condenser, magnetic stirrer, and thermometer. A serum cap covered one neck. Bis(dimethylamino)dimethylsilane, 9.12 g (0.062 mole), was added in 0.50-ml increments at 3- to 5-minute intervals through the serum cap by means of a hypodermic syringe. The temperature was increased to 110°C during the first hour of the 2-hour addition. After the addition was completed, the temperature was reduced to 95°C, and held there overnight. The reaction mixture was distilled at reduced pressure through a small Claisen head. The first fraction, which was largely the amine salt of the adduct, distilled at 62-74°C, at 2.7 mmHg. The fraction weighed 62.3 g. The second fraction distilled at 106-121°C at 1.2 mmHg and weighed 28.50 g (57% yield). The product, the silylated hexafluoroacetone-propylene adduct, was redistilled through a 3-in. Vigreux column. The portion that distilled at 103-4°C at 0.02 mmHg was submitted for analysis.

Anal. Calculated for $C_{20}H_6F_{24}O_4Si$: C 29.93, H 1.76, M.W. 804
Found: C 29.99, H 1.82, M.W. 786

d. 1,4-Bis(dimethylaminodimethylsilyl)benzene

1,4-Bis(dimethylaminodimethylsilyl)benzene was prepared by the method described earlier.[1]

e. Bis(dimethylamino)dimethylsilane

Bis(dimethylamino)dimethylsilane was prepared by the method described earlier.[1]

2. Preparation of polymers

a. Hexafluoroacetone-isobutylene-silphenylene polymer

The preparation of the hexafluoroacetone-isobutylene-silphenylene polymer was described earlier[1] and is repeated here.

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 additional 0.018-g portions 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 the flask had been cooled, 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 Å
$\bar{A}_w$ = 738 Å
$\bar{A}_w/\bar{A}_n$ = 2.65

---

* Determined by ArRo Laboratories, Joliet, Illinois.

b. Hexafluoroacetone-propylene-silphenylene polymer

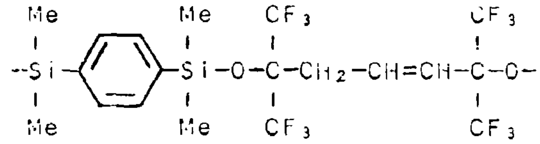
(1) Preparation

The hexafluoroacetone-propylene-silphenylene polymer was prepared by the method first described for the HFA-isobutylene-silphenylene polymer. The highest inherent viscosity obtained in any of the hexafluoroacetone-propylene-silphenylene polymers was 0.33 dl/g,* but this material was degraded by standing in the presence of the dimethylamine by-product. The large batch, 34 g, had an inherent viscosity of 0.20 dl/g when it was isolated.

(2) Physical properties

The solubility parameter of the hexafluoroacetone-propylene-silphenylene polymer was calculated by the method of Small.[4] The molar attraction constants of the various components, except for the trifluoromethyl group, were values given by Small. The values for trifluoromethyl were determined by plotting values given for trihalomethyl groups in the series, I, Br, and Cl, according to atomic number and extrapolating to obtain a value for trifluoromethyl groups.

The elastomer,



was separated into its components according to Table II. The molar attraction constants were combined according to the expression:

$$\delta = d\frac{\Sigma N_i G_i}{\bar{M}_n}$$

in which δ = solubility parameter in $cal^{1/2}/cc^{1/2}$

G_i = molar attraction constant of the individual component, i, of the repeating unit in $cal^{1/2}/cc^{1/2}$

N_i = number of times a component, i, occurs in the repeating unit

$\bar{M}_n$ = formula weight of the repeating unit in g/mole

d = density in g/cc

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4. See References, page 22.

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

For this elastomer, d = 1.25 g/cc and $\bar{M}_n$ = 564. Thus the solubility parameter calculated was 9.2 $cal^{1/2}/cc^{1/2}$.

Table II. Molar Attraction Constants of Polymer Components

Functional group	No. of groups in repeating unit, N_i	Molar attraction constant, G_i, $cal^{1/2}/cc^{1/2}$	N_iG_i
$-CH_3$	4	214	856
-Si-	2	-38	-76
	1	735	735
-O-	2	70	140
F (tripled $-CF_3$)	12	225	2700
$-\overset{\vert}{\underset{\vert}{C}}-$	6	-93	-558
-CH=	2	111	222
$-CH_2-$	1	133	133
			4152

ArRo Laboratories, Joliet, Illinois, performed the differential thermal analyses to determine the glass-transition temperature, -12°C, and they determined the molecular dimensions by gel-permeation chromatography. The results were as follows:

$\bar{A}_n$ = 604 Å
$\bar{A}_w$ = 1031 Å
$\bar{A}_w/\bar{A}_n$ = 1.71

c. <u>Hexafluoroacetone-propylene-dimethylsiloxane</u>

(1) <u>Via</u> diol-diaminosilane reaction

The hexafluoroacetone-propylene-dimethylsiloxane polymer was prepared from the silylated hexafluoroacetone-propylene adduct (Section II.B.1.c.) and bis(dimethylamino)dimethylsilane by the method described for the preparation of the hexafluoroacetone-isobutylene-silphenylene (Section II.B.2.a.).

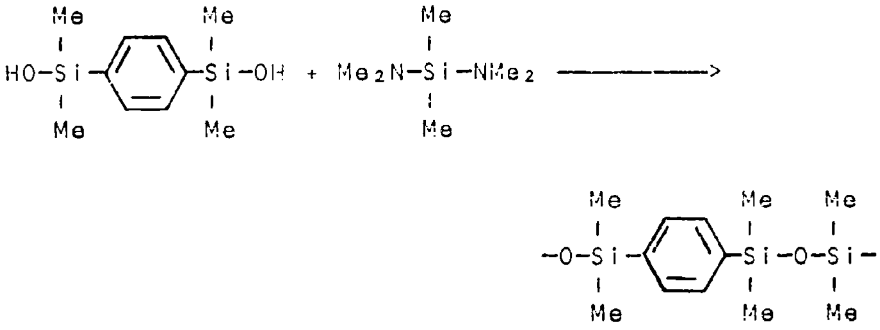
(2) Via disodium derivative of diol

The disodium salt of the hexafluoroacetone-propylene adduct (Section II.B.1.b.) was treated with dimethyldichlorosilane in the following manner: To 9.83 g (0.0233 mole) of the disodium salt of the diol dissolved in 50 ml of ether was added dropwise with stirring 3.03 g (0.0235 mole) of freshly distilled dimethyldichlorosilane. A white precipitate formed as soon as addition was started. The precipitate was filtered off and washed with ether to yield 2.3 g of white solid. (The theoretical amount of sodium chloride was 2.7 g.) The clear ether solution was evaporated to yield 7.8 g of an oily product. The theoretical yield of polymer or cyclic compound was 10.1 g. The oily product was heated to 160°C at 0.05 mmHg, and 2.6 g was distilled off. The inherent viscosity of the residue was 0.01 dl/g, which indicates a very low degree of polymerization.

III. SILPHENYLENE-DIMETHYLSILOXANE ELASTOMER

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.[5]



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

"silphenylene-dimethylsiloxane polymer"

The silphenylene-dimethylsiloxane elastomer can be cured at room temperature, and it is superior to room-temperature-vulcanizing silicone elastomers in tensile properties and sand-abrasion resistance as shown in Table III. The glass-transition temperature of the silphenylene-dimethylsiloxane elastomer is -60°C, but its fuel and solvent resistance, which are comparable with those of the RTV silicones, are below the desired level.

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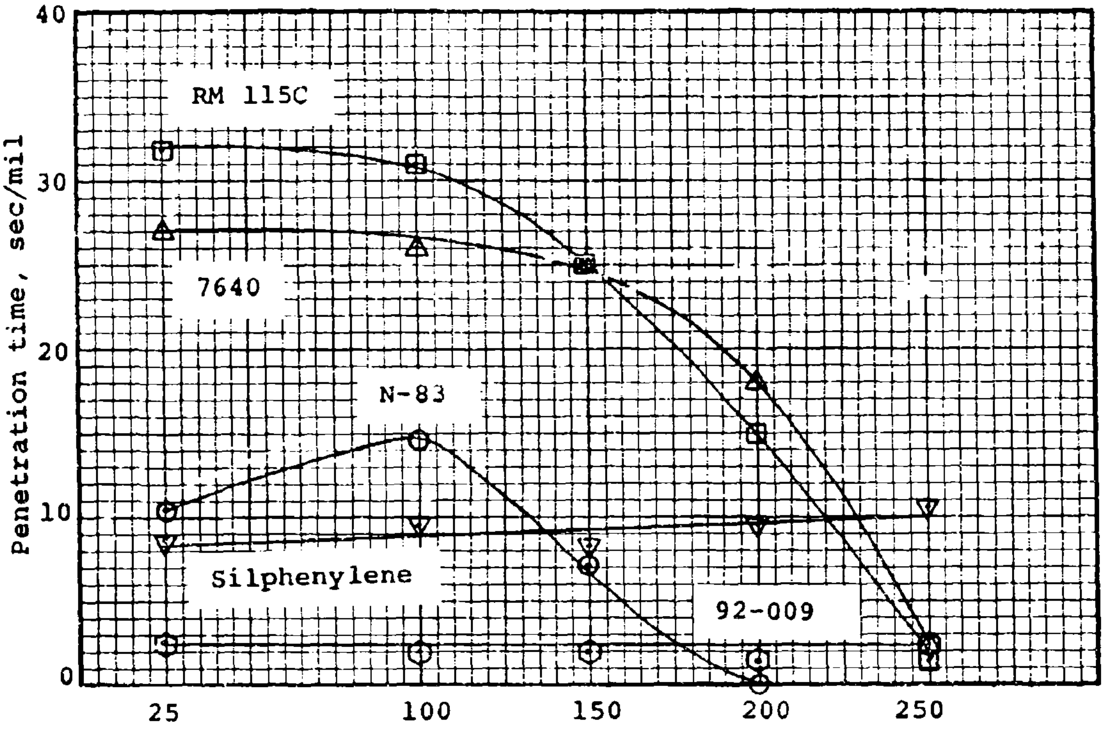
5. See References, page 22.

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

Elastomer	Penetration time, sec/mil, after 4 hours heating at				
	25°C	100°C	150°C	200°C	250°C
Neoprene N-83	10.6	14.8	7.2	0	0
Polyurethane 7640	27	26	25	18	2.3
Polyurethane RM115C	32	31	25	15	1.5
DC 92-009 (silicone)	2.5	2	2	1.4	2.3
5119-111-1 (silphenylene-dimethylsiloxane)	8.5	9.5	8.2	9.3	10.5

The silphenylene-dimethylsiloxane polymer has been reinforced with silica and cured with ethyl silicate and dibutyltin diacetate to form films with tensile strengths up to 1720 psi (nominal) and 600% elongation, which give a tensile product of 1,032,000. These high tensile values suggested trials of resistance to sand abrasion as described earlier.[1] More recently, a comparison was made with two polyurethane coatings given us by the Air Force (Polyurethanes 7640 and RM115C) and with a silicone spray coating (DC 92-009) suggested by the Dow Corning Corporation. The data, which are summarized in Table III and the figure, show the sand-abrasion resistances of a silicone, a silphenylene, a neoprene, and two polyurethanes after heating at temperatures up to 250°C for 4 hours. The silphenylene-dimethylsiloxane coating was superior to all of the others tried after they were heated at 250°C for 4 hours. Neither the silphenylene-dimethylsiloxane nor the silicone was affected appreciably by heating at any of the temperatures up to 250°C. The polyurethanes were affected by heating, but they were superior to the others after being heated 4 hours at temperatures up to and including 200°C. The neoprene N-83 lost its resistance at 150°C. The silphenylene-dimethylsiloxane coating cures at room temperature, and it can be sprayed on in layers about 2 mils thick with only 3 to 5 minutes between coats. We have no information on the requirements for application of the polyurethane coatings.

The results of sand abrasion suggested that the silphenylene elastomer should be evaluated in simulated rain erosion. To prepare samples, it was necessary to develop a method of applying the coating to airfoil substrates of the type used by the Air Force Materials Laboratory, who had agreed to perform the test. Because of the small amounts of polymer available, we used a "Paasche F 2-in-1 Air Brush". We milled silica and ethyl silicate



Sand-Abrasion Resistance of Elastomers After Being Heated for 4 Hours at Temperatures up to 250°C

□ Polyurethane RM115C
△ Polyurethane 7640
○ Neoprene N-83
▽ Silphenylene dimethylsiloxane 5119-111-1
⬡ Silicone DC 92-009

into a polymer and then dissolved it in toluene by shaking with glass beads. The catalyst, dibutyltin diacetate, was mixed in just before spraying. Trials of eight primers, which were evaluated by measuring the peel strengths of coated samples, revealed that General Electric SS-4044 performed the best of those tried. The data are in Table IV. Elastomer coatings were applied to a thickness of about 12 mils in six coats with 3 to 5 minutes between coats. The results of the rain-erosion tests have not been received.

Table IV. Evaluation of Primers

Primer	Peel or stripping strength,[a] lb/in.
None	1.5
Chemlock 607	3.4
Dow Corning 1200	3.8
Dow Corning 4094	1.7
Dow Corning Z6040	1.5
Dow Corning Z6075	2.1
General Electric SS-4044	>3.8[b]

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[a] Expressed in pounds per inch of width for separation at 6 in. per min.

[b] The peel strength exceeded the tensile strength and the film broke.

B. Experimental Details

1. Preparation of polymer

Poly[1,4-bis(oxydimethylsilyl)benzene dimethylsilane] was prepared as described earlier by the reaction of 1,4-bis(dimethylhydroxysilyl)benzene and bis(dimethylamino)dimethylsilane.[1]

2. Formation of coatings

a. Spraying technique

An elastomer formulation was prepared by milling the following on stainless steel rolls: silphenylene-dimethylsiloxane polymer, silica (Cab-O-Sil H-5, Cabot Corporation, 30% of the weight of the polymer), and ethyl silicate (ES 40, Union Carbide

Corporation, 15% of the weight of the polymer). The milled formulation was shaken with glass beads and 3.1 times its weight of toluene until solution was complete. Just prior to application, the solution was mixed with toluene to reduce the viscosity and a 10% solution of catalyst (dibutyltin diacetate) in toluene. The final formulation was a 21.4% solution of the elastomer ingredients in toluene. The composition of the elastomer ingredients was 66.8% silphenylene-dimethylsiloxane polymer, 20.2% Cab-O-Sil H-5, 10% ES 40, and 2.8% dibutyltin diacetate. The solution was sprayed with a "Paasche F 2-in-1 Air Brush" to form a 2-mil film, and the next coat was sprayed on after 3 to 5 minutes.

b. Primer evaluation

Six primers were evaluated by measuring the peel strengths of coatings applied to primed epoxy panels. Peel strengths were measured with a modification of ASTM Method D903 (Testing for Peel or Stripping Strength of Adhesives). The major modification was in the width of the sample; the scarcity of elastomer necessitated the use of 0.25-by-4-in. strips instead of 1-by-12-in. strips. The polyester glass-fiber laminate (Brunswick Corporation, Chicago) was sand blasted and cut into 0.75-by-4-in. strips. The primers were brushed onto the lower halves of the strips, and allowed to dry in air for 1 to 2 hours. Then the elastomer was sprayed to a thickness of 6 to 7 mils by the technique described in the preceding section. The films were allowed to cure overnight, and a straight-edge and razor were used to cut two adjacent 0.25-in. strips of cured elastomer. The elastomer on the unprimed area was peeled so it could be clamped in the lower jaws of the Instron Tester, while the upper edge of the panel was clamped in the upper jaws. Preliminary testing eliminated two primers, Dow Corning 1201 and A-4014, because they peeled so easily. The results, which are the averages of two values, are listed in Table IV.

3. Tensile properties of films

A 7-mil film of the silphenylene-dimethylsiloxane polymer formulated as described in the preceding section was sprayed onto an unprimed polyester laminate. After air curing for 2 days, the tensile properties were measured on the Instron tester. The nominal tensile strength of the film (5724-27-1) was 1925 psi, the elongation was 460%, and the ultimate tensile strength was 8850 psi (tensile product, 885,000).

4. Sand-erosion tests

A devic for producing a small, high-speed, airborne stream of an abrasive has been used as a preliminary method of evaluating the abrasion resistance of experimental polymers. The device ("Airdent", Model H) was built by S. S. White Dental Manufacturing Company as a dental drill, and it can be used to compare the abrasion resistances 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 were developed.

To use the "Airdent" the pressure of the carrier gas and the feed rate of the abrasive are adjusted so as to penetrate a film of Scotch Brand electrical tape (No. 33, 3M Company) in 30±2 seconds. Then the penetration times of the experimental films are measured alternatively 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 III and the figure.

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UNCLASSIFIED
Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)
Southern Research Institute
2000 Ninth Avenue South
Birmingham, Alabama 35205

2a. REPORT SECURITY CLASSIFICATION
Unclassified

2b. GROUP

3. REPORT TITLE

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

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)
Final Report - 15 April 1969 to 14 January 1970

5. AUTHOR(S) (First name, middle initial, last name)

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

6. REPORT DATE March 30, 1970	**7a. TOTAL NO. OF PAGES** 21	**7b. NO. OF REFS** 5

8a. CONTRACT OR GRANT NO.
N00019-69-C-0258

b. PROJECT NO.

c.

d.

9a. ORIGINATOR'S REPORT NUMBER(S)
10059-2258-V

9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)

10. DISTRIBUTION STATEMENT

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11. SUPPLEMENTARY NOTES

12. SPONSORING MILITARY ACTIVITY
Department of the Navy
Naval Air Systems Command
Washington, D. C.

13. ABSTRACT

~~This~~ research on development of a thermally stable, rain-erosion-resistant coating has involved, mainly, three types of polymers made from hexafluoroacetone, alkenes, and silicon-containing compounds. In addition, a silphenylene-dimethylsiloxane elastomer has been given a preliminary evaluation. The polymers based on hexafluoroacetone cure at room temperature to elastomers that have good resistance to heat and liquid fuels. More work is needed to increase molecular weights and improve tensile properties. The silphenylene-dimethylsiloxane elastomer was more resistant to sand abrasion than any high-temperature-resistant elastomer that could be cured at room temperature. Work is being continued under Contract N00019-70-C-0030 on the silicon-containing elastomers to improve their toughness and to find satisfactory methods of application.

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Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Rain-erosion-resistant coatings Hexafluoroacetone-alkene adduct Elastomers Thermally stable elastomers Fluorinated elastomers Silphenylene-siloxanes Silphenylene elastomers Hexafluoroacetone-alkene-sliphenylene polymer Hexafluoroacetone-alkene-dimethylsiloxane polymer						