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DEVELOPMENT OF POLYMERIC FUEL TANK SEALANTS FOR ADVANCED AEROSPACE VEHICLES

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16. ABSTRACT

This report describes the current in-house studies directed toward the development of a polymeric material capable of functioning as a fuel tank sealant in hypersonic aircraft. The preparation of a number of organic intermediates is outlined which encompasses a variety of systems including aryl-fluorinated compounds and aromatic polycyclic structures. Preliminary results indicate that incorporation of fluorine atoms into the basic polymer structure imparts a degree of aviation fuel resistance, a property which the sealant must of necessity possess. The rationale supporting the selected polymeric systems chosen for study and investigation is outlined in detail along with other pertinent factors involved in the selection of candidate materials. The Monsanto Research Corporation, Dayton, Ohio, under contract NAS8-21401 has been engaged in supplemental studies involving the development of thermally resistant polymers as fuel tank sealants. This program has been designated Task A and is an integral part of a three-phase contracted system designed to provide a workable polymeric sealant for hypersonic aircraft. The functions of Tasks B and C, under contracts NAS8-21399 and NAS8-21398 to Monsanto Research Corporation and Battelle Memorial Institute, Columbus, Ohio, respectively, are outlined within the body of this report.

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TABLE OF CONTENTS

TECHNICAL MEMORANDUM X- 53970

DEVELOPMENT OF POLYMERIC FUEL TANK SEALANTS FOR ADVANCED AEROSPACE VEHICLES

INTRODUCTION

The need for a new family of polymeric materials for sealant application in advanced aerospace structures has been emphasized by the marginal performance of commercially available fuel tank sealants in the presently configured supersonic transport aircraft. These sealants are required to function in thermo-oxidative environments up to 500°F in the presence of hydrocarbon fuels for periods equivalent to the service life of the aircraft, approximately 50,000 hours. Additionally, the sealant must not contribute to stress corrosion of titanium alloys, notably the 6Al-4V alloy, used in fuel tank construction.

For some time the development of improved polymeric sealant materials to meet the stringent requirements imposed by the SST has been the subject of an intensive study being conducted by this Center. The in-house program is now supported by three contracted investigations with the goal of the overall program being the development of improved thermally resistant sealant materials for use in the fuel tanks of advanced high speed aircraft. Task A, being carried out by Monsanto Research Corporation, Dayton, Ohio, under contract NAS8-21401, encompasses the development of new or improved thermally stable polymers which are suitable for processing into sealants in critical metal joints in fuel tanks on advanced aircraft.

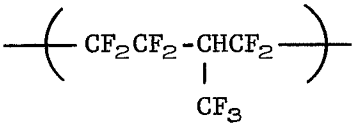
Task B, also under contract (NAS8-21398) to Monsanto Research Corporation, has as its objective the formulation, application, evaluation, and process engineering of new sealant materials. Additionally, a second objective of this task will be a definitive study of the enhancement of titanium stress corrosion susceptibility by highly fluorinated polymer systems. It is hoped that this study will determine unequivocally if fluorinated polymers, regardless of structure, inherently enhance this stress corrosion, or if the phenomenon is completely dependent on polymer structure or chemistry.

Task C, formerly under contract NAS8-21399 to Battelle Memorial Institute, Columbus, Ohio, has as its goal the combination of relevant theory and experimental data to provide a basis for predicting the performance of sealant materials during long duration service. A practical goal of this study will be to devise a meaningful short term test which will give rapid information indicating the relative and, preferably, the absolute performance of sealants over a much more protracted period.

Through the combined efforts of the in-house program and Tasks A, B, and C, it is anticipated that a series of polymeric materials will be developed which will function as fuel tank sealants in the hostile thermo-oxidative environment of the hypersonic aircraft now under development.

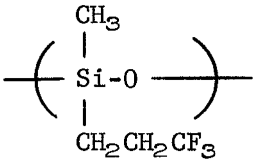
DISCUSSION

The basic requirement of minimum degradation of polymeric sealant materials in hydrocarbon fuels is most dramatically met by incorporation of fluorine, either along the polymer backbone or in pendant groups. Examples of this are the commercially available Viton fluorocarbon,



$$-\!\!\left(CF_2CF_2\text{-}\underset{\substack{|\\ CF_3}}{CH}CF_2 \right)\!\!-$$

and fluorosilicone

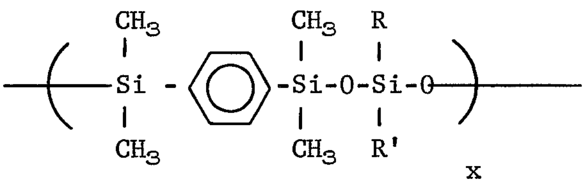


$$-\!\!\left(\underset{\substack{|\\ CH_2CH_2CF_3}}{\overset{\substack{CH_3\\ |}}{Si}}\text{-}O \right)\!\!-$$

both of which are currently under study as potential fuel tank sealants. However, inherent weaknesses are present in both materials. The Viton polymer has fluorine and hydrogen on adjacent carbon atoms, which would encourage the facile elimination of HF to promote stress corrosion of titanium alloys. While the HF elimination is not a proven mode of stress corrosion, the high stress corrosion tendencies of the Viton polymer are well documented.

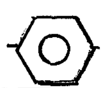
The fluorosilicone polymer has a similar structural deficiency but does not contribute to titanium stress corrosion nearly to the extent of Viton. A more serious shortcoming is the marginal thermal stability of this polymer at 500°F for extended periods.

An experimental aryl silicone polymer was under development in-house at the time of initiation of the sealant program. This polymer can be represented by the following formula,



where R and R' are normally methyl or phenyl, and is termed polysilphenylenesiloxane. Comparative weight loss measurements between the silphenylenesiloxane and silicone polymers following isothermal aging at 500 and 600°F predicted a higher thermal-oxidative stability for the former material, as depicted in the table below.

TABLE I. Isothermal Aging of Silphenylenesiloxane Polymers

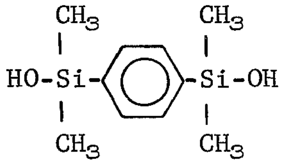
	Percent Weight Loss		
Temperature	Polymer 1 $R = R' = CH_3$	Polymer 2 $R = R' =$ 	Commercial RTV Silicone
500°F	5	2	7
600°F	15	8	18

These uncured polymers were aged in an air environment for 7 hours prior to measurement of weight loss. The basic silphenylsiloxane polymer is formed through a condensation polymerization of a disilanol with a diaminosilane such that both monomers can be synthesized to contain desirably structured, fluorine-containing groups.

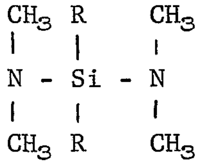
Thus, the current emphasis of the in-house sealant program has been the development of fluorinated silphenylenesiloxane polymers as candidate fuel tank sealants. This report describes the current status of the in-house sealant program, in which the predominant effort has been the preparation of suitable fluorine-containing intermediates for polymerization. Preliminary polymerization and cure studies are reported, as well as evaluation of the polymers as potential sealants.

Formation of Polymer Intermediates

The silphenylenesiloxane polymer is normally formed from a disilanol,

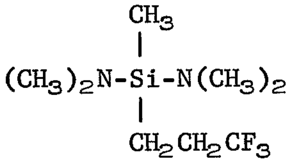


and a diaminosilane,



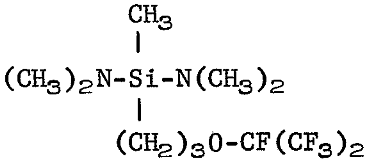
$$\begin{array}{ccccc} CH_3 & & R & & CH_3 \\ | & & | & & | \\ N & - & Si & - & N \\ | & & | & & | \\ CH_3 & & R & & CH_3 \end{array}$$

and both monomers can be modified to incorporate fluorination. The diaminosilane lends itself most readily to fluorine substitution through the R-groups. The intermediate is formed by dimethylamination of its precursor, the dichloride. At least two fluorine-containing dichlorosilanes, 3,3,3-trifluoropropylmethyldichlorosilane and 3-(heptafluoroisopropoxy)propyl methyldichlorosilane, were commercially available and provided a convenient starting point to assess the effect of various fluorine groups in the resulting polymer. Thus, the corresponding diaminosilanes, 3,3,3-trifluoropropylmethyl-bis(dimethylamino)silane (I) and 3-(heptafluoroisopropoxy)propylmethyl-bis(dimethylamino)silane (II) were readily prepared in high purity.



$$(CH_3)_2N\text{-}\overset{CH_3}{\underset{CH_2CH_2CF_3}{Si}}\text{-}N(CH_3)_2$$

(I)

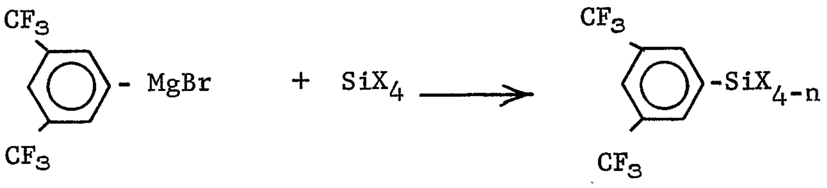


$$(CH_3)_2N\text{-}\overset{CH_3}{\underset{(CH_2)_3O\text{-}CF(CF_3)_2}{Si}}\text{-}N(CH_3)_2$$

(II)

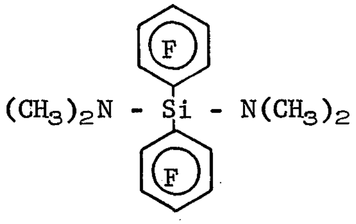
The utilization of these and other intermediates in polymer formation is discussed in a subsequent section.

The fluorination in the above intermediates, while not sufficient to stabilize the silphenylenesiloxane polymers toward hydrocarbon fuels, provided a reference point for assessment of experimental fluorinated intermediates. The first approach toward increased fluorination in a stable configuration involved the intermediate 3,5-di(trifluoromethyl)-phenylbromide. The Grignard reagent of this compound was prepared through exchange with ethylmagnesiumbromide (Ref. 1) and condensed with both tetrachlorosilane and tetraethoxysilane in an effort to prepare disubstituted silicon intermediates of the type $(R_f)_2SiX_2$. These products would be converted to the bis(dimethylamino)silane polymer precursors. Numerous condensations of the Grignard with $SiCl_4$ or $Si(OCH_2CH_3)_4$ invariably resulted in undesirably high degrees of substitution of the fluorinated moiety and the disubstitution product was formed in very low yield,



X = Cl, OCH_2CH_3; n = 1-4.

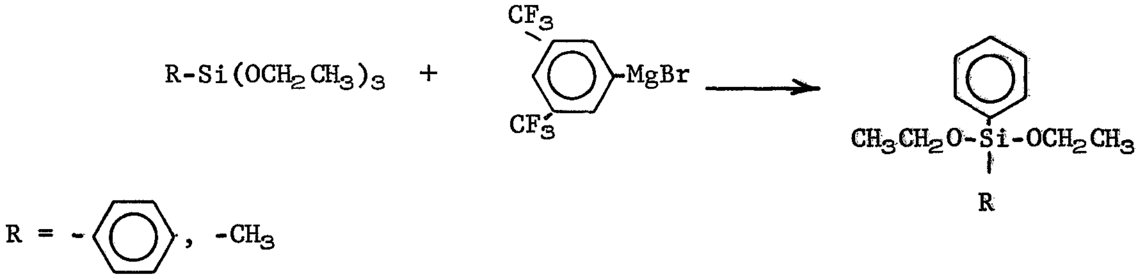
Fluorine apparently serves to enhance the reactivity of the mono- and disubstitution products so that they are more reactive toward the Grignard condensation than the unsubstituted compounds, driving the condensation process to tri- and tetra-substituted intermediates. This phenomenon was also observed by Whittingham et al. (Ref. 2) in similar condensations involving the pentafluorophenyl group. These workers were able to prepare bis(pentafluorophenyl)diethoxysilane (III) by a solvent addition method and convert it to bis(pentafluorophenyl)dichlorosilane (IV) by treatment with acetyl chloride. Compounds (III) and (IV) were prepared in this laboratory with the intention of converting the dichloride to the bis(dimethylamino)derivative, bis(pentafluorophenyl)-bis(dimethylamino)-silane (V).



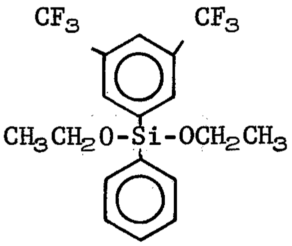
(V)

Compound (V) was prepared in very low yield with evidence of decomposition. The 3,5-di(trifluoromethyl)phenyl derivatives would not form under the conditions utilized for preparation of the pentafluorophenylethoxysilanes and this approach was discontinued.

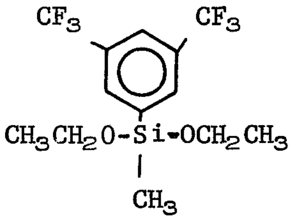
The apparent requirement to reduce the reactivity or functionality of the silicon intermediate during the Grignard condensation prompted several alternate approaches. The initial attempt involved reduction of functionality of the alkoyxsilane intermediate. Thus, methyltriethoxysilane and phenyltriethoxysilane were utilized in place of tetraethoxysilane in the Grignard condensation:



It was found in this case that the diethoxy derivatives could be formed in satisfactory yields with less tendency to proceed to higher degrees of substitution. In this fashion phenyl-3,5-di(trifluoromethylphenyl)-diethoxysilane (VI) and methyl-3,5-di(trifluoromethylphenyl)diethoxysilane (VII) were prepared.



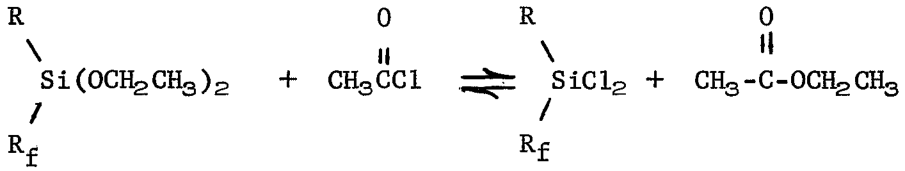
(VI)



(VII)

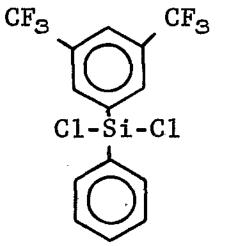
These condensations were found to be rather sluggish under tetrahydrofuran reflux conditions and required prolonged reflux to effect monosubstitution. An optimization study of the Grignard reagent for this reaction was also carried out. Direct preparation of the Grignard was carried out in tetrahydrofuran for comparison of the yield of Grignard prepared by the exchange method. Hydrolyses were carried out in dilute acid and the relative quantities of hydrolysis product were compared by gas chromatography. The exchange method resulted in 90-95% of the theoretical quantity of Grignard, whereas the direct method produced only 50-60% Grignard accompanied by formation of the coupling product, bis(3,5-di(trifluoromethyl)-biphenyl.

The conversion of compounds (VI) and (VII) to the dichlorides was carried out by the published procedure (Ref. 2) utilizing acetylchloride:

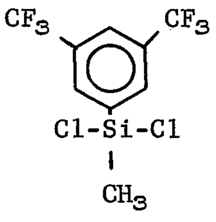


$$\overset{R}{\underset{R_f}{\diagdown\!\!\!\!\diagup}}\,Si(OCH_2CH_3)_2 + CH_3\overset{\overset{O}{\|}}{C}Cl \rightleftharpoons \overset{R}{\underset{R_f}{\diagdown\!\!\!\!\diagup}}\,SiCl_2 + CH_3\text{-}\overset{\overset{O}{\|}}{C}\text{-}OCH_2CH_3$$

This equilibrium reaction yielded phenyl-3,5-di(trifluoromethyl)phenyl-dichlorosilane (VIII) and methyl-3,5-di(trifluoromethyl)phenyldichlorosilane (IX).

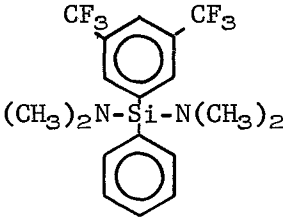


(VIII)

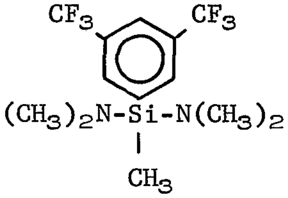


(IX)

The purification of these dichlorides proved quite difficult due to residual ethoxy-functional substituents, and purification by preparative gas chromatography was normally necessary to produce analytically pure samples. The dimethylamination of (VIII) and (IX) proceeded readily to provide the desired polymer precursors, phenyl-3,5-di(trifluoromethyl)-phenyl-bis(dimethylamino)silane (X) and methyl-3,5-di(trifluoromethyl)-phenyl-bis(dimethylamino)silane (XI).

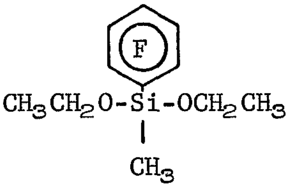


(X)



(XI)

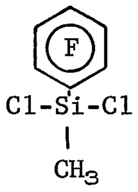
Additionally, the pentafluorophenyl derivative was prepared by this general procedure. Attempts to prepare this pentafluorophenyl-analog of compound (VII) by condensation of pentafluorophenylmagnesium-bromide with methyltriethoxysilane were unsuccessful when carried out at the tetrahydrofuran reflux temperature, as no salt formed as evidence of reaction. When methylchlorodiethoxysilane was substituted, the Grignard preferentially reacted with the chloride to form the desired product, methylpentafluorophenyldiethoxysilane (XII).



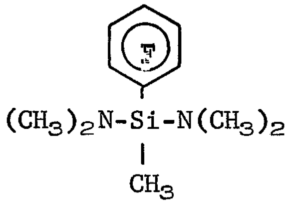
(XII)

The inconsistent reactivity of 3,5-di(trifluoromethyl)phenylmagnesium bromide versus pentafluorophenylmagnesium bromide when reacted with methyltriethoxysilane is not explainable at this time.

The diethoxy compound (XII) was converted in the previously described fashion to pentafluorophenylmethyldichlorosilane (XIII) and pentafluorophenyl-bis(dimethylamino)silane (XIV).



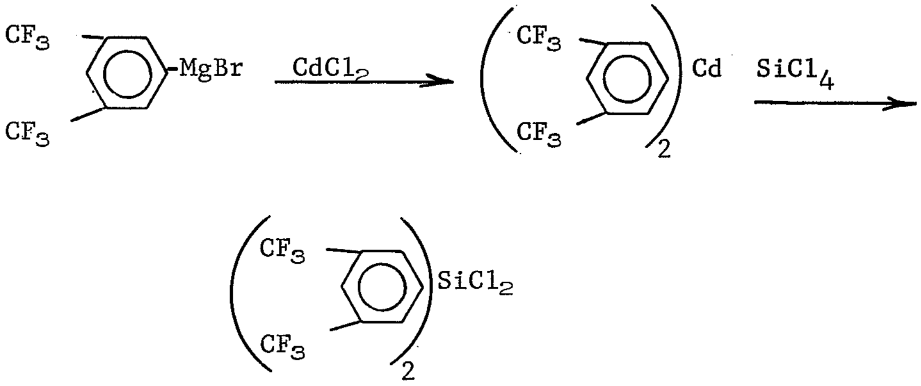
(XIII)



(XIV)

Numerous attempts were made to prepare compounds (XII, (XIII), and (XIV), in which the methyl group is replaced by the phenyl ring. However, these attempts were not successful.

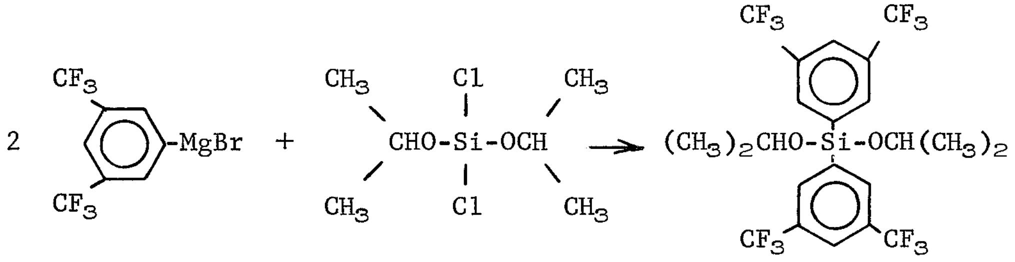
It was shown through preliminary fuel exposure tests (to be discussed in a later section) of polymers prepared from intermediates (X) and (XI) that increased fluorination was desirable to further reduce their swelling characteristics in fuels. One approach to the preparation of bis(fluoroaryl) derivatives involved substitution of a less reactive intermediate than the Grignard reagent for condensation with $SiCl_4$:



Reactive organometallic derivatives, such as Grignard reagents, yield the trialkylphosphine when treated with phosphorus trichloride; no mono- or di-substituted products are obtained. Fox (Ref. 3) reported the synthesis of alkyldichlorophosphines through treatment of phosphorus trichloride with the less reactive organo-cadmium derivatives. Although the addition of PCl_3 to the organocadmium derivative yields a mixture of mono-, di-, and tri-substituted products, reverse addition, i.e., the addition of the cadmium compound to an excess of phosphorus trichloride, gave little evidence of reaction with more than one halogen atom. In view of the similarity between PCl_3 and $SiCl_4$, and through adjustment of the stoichiometry of the reactants, it seemed logical to assume that reaction of the organo-cadmium derivative with silicon tetrachloride would lead to the desired di-substituted derivative. Essentially, the reaction consists of three steps: preparation of the appropriate Grignard reagent, conversion to the corresponding organo-cadmium compound, and reaction of the cadmium derivative with silicon tetrachloride at -20°C (while no systematic study to determine the optimum conditions for the reaction was carried out, Fox determined that the best yields of the dichlorophosphines were obtained by the addition of the dialkylcadmium to the phosphorus trichloride at a rate consistent with the maintenance of reaction temperature in the vicinity of this temperature).

Unfortunately, it was found through a number of experiments that even when the fluorinated organo-cadmium derivative was added to a large excess of $SiCl_4$ at sub-zero temperatures, multiple substitution on the silicon atom occurred yielding a mixture of di- and tri-aryl silanes. This mixture could not be separated when subjected to fractional distillation *in vacuo* through a 15-inch packed column. It can only be surmised that the enhanced reactivity of the organo-cadmium derivative through the presence of the fluorine atoms was responsible for the observed results.

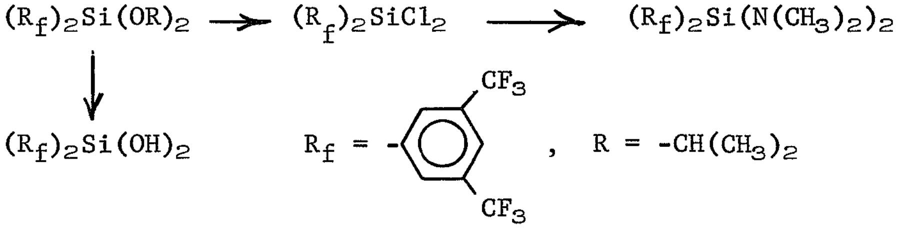
An alternate approach to this synthesis involved blocking 2 of the 4 available chlorines in $SiCl_4$ by substituting sterically hindered, less reactive groups. The intermediate, diisopropoxydichlorosilane (Ref. 4), was prepared for this purpose and the following condensation was effected:



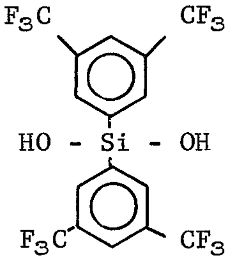
(XV)

In this manner the desired product, bis(3,5-di(trifluoromethyl)-phenyldiisopropoxysilane (XV), was prepared in 35% yield. The isopropoxy group contributed sufficient steric hinderance that the substitution on silicon was limited to 2. The drastic reduction in reactivity of the isopropoxy group compared to the ethoxy group was evidenced by the fact that prolonged reflux at 135°C could be maintained without significant formation of higher substitution products. The steric properties of the isopropoxy group apparently accounted for the low yield of product. It is anticipated that diisobutoxydichlorosilane, having the isopropyl radical on the beta-carbon, would provide a better combination of steric hinderance and reactivity when condensed with the Grignard reagent.

The utility of compound (XV) in providing two possible routes to the silphenylenesiloxane polymer is demonstrated in the reaction sequence below:

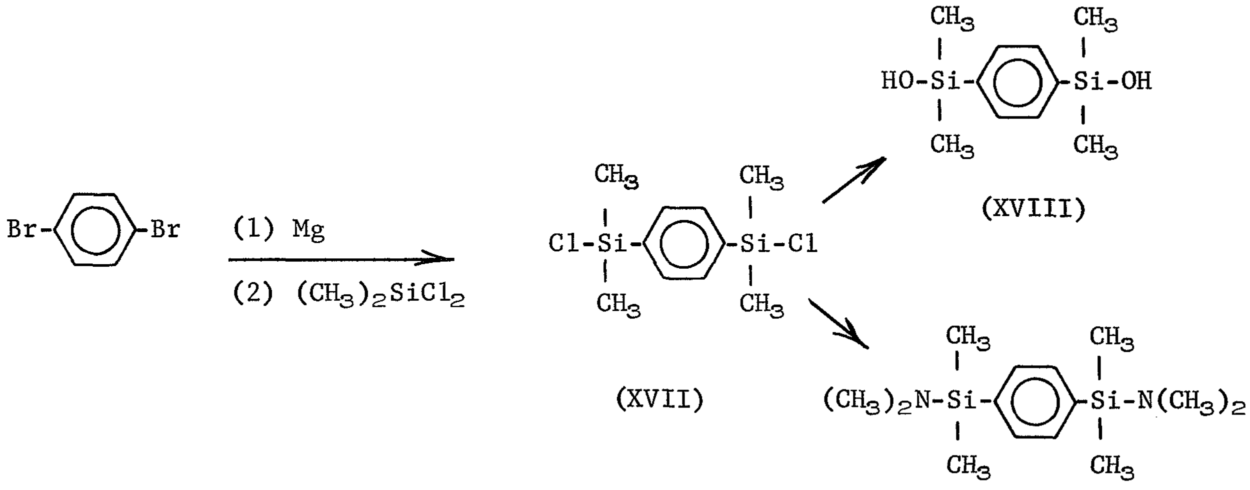


This compound (XV) is being considered as a precursor both for diaminosilane and disilanol monomers. Treatment of (XV) with acetyl chloride was carried out stepwise with the isopropyl acetate removed after each treatment. The reaction could be driven essentially to completion in this fashion. As in the case of the ethoxy derivatives, however, the residual isopropoxy and chloro derivatives have been extremely difficult to separate by conventional distillation. The hydrolysis of (XV) appears a more straight forward approach and has been studied in some detail. In order to establish the general conditions for hydrolysis of (XV) its nonfluorinated counterpart, diphenyldiisopropoxysilane, was prepared and successfully hydrolyzed to diphenyldihydroxysilane in high yield by treatment with methanolic sodium hydroxide solution followed by precipitation from a potassium dihydrogenphosphate solution (Ref. 5). Compound (XV) was hydrolyzed by this procedure and the resultant oil had the expected infrared spectrum for a disilanol. A modification of the above hydrolysis resulted in precipitation of a white solid tentatively characterized as the desired diol, bis(3,5-di(trifluoromethyl)-phenyl)dihydroxysilane (XVI).



(XVI)

This diol is to be polymerized with a bis(aminosilane) incorporating the silphenylene moiety. The preparation of the silphenylene intermediate is outlined below:



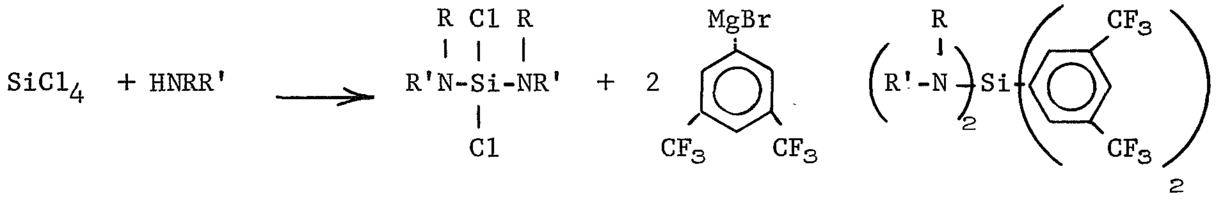
(XVII)

(XVIII)

(XIX)

The diol, 1,4-bis(hydroxydimethylsilyl)benzene (XVIII) is the basic monomer utilized with the fluorinated bis(aminosilane) described earlier. Its preparation has been studied in detail and can be obtained in high purity by this procedure (Ref. 6). Conversely, if fluorination is incorporated into the diol rather than the bis(aminosilane) as in the case of compound (XVI), then the silphenylene moiety can be incorporated into a bis(aminosilane), 1,4-bis(dimethylaminodimethylsilyl)-benzene (XIX). This compound is readily prepared from the dichloride and can be fractionated to an acceptable purity for polymerization.

As an alternate approach to limiting the reactivity of the silicon intermediate, it was envisioned that use of a hindered amine in the reaction with silicon tetrachloride might lead to the formation of a disubstituted derivative which could be subsequently allowed to condense with a fluorinated Grignard reagent;



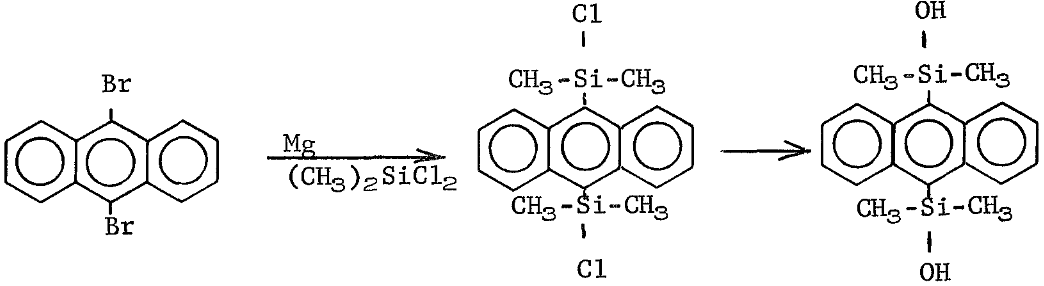
The product of these reactions would be a derivative which would lend itself to direct reaction with a silane diol to eliminate amine and form the desired fluorinated polysilphenylenesiloxane.

The use of hindered amines to limit the degree of substitution on a particular chlorinated atom is not novel. In their work with tetrameric phosphonitrilic chlorides, John et al. (Ref. 7) prepared tetra-substituted derivatives employing N-methylaniline in moderate yield the substitution being entirely non-geminal as substantiated through $^{31}P_{nmr}$ spectra. Later, Berlin et al. (Ref. 8) prepared 2,4,6,8-tetrachloro-2,4,6,8-tetramethylcyclohexylaminotetraphosphazine in quantitative yield employing N-methylcyclohexylamine, and showed through n.m.r. studies that the derivative was non-geminally substituted.

In these studies, the reaction between stochiometric amounts of silicon tetrachloride and N-methylcyclohexylamine gave rise to the formation of a disubstituted derivative* in excellent yield. Characterization was made through both chemical and spectral data. However, subsequent reactions of the disilazane with appropriate fluorinated Grignard reagents gave rise to either intractable or unstable compounds, or to no reaction at all occurring. Consequently, this approach was abandoned in favor of more promising routes to the desired intermediates.

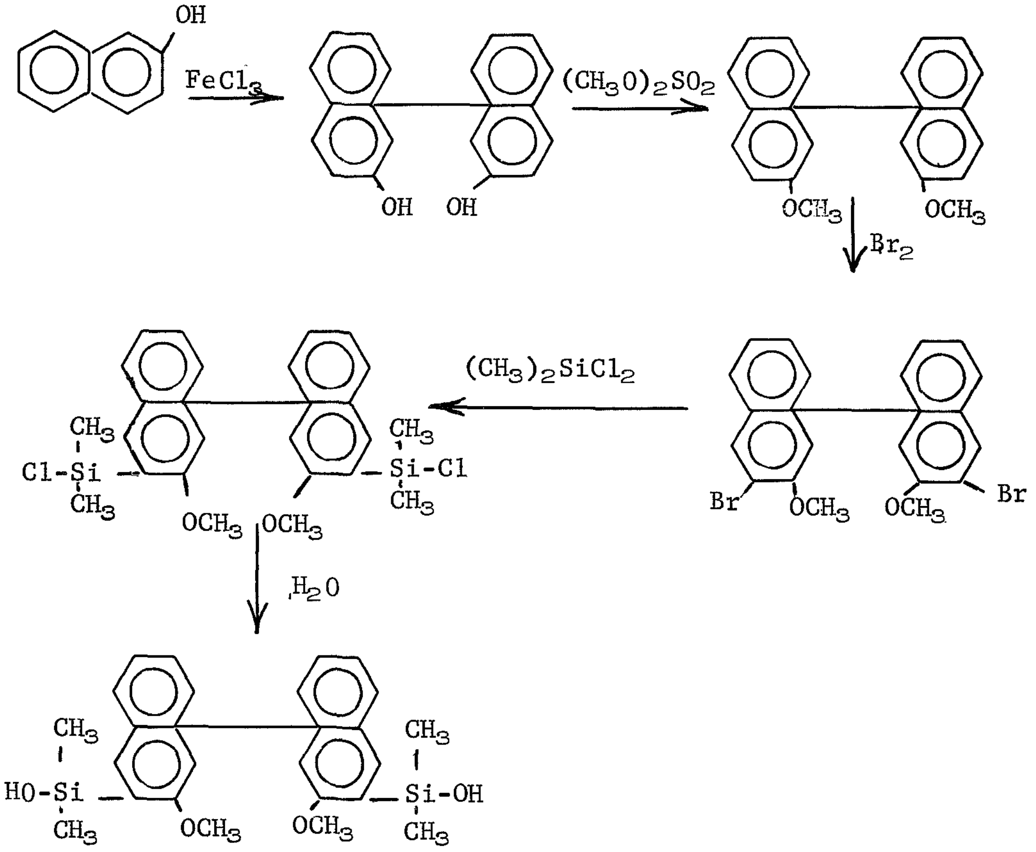
Several additional approaches were investigated to incorporate increased fuel resistance into the disilanol moiety. A series of disilanols has been studied which had increased aromatic content.

A representative difunctional monomer of this class of compounds is the product arising from the reaction of 9, 10-dibromoanthracene with a mixture of magnesium and dimethyldichlorosilane in THF solvent followed by hydrolysis:



In this type of reaction, it was found that attempting to preform the di-Grignard reagent for subsequent reaction with the dichlorosilane was not feasible. In a number of reactions it was impossible to effect reaction between the magnesium and the 9, 10-dibromoanthracene in THF. However, when the latter compound was added portionwise (neat) to a mixture of the magnesium and dichlorosilane containing a crystal of iodine, a self-sustaining exothermic reaction ensued which lasted throughout the addition of the aromatic compound. When addition was complete, a clear homogeneous solution was obtained from which MgBrCl separated upon cooling to room temperature. The crude product isolated from the solution proved difficult to purify and was therefore used as-is in the hydrolysis step. At the time of this writing, the recrystallization of the crude product (brown solid) is being studied, and the purified product will be characterized through both chemical and spectral analyses.

In a related effort, β -naphthol was used as the starting material in a series of reactions designed to give a silane diol capable of acting as a monomer in polymerization reactions:

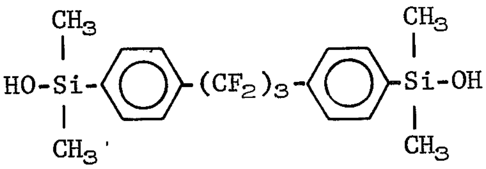


The reactions were successfully carried out up to the point of the preparation of the dichloro derivative. From this reaction was isolated an oily product which could not be induced to crystallize and which decomposed upon attempted distillation at very low pressure. This approach has not been entirely abandoned and will be re-examined sometime in the near future.

An alternate approach to the fluorinated diols has been incorporation of perfluoroalkyl segments. The basis for this work was performed by McLoughlin et al. (Ref. 9) in which they prepared diarylhexafluoropropanes by a coupling reaction of 1,3-diiodohexafluoropropane and an aromatic halide in an aprotic solvent in the presence of activated copper (Ref. 10). The ease of displacement of halogen from the aromatic halide is I Br Cl, and this differential reactivity has been utilized to form the precursor of the desired fluorinated disilanol. Thus, the coupling reaction between p-bromoiodobenzene and 1,3-diiodohexafluoropropane was carried out under carefully controlled conditions to avoid coupling the bromide and resulted in the desired 1,3-bis(p-bromophenyl)-hexafluoropropane (XX):

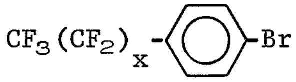
(XX)

The diodide for this reaction was prepared by the method of Krespan (Ref. 11). Compound (XX) has been prepared in 40-50% yield. Current efforts have been directed toward preparation of the analogous disilanol depicted below:



by (1) preparation of the di-Grignard reagent of compound (XX), (2) condensation with ethoxychlorodimethylsilane, and (3) hydrolysis of the diethoxy condensation product to the desired disilanol. Preliminary experiments have indicated that compound (XIX) forms the di-Grignard reagent in a normal fashion.

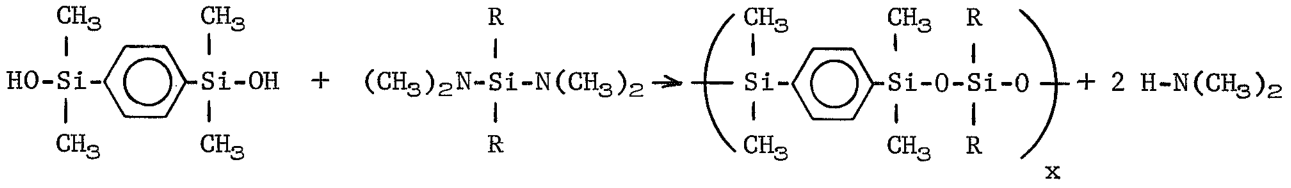
As an extension of this coupling reaction, fluorinated aromatic halides of the type



have been prepared in 50-55% yield by reaction of perfluoropropyl iodide with p-iodobromobenzene. Since the perfluoroalkyl chain length can be increased as desired, this offers a convenient method for incorporating additional fluorination into the polymer. The preparative sequences discussed earlier for the 3,5-di(trifluoromethyl)phenyl derivatives should hold for this intermediate also.

Silphenylenesiloxane Polymer Formation

The basic polymerization reaction for the formation of this type polymer is depicted below:



This is a condensation polymerization which generates dimethylamine as a result of nucleophilic displacement at the silicon site. The polymer illustrated above in which the R-groups are methyl or phenyl can be prepared in relatively high weight average molecular weights up to 500,000-600,000, estimated from viscosity values. The polymerizations are carried out in toluene at 95-100°C. The reaction becomes noticeably exothermic at 50-60°C with a large evolution of dimethylamine. This rapid volatization of the amine tends to remove some of the bis(dimethylamino)silane monomer leading to an imbalance in the monomer stoichiometry. Also, the aminosilane monomer is very moisture sensitive and an initial weighing of this reactant to the correct stoichiometry would invariably result in some hydrolysis. Thus, a syringe addition method has been utilized in which the required amount of disilanol and 93-95% of the required amount of bis(dimethylamino)silane are combined initially.

Then the remaining quantity of the aminosilane plus a 5 percent excess are added to a syringe for subsequent addition after the initial exotherm subsides. The incremental addition of the remaining monomer can be adjusted to control the molecular weight of the growing polymer chain. It is desirable to limit the weight average molecular weight ($\bar{M}_w$) to 75,000-100,000 to facilitate curing or crosslinking. This represents the best compromise between mechanical properties and cure characteristics. The increasing $\bar{M}_w$ can be estimated conveniently by measuring inherent viscosity of the polymer following the incremental additions of aminosilane. The desired $\bar{M}_w$ range corresponds to an inherent viscosity of 0.4-0.5, measured in tetrahydrofuran at 30°C. The polymers produced by this method are normally refluxed in toluene in the presence of water to convert any residual dimethylaminosilane to silanol. This procedure removes the hydrolytically unstable groups from the polymer and provides an effective silanol end group concentration for crosslinking purposes.

The fluorinated aminosilane intermediates discussed earlier are generally adaptable to this procedure. The purity of these intermediates had to be at least 99% to attain high molecular weight polymers. Polymers of varying molecular weights were obtained from the fluorinated intermediates as summarized in Table II:

TABLE II. Fluorinated Silphenylenesiloxane Polymers

Polymer	Disilanol	Aminosilane	Inherent Viscosity (η_{inh})*	Aminosilane Purity %
1	XII	I	0.873	99
2	XII	II	0.246	98.5
3	XII	VIII	0.029	--
4	XII	IX	0.09	95
5	XII	XIV	0.11	-

* Measured in tetrahydrofuran at 30°C, 1.0 gram/deciliter.

The dependence of the molecular weight of these polymers on monomer purity is evidenced by the above table. In the case of polymers 3, 4, and 5, the molecular weight problem is further aggravated by the preparative method common to these respective monomers, which very likely results in formation of monofunctional aminosilane as one of the impurities.

This constituent would act very effectively as a chain terminating agent to limit the molecular weight.

In an effort to assess the inductive effect of the fluorine substituents on the aminosilane-silanol polymerization, a comparative study was carried out utilizing phenylmethyl-bis(dimethylamino)silane and 3,5-di(trifluoromethyl)phenylmethyl-bis(dimethylamino)silane in which the dimethylamine condensation product was monitored as a function of polymerization time. For this purpose, a constant purge of dry nitrogen was swept through the polymerization vessel. The diol, 1,4-bis(dimethylhydroxysilyl)benzene (XII), was allowed to dissolve in 100 ml. of dry toluene at 95 ± 1°C and the appropriate bis(aminosilane) was added. The polymerization flask was fitted with tubing terminating in a gas dispersion tube which extended to the bottom of a flask containing 500 ml. of an H_2SO_4 solution of known normality. The solution was stirred constantly and maintained at 0-2°C. As the polymerization progressed, 5 ml. aliquots were removed and titrated to a methyl red endpoint with standard base. The change in normality of the acid solution with time was proportional to the moles of dimethylamine absorbed. The rates of polymerization involving the nonfluorinated and fluorinated aminosilanes are depicted on the graph below.

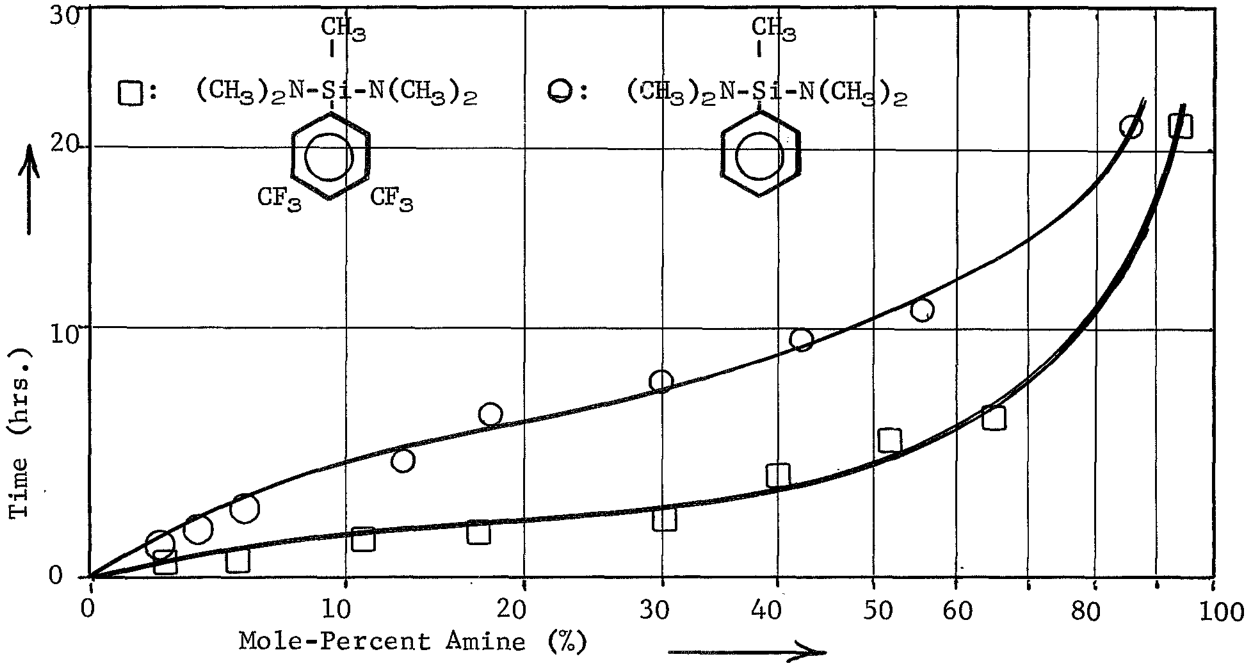


FIGURE 1. Polymerization Rates of Aminosilanes

The initial results of this study indicate a more efficient polymerization involving the fluorinated aminosilane. This seems logical since the inductive effect of the fluorine atoms results in a more effective positive charge on the silicon atom of the aminosilane which is the site of the nucleophilic displacement. However, this contradicts the previous notion that the formation of lower molecular weight polymers from the fluorinated monomers resulted in part from the deactivating influence of the fluorine atoms. Thus, the problem of attaining low molecular weights seems to be predominantly monomer impurity.

Polymer Curing and Processing

The basic curing or crosslinking method for the silphenylenesiloxane polymer utilizes an alkoyxsilane crosslinking agent and a metal salt catalyst. Normally, tetraethoxysilane or its partially hydrolyzed counterparts together with dibutyltindiacetate will effect a room temperature conversion of the linear polymer to a thermoset product, although the crosslinking process appears to depend on the availability of the silanol endgroups on the polymer. The rate of cure is quite dependent on polymer molecular weight which controls the silanol group concentration. One polymer in which the residual silanol groups were removed by treatment with N,N-bis(trimethylsilyl)acetamide failed to give any evidence of cure under standard curing conditions. It seems at first that the silanol group participates in a straight forward condensation reaction with the alkoxysilane group of the curing agent to provide the crosslink sites. However, the methyl-substituted polymers represented by the desirable inherent viscosity range of 0.4-0.6 have reasonably high molecular weights as shown on the figure below.

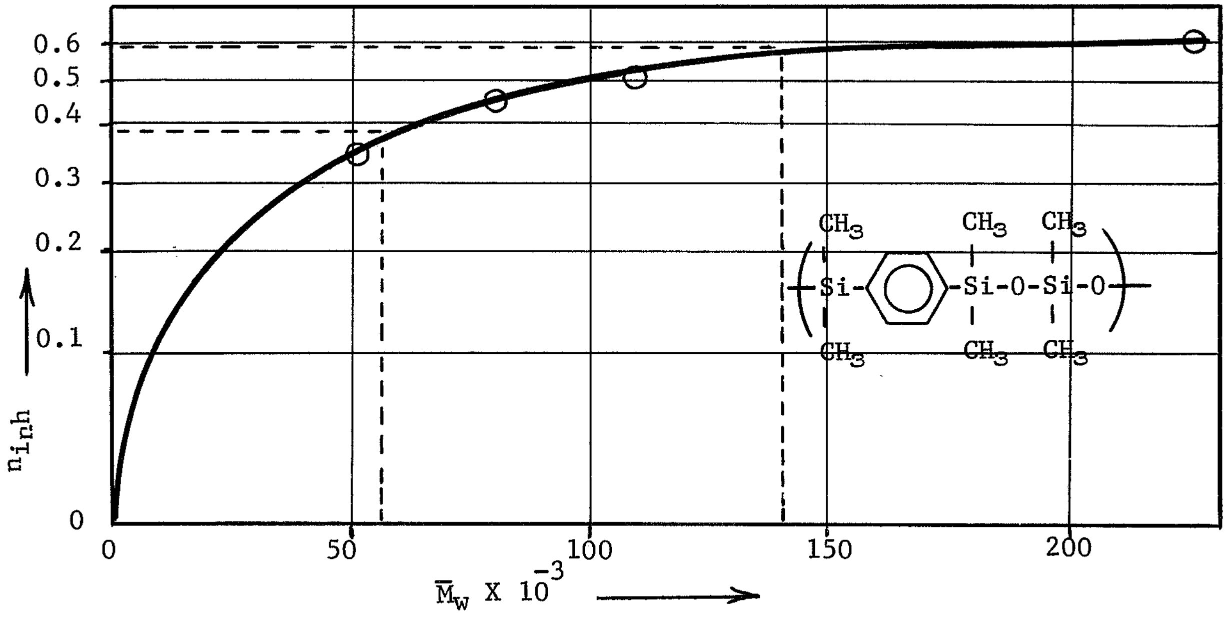


FIGURE 2. Optimum Molecular Weight Range for Cure Processes

Thus the silanol group concentration in this range would be quite low, yet the crosslinking process proceeds readily. Since the ethoxysilane crosslinking agent must be used in quantities of 10% by weight of the polymer for effective curing, the effect of the silanol end group must be catalytic to some extent. A more plausible speculation for the crosslinking process is generation of a nucleophilic species by the metal salt catalyst which can initiate cleavage of the siloxane chains and result in crosslinking at these sites.

A detailed study has been made of the curing characteristics of the methyl and phenyl substituted silphenylenesiloxane polymers by this method. The optimum concentrations of tetraethoxysilane hydrolyzate (ES-40) and dibutlytindiacetate (DBTDA) were found to be 10/2 and 20/10 for the methyl and phenyl substituted polymers, respectively. These values represent weight percent based on the weight of polymer. The fluorinated polymers were generally cured using the optimum curing ratios determined for their nonfluorinated counterparts. The efficiency of the crosslinking process is dependent both on the functionality of the alkoxide and the type of metal salt. Phenyltriethoxysilane and 1,4-bis(methyldiethoxysilyl)benzene (Ref. 12) effected complete cures of the polymers but more sluggishly than the more highly functional ES-40. The rate of cure could be greatly increased by substituting lead octoate for DBTDA.

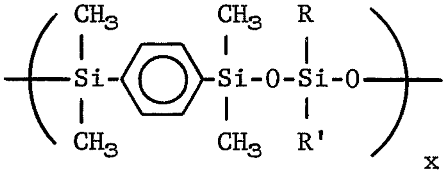
The rate of cure of these polymers varied widely with the substituent groups along the polymer backbone. The methyl-substituted polymer gelled quickly, whereas pendant fluorination as well as phenyl substituents increased the gell time. An absolute assignment of cure reactivity of the various polymers cannot be made at this point, as the polymers vary in molecular weight and the cure process is quite dependent on this parameter.

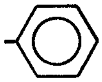
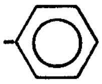
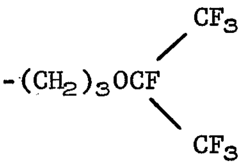
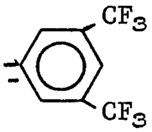
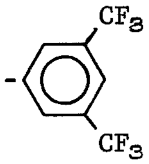
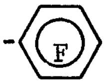
Elastomers were prepared from a series of silphenylenesiloxane polymers by casting them as toluene solutions containing the appropriate concentrations of curative. The solutions were allowed to air dry at room temperature for at least three days to obtain tack-free elastomers. The elastomers prepared to date are summarized in Table III.

The poor mechanical properties of the fluorinated elastomers obtained to date are largely attributable to low molecular weight of the linear polymers. The purity of polymer precursors is a limiting factor, and efforts are currently underway to overcome purification problems.

The processing characteristics of the methyl-substituted silphenylenesiloxane polymer are such that it lends itself to application to metal substrates as a solvent-free catalyzed mix. However, the polymers with fluorinated phenyl groups are necessary for increased thermal stability and fuel resistance. Introduction of these aromatic groups along the polymer chain results in a non-flowing linear polymer which

TABLE III. Cured Silphenylenesiloxane Elastomers



	R	R'	ES-40*	DBTA*	Elastomer Appearance
(1)	$-CH_3$	$-CH_3$	10	2	Flexible, tough elastomer
(2)			20	10	Stiff elastomer
(3)	$-CH_3$	$-CH_2CH_2CF_3$	10	2	Flexible elastomer
(4)	$-CH_3$	 $-(CH_2)_3OCF(CF_3)_2$	10	2	Weak elastomer
(5)	$-CH_3$		15	5	Weak elastomer
(6)	-		20	10	Weak elastomer
(7)	$-CH_3$		10	2.5	Cheesy elastomer

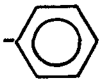
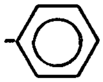
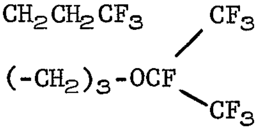
* Weight percent based on weight of polymer.

cannot be readily applied as a solvent-free system. This polymer can be mixed with the alkoxysilane curative while as a solution in toluene, after which the toluene is removed. The curative has the effect of a diluent, reducing the viscosity of the polymer to a workable, applicable consistency. Crosslinking does not occur until the metal salt catalyst is added. The mechanical strength of the silphenylenesiloxane polymer is readily increased by incorporation of reinforcing fillers such as Cab-O-Sil.

Sealant Evaluation Studies

While the polymers prepared to date do not reflect optimum mechanical properties, a preliminary evaluation has been carried out to serve as a basis for further development. The mechanical properties of various silphenylenesiloxane polymers have been determined by pressing sheets of the filled formulations between metal plates separated by 1/16-inch shims. Microtensile specimens were then cut from the cured elastomers. Cab-O-Sil, 30% by weight, was used as the reinforcing filler. Elastomers (1), (3), and (4) from Table III were prepared in this manner. Elastomer (3) was unfilled as its viscosity increased prohibitively at the required filler levels. The remaining elastomers have not been prepared in sufficient quantity to date to allow this evaluation. Table IV describes the tensile properties of potential sealant polymers measured at room temperature.

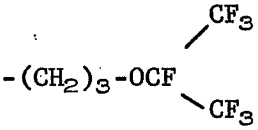
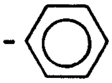
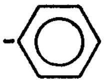
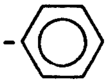
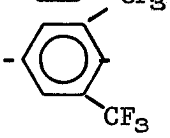
TABLE IV. Tensile Properties of Sealant Materials

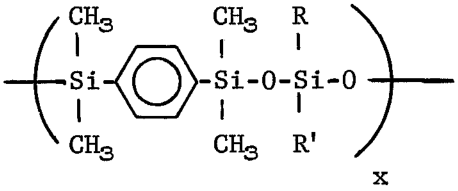
	Experimental Polymers	Elongation(%)	Ultimate Tensile (psi)
(1)	R = $-CH_3$, R' = $-CH_3$	480	9150
(2)	R = , R' = 	530	4550
(3)	R = CH_3, R' = $-CH_2CH_2CF_3$	230	2025
(4)	R = $-CH_3$, R' =  $(-CH_2)_3-OCF(CF_3)_2$	185	842
	Commercial Polymers		
(1)	Viton C-10 fluorocarbon	650	1240
(2)	77-028 Fluorosilicone	170	558

The commercial fluorocarbon and fluorosilicone formulations in Table IV represent the most promising state-of-the-art sealants being studied by Monsanto Research Corporation, who performed the tensile measurements on the two materials (Ref. 13).

A study was carried out to assess the effect of various fluorinated pendant groups on the swelling characteristics of the cured silphenylene-siloxane sealant materials. Unfilled films of each elastomer were prepared and specimens of 1 square inch in area were soaked in JP-4 hydrocarbon fuel (containing 10-12% aromatic moieties) at room temperature for 24 hours. The percent change in area was determined as an index of the swelling characteristics.

TABLE V. Sealant Swelling Tests in Hydrocarbon Fuel

Polymer	R	R'	Area Change, %
1	$-CH_3$	$-CH_3$	164
2	$-CH_3$		66
3			42
4			13



The fluorinated aromatic moieties contribute significantly toward stabilization of the sealant against swelling. This evaluation supports the studies discussed in the section on intermediates, which were directed toward fluoroaryl substituents in the R and R' positions on the polymer.

EXPERIMENTAL

The starting silicon- and fluorine-containing compounds were obtained from Peninsular ChemResearch, Gainesville, Florida, or Pierce Chemical Company, Rockford, Illinois, and were used without further purification. The infrared spectra were obtained from smears or solutions in CCl_4 and recorded in the 25-15.0 μ region with a Perkin-Elmer model 137 double beam spectrophotomer equipped with sodium chloride optics. Purity of the intermediates was determined by gas-liquid phase chromotography. Molecular weights were determined at 55°C in toluene with a Hitachi Perkin-Elmer model 115 molecular weight apparatus. Mass spectra were obtained from a CEC model 21-104 mass spectrometer.

Preparation of (3,3,3-Trifluoropropyl)methyl-bis(N,N-dimethylamino)silane (I)

(3,3,3-Trifluoropropyl)methyldichlorosilane (100 g., 0.47 mole) was added dropwise with stirring to a solution of dimethylamine (200 g., 4.4 moles) in 500 ml. of ether at -5 to 0°C. The reaction mixture was allowed to stir overnight at room temperature. Separated solid was removed by filtration and the filtrate concentrated <u>in vacuo</u> on a rotary vacuum evaporator. The weight of the salt corresponded to a quantitative yield of dimethylamine hydrochloride. The residue from the evaporation of the filtrate was distilled through a 15-inch vacuum-jacketed Vigreux column and the fraction collected with a boiling range of 163-165°C. Yield: 87.3 g., 81%. Vapor phase chromotography indicated 99.5% purity.

Anal. Calcd. for $C_8H_{19}F_3N_2Si$: C, 42.08; H, 8.39; N, 12.27. Found: C, 41.19; H, 8.89; N, 12.36.

Preparation of 3-(Heptafluoroisopropoxy)-propylmethyl-bis(N,N-dimethylamino)-silane (II)

3-(Heptafluoroisopropoxy)propylmethyldichlorosilane (102 g., 0.03 mole) was added dropwise with stirring to a cold (0-5°C) solution of dimethylamine (100 g.) in 300 ml. of anhydrous ether. When addition was complete, the ice-salt bath was removed and the system allowed to warm to room temperature. After stirring for 24 hours, the separated amine salt was removed by filtration and the filtrate concentrated <u>in vacuo</u>. Distillation of the residue through a short column afforded a main fraction with boiling point of 103-105°C/30 mm Hg which was collected and weighed. Yield: 81.7 g., 75%. Anal. Calcd. for $C_{11}H_{21}F_7N_2OSi$: N, 7.82%. Found: 7.57%.

Reaction of 3,5-di(trifluoromethyl)phenylmagnesiumbromide with Ethyl Silicate

To a solution of ethylmagnesium bromide prepared from ethyl bromide (57.0 g. - 0.52 mole), Mg (13.30 g.- 0.55 g.- atom) and THF (500 ml.), was added 3,5-di(trifluoromethyl)bromobenzene (146.5 g., 0.5 mole) dropwise with stirring. After two hours, the exchanged Grignard reagent was added dropwise with stirring to a cold (0°C) solution of ethyl silicate (52.1 g., 0.25 mole) in 250 ml. of THF. When addition was complete, the cooling bath was removed and the mixture allowed to stir at room temperature for 3 days. At the end of this time, the reaction mixture consisting of solid and liquid was evaporated to dryness *in vacuo* and the residue exhaustively extracted with cyclohexane in a Soxhlet apparatus. The extracts were concentrated *in vacuo*; the crude oily product which solidified upon standing at room temperature, was recrystallized from 30-60° petroleum ether, melting point 58-60°C. Mass spectral data indicated that the product was not the expected disubstituted derivative, but tris(3,5-di(trifluoromethyl)phenyl)-ethoxysilane. Anal. Calcd. for $C_{26}H_{14}F_{18}OSi$: M.W., 713. Found: M.W., 700.

Preparation of Bis(pentafluorophenyl)diethoxysilane (III)

Compound (III) was prepared by the method of Whittingham (Ref. 2). Fractional distillation resulted in a 35% yield, b.p. = 125-128°C/1 torr, literature boiling point = 132°C/3 torr.

Preparation of (Bis(pentafluorophenyl)dichlorosilane (IV)

Compound (IV) was prepared by the method of Whittingham (Ref. 2) by treatment of compound (III) with a four molar excess of acetyl chloride at room temperature. Fractional distillation resulted in a 40% yield, b.p. = 87-90°C/0.08 torr, literature boiling point 180-185°C/16 torr.

Preparation of Bis(pentafluorophenyl)-bis(N,N-dimethylamino)-silane (V)

Compound (IV), 10 grams, was added dropwise to a stirred solution of excess dimethylamine in ether which was maintained at 0°C. The mixture was refluxed for one hour following the addition and filtered to remove the amine hydrochloride. Compound (V) was recovered by fractional distillation as a colorless oil in 22% yield, b.p. = 108-110°C/0.05 torr. Anal. Calcd. for $C_{16}H_{12}F_{10}SiN_2$: C, 42.66%; H, 2.69%; Si, 6.24%. Found: C, 45.2%; H, 2.74%; Si, 6.39%.

Preparation of 3,5-di(trifluoromethyl)phenyldiethoxyphenylsilane (VI)

To a solution of ethylmagnesium bromide prepared from ethyl bromide (57.0 g., 0.52 mole), Mg (13.3 g., 0.55 g.-atom), the THF (500 ml.) was added dropwise with stirring a solution of 3,5-di(trifluoromethyl)-bromobenzene (146.5 g., 0.5 mole) in 150 ml. of THF. After stirring at room temperature, the Grignard reagent was added in one portion to a solution of phenyltriethoxysilane in 250 ml. of THF. The reaction solution was heated at reflux overnight with stirring. Solid commenced to separate after several hours of heating. The two-phase system was concentrated <u>in vacuo</u> and the residue exhaustively extracted with cyclohexane in a Soxhlet apparatus. The extracts were fractionally distilled at 5 mm Hg to give a fraction with boiling point of 93-114°C and a second fraction with boiling point of 114-121°C. The first fraction was redistilled and the 114-121°C distillate added to the second fraction. Fraction two was then distilled through a 15-inch vacuum jacketed Vigreux column and the fraction collected with b.p. of 118-121°C/5 mm Hg. Yield: 88 g., (43%). The infrared spectrum was consistent with the proposed structure. Anal. Calcd. for $C_{17}H_{18}F_6O_2Si$: C, 52.94; H, 4.44%. Found: C, 52.19; H, 4.34%.

Preparation of 3,5-di(trifluoromethyl)phenyldiethoxymethylsilane (VII)

To a solution of ethylmagnesium bromide prepared from ethyl bromide (11.4 g., 0.104 mole), Mg (2.7 g., 0.11 g. atom), and THF (100 ml.) was added dropwise with stirring a solution of 3,5-di(trifluoromethyl)-bromobenzene (29.3 g., 0.1 mole) in 200 ml. of THF. After stirring at room temperature for four hours, the exchanged Grignard reagent was added dropwise with stirring to a refluxing solution of methyltriethoxysilane (53.5 g., 0.3 mole) in 200 ml. of THF. Solid started separating after about one-third of the Grignard reagent had been added. The resulting mixture was heated at reflux with stirring for 12 hours after addition was complete. The system was freed of solvent on a rotary vacuum evaporator and the residue exhaustively extracted with cyclohexane in a Soxhlet apparatus. The extracts were concentrated <u>in vacuo</u> and the residue distilled <u>in vacuo</u> through a 15-inch vacuum-jacketed Vigreux column and the fraction collected with b.p. 112-116°C/37 mm Hg. Yield: 16.3 g. (47%). The infrared spectrum was consistent with the proposed structure showing a strong absorption band at 1370 cm^{-1} characteristic of Si-Ø. Anal. Calcd. for $C_{13}H_{16}F_6O_2Si$: C, 45.1; H, 4.6%. Found: C, 44.6; H, 4.5%.

Preparation of 3,5-di(trifluoromethyl)phenyldichlorophenylsilane (VIII)

A solution of (3,5-di(trifluoromethyl)phenyl)diethoxysilane (85 g., 0.21 mole) in 200 ml. of acetylchloride was stirred at room temperature for 48 hours under protection of a calcium chloride packed drying tube. At the end of this time, excess acetyl chloride and by-product ethyl acetate were removed by distillation at atmospheric pressure, the two compounds co-distilling between 50 and 78°C. The residue was distilled through a 15-inch Vigreux column and the fraction collected with b.p. 112-116°C/5 torr. Yield: 64.0 g., (78%). The infrared spectrum showed only a trace of Si-O absorption at 970 cm^{-1}. Vapor phase chromotography indicated a purity of 98%. The extreme reactivity of the dichlorosilane prevented the attainment of satisfactory elemental analysis.

Preparation of Methyl-3,5-di(trifluoromethyl)phenyldichlorosilane (IX)

Methyl-3,5-di(trifluoromethyl)phenyldiethoxysilane (16.3 g., 0.04 mole) was dissolved in 40 ml. of acetylchloride and the resulting solution allowed to stir at room temperature for 48 hours under protection of a calcium chloride packed drying tube. At the end of this time, the solution was distilled at atmospheric pressure thorugh a short fractionating column. Excess acetylchloride and ethyl acetate co-distilled between 51 and 77°C, and this fraction was collected and discarded. The pot residue was distilled *in vacuo* through a 15-inch vacuum-jacketed Vigreux column and the fraction collected with b.p. of 100-106°C/33 torr. Yield: 9.8 g., (64%). The infrared spectrum was consistent with the proposed structure and showed the absence of Si-O-C absorption at 970 cm^{-1}. Vapor phase chromotography indicated a purity of 98+%. An alcoholic silver nitrate test was strongly positive. Because of the extreme reactivity of this derivative, satisfactory elemental analysis could not be obtained.

Preparation of Phenyl-3,5-di(trifluoromethyl)phenyl-bis(N,N -dimethylamino) silane (X)

A solution of phenyl-3,5-di(trifluoromethyl)phenyldichlorosilane (63 g., 0.16 mole) in 75 ml. of anhydrous ether was added dropwise with stirring to a solution of cold (0-5°C) dimethylamine (100 g.) in 500 ml. of anhydrous ether. When addition was complete, the cooling bath was removed and the solution allowed to stir at room temperature over the weekend. At the end of this time, amine salt (20 g., 77%) was removed by filtration and the filtrate evaporated to dryness. The crude product was distilled and the fraction collected with b.p. of 119.5-120°C/5 torr. Yield: 31.6 g., (49%). The infrared spectrum showed a strong absorption band at 1000 cm^{-1} characteristic of the $SiNR_2$ group. Anal. Calcd. for $C_{18}H_{20}N_2SiF_6$: C, 53.19; H, 4.96%. Found: C, 52.44; H, 4.67%.

Preparation of (3,5-di(trifluoromethyl)phenyl)methyl-bis(N,N-dimethylamino)silane (XI)

3,5-di(trifluoromethyl)phenyldichloromethylsilane (20 g., 0.06 mole) was added dropwise with stirring to a cold (0-5°C) solution of dimethylamine (100 g) in 150 ml. of THF. The temperature was maintained in this region until addition was complete at which time the external ice water-salt bath was removed and the temperature allowed to rise to ambient. Separation of amine salt was instantaneous upon addition of the dichlorosilane. After stirring at room temperature for 24 hours, the separated solid was removed by filtration, dried, and weighed. Yield: 8.2 g., (90%). The filtrate was evaporated to dryness, the residue distilled in vacuo, and the fraction with b.p. of 117-122°C/ 31 torr was collected. Yield: 10.6 g., (52%). Considerable loss of product occurred due to decomposition during the distillation. The infrared spectrum was consistent with the proposed structure and exhibited a strong absorption band at 1000 cm^{-1} characteristic of the $Si(N(CH_3)_2)_2$ group. Anal. Calcd. for $C_{13}H_{18}F_6N_2$: C, 45.34; H, 5.27; N, 8.14%. Found: C, 45.01; H, 5.25; N, 8.07%.

Preparation of Chlorodiethoxyphenylsilane

In a 1000 ml. three-neck flask equipped with an addition funnel, mechanical stirrer, thermometer, and a dry ice cold finger was placed trichlorophenylsilane (106 g., 0.5 mole). The contents of the flask were cooled to 0°C and maintained at that temperature while ethanol (46.1 g., 1.0 mole) was added dropwise to the rapidly stirred solution over a 3.5-hour period. A slow nitrogen purge was maintained throughout the course of the reaction. After all of the ethanol had been added, the temperature of the system was slowly raised to 60°C over a three hour period. Nitrogen purging and heating at 60°C was continued for an additional hour. At the end of the heating period, the reaction product was distilled through a 15-inch vacuum jacketed column packed with berl saddles and the fraction collected with b.p. of 127-130°C/ 25 torr. (Literature b.p. 124-126°C/20 torr.) Yield: 91.5 g., 78%.

In a similar fashion, chlorodiethoxymethylsilane was prepared from methyltrichlorosilane (74.9 g., 0.5 mole) and ethanol (46.1 g., 1.0 mole) b.p. 117-120°C. Yield: 67 g., 80%.

Preparation of Pentafluorophenylmethyldiethoxysilane (XII)

To a solution of ethylmagnesium bromide prepared from ethylbromide (57.0 g., 0.52 mole), Mg (13.3 g., 0.55 g.-atom), and THF (500 ml.) was added dropwise with stirring a solution of pentafluorobromobenzene (123.5 g., 0.5 mole) in 125 ml. of THF. After four hours of stirring at room temperature, the Grignard reagent was added dropwise with stirring to a solution of chlorodiethoxymethylsilane (85.5 g., 0.5 mole) in 300 ml. of THF. The mixture was stirred at room temperature for 24 hours and then evaporated to dryness in vacuo. The heterogeneous residue was exhaustively extracted with cyclohexane in a Soxhlet apparatus; the extracts were then concentrated in vacuo. The crude product was distilled and the fraction collected with boiling point of 57-60°C/0.3 torr. Yield: 44.0 g., 30%. The pot residue solidified upon cooling to room temperature indicating that di- and tri-aryl substitution on the silicon atom had probably occurred also.

Preparation of Pentafluorophenylmethyldichlorosilane (XIII)

Pentafluorophenylmethyldiethoxysilane (27.0 g., 0.09 mole) was dissolved in 85 ml. of acetyl chloride and the resulting solution allowed to stir at room temperature for 48 hours under protection of a calcium chloride packed drying tube. Excess acetyl chloride and by-product ethyl acetate were removed through distillation (50-77°C) and the residue distilled in vacuo through a 15-inch Vigreux column. The fraction was collected with a b.p. of 44-47°C/0.3 torr. Yield: 17.2 g., (66%). An alcoholic silver nitrate test was strongly positive.

Preparation of Pentafluorophenylmethyl-bis(N,N-dimethylamino)silane (XIV)

A solution of pentafluorophenylmethyldichlorosilane (17.0 g., 0.06 mole) in 25 ml. of THF was added dropwise with stirring to a cold (-5 to 0°C) solution of dimethylamine in 125 ml. of THF. When addition was complete, the ice-salt bath was removed and the mixture allowed to stir at room temperature for 24 hours. Salt was removed by filtration and the filtrate concentrated in vacuo. Distillation of the residue at 0.35 torr afforded a main fraction, b.p. 63-65°C. The infrared spectrum of the distillate showed only a very weak absorption band at 970 cm^{-1} (Si-O-C).

Preparation of Phenylpentafluorophenyldiethoxysilane

To a solution of ethylmagnesium bromide prepared from ethyl bromide (5.7 g., 0.052 mole), Mg. (1.33 g., 0.055 g. -atom), and THF (50 ml.) was added dropwise with stirring a solution of pentafluorobromobenzene (12.4 g., 0.05 mole) in 25 ml. of THF. After four hours of stirring at room temperature, the solution of pentafluorophenylmagnesium bromide was added by means of positive nitrogen pressure to a stirred solution of chlorodiethoxyphenylsilane (11.5 g., 0.05 mole) in 100 ml. of THF. After stirring overnight at room temperature, the solid which had separated was removed by filtration and the filtrate concentrated in vacuo. The crude product decomposed upon attempted vacuum distillation at 0.7 torr.

When the reaction was re-run and the solution heated at THF reflux, solid separated after approximately one hour. After an additional heating period of two hours, the crude product was isolated as described above. Attempted vacuum distillation also resulted in decomposition of the product.

In a third run, the entire reaction mixture was freed of solvent and exhaustively extracted with 30-60° petroleum ether in a Soxhlet apparatus for 24 hours. The extracts were evaporated to dryness and the residual oil was used in subsequent reactions "as is." Yield: 24.4 g., 67%. An alcoholic silver nitrate test was negative.

Attempted Preparation of Phenylpentafluorophenyldichlorosilane

A solution consisting of pentafluorodiethoxyphenylsilane (18.1 g., 0.05 mole), benzoylchloride (42 g., 0.3 mole), and 1 ml. of pyridine was heated at reflux with stirring for 8 hours. The resultant dark colored solution decomposed upon attempted vacuum distillation at 0.2 torr.

A solution consisting of the same reactants in the same quantities as described above was heated at 150°C for an eight hour period. Fractional distillation of the reaction mixture yielded a negligible (ca. 4 g.) amount of distillate, b.p. 80-120°C/0.05 torr, which was not further characterized or investigated.

A solution of pentafluorodiethoxyphenylsilane (18.1 g., 0.05 mole), acetylchloride (23.6 g., 0.3 mole), and triethylamine was heated at reflux for six hours. Atmospheric distillation of the reaction solution afforded only unreacted acetyl chloride with no ethyl acetate being detected.

Attempted Preparation of Phenylpentafluorophenyldichlorosilane

To a mixture of activated Mg (1.33 g., 0.055g.-atom) and phenyltrichlorosilane (42.3 g., 0.2 mole) in 50 ml of THF was added dropwise with stirring a solution of pentafluorobromobenzene (12.35 g., 0.05 mole) in 75 ml. of THF. The reaction solution darkened considerable and no salt was observed to separate. When addition was complete, the solution was heated at reflux for two hours. After removal of the solvent, fractional distillation <u>in vacuo</u> of the residue afforded recovery of only unreacted phenyltrichlorosilane (100°C/31 torr).

Attempted Preparation of bis(3,5-di(trifluoromethyl)phenyl)dichlorosilane

To a solution of ethylmagnesium bromide prepared from ethyl bromide (54.5 g., 0.5 mole), Mg. (12.2 g., 0.5 g. atom), and THF (500 ml.) was added dropwise with stirring a solution of 3,5-di(trifluoromethyl)bromobenzene (146.5 g., 0.5 mole) in 100 ml. of THF. After stirring for two hours at room temperature, the solution was cooled to 10°C by means of an ice-salt bath and treated in one portion with cadmium chloride (45.8 g., 0.25 mole) which had been previously dried at 110°C for two hours. The resulting mixture was stirred at 10-15°C for four hours at the end of which time the entire contents of the flask, including the precipitate, were added by means of a positive nitrogen pressure to a stirred solution of silicon tetrachloride (106.2 g., 0.625 mole) in 200 ml. of THF maintained at -20°C. When addition was complete, the cooling bath was removed and the reaction mixture allowed to stir at room temperature for three days. The two-phase system was concentrated in vacuo and the residue exhaustively extracted with cyclohexane in a Soxhlet apparatus. The extracts were evaporated to dryness and the crude product distilled through a 15-inch vacuum jacketed column packed with berl saddles. The fraction was collected with b.p. of 137-149°C/15 torr (54.0 g.); a forerun with b.p. of 47-83°C/15 torr was collected and discarded. The main fraction was re-distilled through the same column and the fraction collected with b.p. of 94-96°C/6 torr. The distillate solidified upon standing to white crystals, m.p. 58-60°C. The product was shown through elemental analysis to be a mixture of mono- and dichloro-substituted silane. Anal. Calcd. for $C_{16}H_{16}Cl_2F_{12}Si$: Cl, 13.50. Calcd. for $C_{24}H_9ClF_{18}Si$: Cl, 5.04%. (Avg. 9.27). Found: Cl, 9.90%.

Repeated distillations were unsuccessful in effecting separation of the mixture into two or more components.

When an equivalent molar amount of ethylsilicate was substituted for the silicon tetrachloride, no reaction occurred with the diaryl cadmium derivative.

Preparation of Bis(3,5-di(trifluoromethyl)phenyl)diisopropoxysilane (XV)

This compound was prepared through condensation of 3,5-di(trifluoromethyl)phenylmagensium bromide with diisopropoxydichlorosilane. The Grignard reagent was prepared as described earlier for the preparation of compound (VI). Diisopropoxydichlorosilane was prepared in 82% yield by the addition of 2 equivalents of anhydrous isopropyl alcohol to 1 equivalent of silicon tetrachloride at 0°C. The product was carefully fractionated at 156-157°C/760 torr, literature boiling point 155°C/745 torr (Ref. 8). To 31.8 g. (0.1 mole) of 3,5-di(trifluoromethyl)-phenylmagnesium bromide in 200 ml. of tetrahydrofuran was added with stirring 10.8 g. (0.05 mole) of diisopropoxydichlorosilane at 65°C. The mixture was refluxed overnight at this temperature and 200 ml. of dibutylether was added. The tetrahydrofuran was distilled off and the reaction temperature was increased to 136°C where it was held overnight. The salts which precipitated during this reaction were filtered off and extracted in a Soxhlet extractor with cyclohexane. The combined filtrates were concentrated to remove the solvents and the residue was fractionated to provide a 34% yield of compound (XV), b.p. 92-95°C/ 0.01 torr. Anal. Calcd. for $C_{22}H_{20}F_{12}O_2Si$: C, 46.15%, H, 3.53%; Si, 4.91%. Found: C, 44.5%; H, 3.10%; Si, 4.45%. Purity: 96.5% by glpc. Theoretical M.W.: 572.21. Found: (Mass Spect.) 572.

Preparation of Bis(3,5-di(trifluoromethyl)phenyl)dihydroxysilane (XVI)

Compound (XVI) was prepared by alkaline hydrolysis of (XV), by a modification of the method of Breed et al. (Ref. 9). Compound (XV), 5.72 g., (0.01 mole) was dissolved in 10 ml. of tetrahydrofuran and heated to reflux. To this warm solution was added a solution containing 2.4 g. of NaOH, 14 ml. of ethyl alcohol, and 2 ml. of water. This mixture was warmed for 5 minutes and treated with a solution of 2.4 grams of NaOH in 16 ml. of water. This mixture was heated at 35-40°C and stirred for one hour after which it was poured slowly into a solution of 20.5 gm. of KH_2PO_4 in 200 ml. of water at 0°C with vigorous shaking. The mixture was kept at 0°C overnight and white crystals formed, melting at 230-240°C with some decomposition. The infrared spectrum showed evidence of silanol absorption at 3300-3400 cm^{-1} and absence of Si-O-C absorption. The crude product was recrystallized from CCl_4 but the melting point, 230-235°C, was always accompanied by decomposition. Anal. Calcd. for $C_{16}H_8F_{12}O_2Si$: C, 39.35%; H, 1.65%; Si, 5.75%. Found: C, 40.6%; H, 1.89%; Si, 5.13%.

Preparation of 1,4-bis(dimethylchlorosilyl)benzene (XVII)

Compound (XVII) was prepared by the method of Burks (Ref. 11) by condensation of the di-Grignard reagent of 1,4-dibromobenzene with excess dimethyldichlorosilane. The solid product was fractionated at 109-110°C/1.5 torr in 35% yield, literature (Ref. 11) 80-93°C/0.5 torr.

Preparation of 1,4-Bis(dimethylhydroxysilyl)benzene (XVIII)

Compound (XVIII) was also prepared by the method of Burks (Ref. 11) by hydrolysis of (XVII) with ammonium hydroxide. The product was recrystallized from CCl_4 in 60% yield, melting point 135.5-136°C, literature: 136-137°C.

Preparation of 1,4-Bis(N,N-dimethylaminodimethylsilyl)benzene (XIX)

Anhydrous dimethylamine, 100 g., (2.22 moles), was dissolved in diethyl ether at 0°C. To this stirred solution was added dropwise a solution of compound (XVII), 26.33 g., (0.1 mole), in diethyl ether while maintaining the reaction temperature between 0-5°C. Following the addition, the amine hydrochloride was filtered and washed with three successive portions of fresh ether. The combined filtrates were concentrated and the residue was fractionated at 100-103°C/0.55 torr in 73% yield. The compound was 98.5% pure by glpc. Anal. Calcd. for $C_{14}H_{28}N_2Si_2$: C, 59.92%; H, 10.08%; N, 9.98%; Si, 20.02%. Found: C, 58.8%; H, 9.75%; N, 9.43%, Si, 20.8%.

Preparation of Bis(N-methylcyclohexylamino)dichlorosilane

A solution consisting of N-methylcyclohexylamine (113.2 g., 1.0 mole) and triethylamine (101.2 g., 1.0 mole) was added dropwise with stirring to a cold (5-10°C) solution of silicon tetrachloride (85.0 g., 0.5 mole) in 1000 ml. of THF. When addition was complete, the cooling bath was removed and the heterogeneous mixture allowed to stir at room temperature overnight. Amine salt (136.8 g., 99%) was removed by filtration and the filtrate evaporated to dryness in vacuo. The crude product was distilled through a 15-inch vacuum-jacketed Vigreux column and the fraction collected with b.p. of 120-122°C/6 torr. Yield: 129.2 g., 80%. Anal Calcd. for $C_{14}H_{28}Cl_2N_2Si$: Cl, 21.9%. Found: Cl, 21.4%.

In a similar fashion bis(N-ethylcyclohexylamino)dichlorosilane was prepared in 52% yield; b.p. 173-177°C/5 torr.

Preparation of Bis(N-methylanilino)dichlorosilane

A solution of N-methylaniline (21.4 g., 0.2 mole) and triethylamine (20.2 g., 0.2 mole) was added dropwise with stirring at room temperature to a solution of silicon tetrachloride (17.0 g., 0.1 mole) in 200 ml. of dry benzene. An exothermic reaction ensued with separation of amine salt. The two phase system was stirred at room temperature for two hours and then heated at reflux for one hour. The amine salt (27.2 g., 99%) was removed by filtration and the filtrate concentrated in vacuo to a light yellow colored oil. The crude product was distilled through a short Vigreux column and the fraction collected with b.p. of 100-102°C/0.075 torr. Yield: 18.4 g., (59%). Anal. Calcd. for $C_{14}H_{16}Cl_2N_2Si$: Cl, 22.78%. Found: Cl, 22.53%.

Attempted Preparation of Bis(N,N -ethylcyclohexylamino)bis(3,5-di(trifluoromethyl)phenyl)silane

A solution of ethylmagnesiumbromide prepared from ethyl bromide (22.8 g., 0.21 mole), Mg. (5.32 g., 0.22 g. atom), and THF (200 ml.) was treated dropwise with stirring with 3,5-di(trifluoromethyl)bromobenzene (0.2 mole). After stirring at room temperature for two hours, the exchanged Grignard was added in one portion to a solution of bis(N-ethylcyclohexylamino)dichlorosilane (0.1 mole). The reaction mixture was stirred at room temperature for 48 hours and then heated at reflux for several hours. At the end of this time, there was still no visible sign of reaction (neither salt formation nor color dissipation). THF was distilled from the flask at atmospheric pressure with the concomitant addition of butylether until the THF had been entirely removed from the system. The solution was then refluxed (142°C) for four hours. Visual examination of the flask still showed no sign of reaction either through salt formation or color dissipation of the Grignard reagent.

Attempted Preparation of Bis(N-ethylcyclohexylamino)-bis(pentafluorophenyl)silane

To a solution of ethylmagensium bromide prepared from ethylbromide (22.8 g., 0.21 mole), Mg. (5.32 g., 0.22 g. atom) and THF (200 ml.) was added dropwise with stirring a solution of pentafluorobromobenzene (49.4 g., 0.2 mole) and 50 ml. of THF. After two hours of stirring at room temperature, the exchanged Grignard solution was added in one portion to a solution of bis(N-ethylcyclohexylamino)dichlorosilane (35.2 g., 0.1 mole) in 200 ml. of THF. The system was heated at reflux with stirring for 24 hours during which time the separation of solid occurred. The mixture was evaporated to dryness *in vacuo* and the residue exhaustively extracted with benzene in a Soxhlet apparatus. The benzene insoluble portion weighed 28 g., and corresponded to a quantitative yield of MgBrCl (theoretical: 27.8 g.). The benzene solution from the extraction was chromatographed on a solumn of neutral grade alumina using additional benzene. Elution with benzene yielded ca. 2.5 g. of cream colored solid, m.p. 170-180°C, which was discarded. No material was eluted from the column with ether. When methanol was used as the eluting agent, 30.7 g., (50% yield) of tan colored solid was obtained which shortly decomposed upon storage *in vacuo* to a dark colored liquid.

Attempted Preparation of Bis(N-methylanilino)-bis(pentafluorophenyl)silane

To a solution of ethylmagnesiumbromide prepared from ethylbromide (22.8 g., 0.21 mole), Mg. (5.32 g., 0.22 g. atom), and THF (200 ml.) was added dropwise with stirring a solution of pentafluorobromobenzene (49.4 g., 0.2 mole) and 50 ml. of THF. After two hours of stirring at room temperature, the exchanged Grignard solution was added in one portion to a solution of bis(N-methylanilino)dichlorosilane (31.1 g., 0.1 mole) in 200 ml. of THF. The reaction solution was heated at reflux with stirring for 12 hours during which time the separation of solid was observed. The reaction mixture was concentrated *in vacuo* and the residue exhaustively extracted with benzene in a Soxhlet apparatus. Concentration of the extracts *in vacuo* afforded an intractable gummy residue which was not further investigated.

Preparation of 9,10-Bis(dimethylchlorosilyl)anthracene

9,10-Dibromoanthracene (33.6 g., 0.1 mole) was added portionwise to a stirred mixture of Mg. (5.35 g., 0.22 g. atom) and dimethyldichlorosilane (56.8., 0.44 mole) in THF (300 ml.). When the exothermic reaction had subsided, the solution was heated at relfux for two hours and then allowed to cool to room temperature. The salt which had separated was removed by filtration and the filtrate concentrated <u>in vacuo</u>. The residue was extracted with 5 X 100 ml. portions of boiling benzene. The extracts were evaporated to dryness and the crude product used directly in the hydrolysis reaction.

Preparation of Di-β-Naphthol

In a three-liter three-necked flask, equipped with a dropping funnel, mechanical stirrer, and reflux condenser, was placed a mixture of β-naphthol (43.2 g., 0.3 mole) and water (1800 ml.) which was heated to reflux. To the boiling system containing liquid β-naphthol in suspension, was slowly added through the dropping funnel, and with vigorous stirring, a solution of hydrated ferric chloride (84 g., 0.31 mole) in 180 ml. of water. After addition was complete, the mixture was refluxed for one hour and the separated solid collected by filtration. The filter cake was washed with boiling water and air dried. After recrystallization from benzene, colorless crystals were obtained, m.p. 217-218°C, (literature m.p. 218°C).

Preparation of di-β-Naphtholdimethylether

To a solution of sodium hydroxide (8.0 g., 0.2 mole) in 500 ml. of water was added di-β-naphthol (28.6 g., 0.1 mole) portionwise. The resulting solution was filtered, the filtrate treated with dimethyl sulfate (25.2 g., 0.2 mole), and then heated to boiling with stirring. After cooling to room temperature, the crude product which had separated was collected by filtration, washed with water until the washings were neutral to alkacid paper and then dried <u>in vacuo</u> over P_2O_5. A quantitative yield of crude product was obtained. The infrared spectrum showed the complete absence of hydroxyl absorption at 3400 cm^{-1}. No solvent or combination of solvents could be found from which to satisfactorily recrystallize the compound.

Preparation of 3,3'-dibromo-di-β-naphtholdimethylether

A stirred solution of di-β-naphtholdimethylether (63 g., 0.2 mole) in 1000 ml. of glacial acetic acid was heated to boiling and treated dropwise with a solution of bromine (64 g., 0.4 mole) in 50 ml. of glacial acetic acid. The reaction solution was maintained at reflux until the evolution of HCl had ceased (ca. 12 hours). The cooled solution was poured into a large excess of water and the solid which separated was collected by filtration, washed with copious quantities of water, and dried *in vacuo* over sodium hydroxide pellets. Yield: 70.8 g., (75%). A small portion of the crude product was recrystallized from glacial acetic acid; m.p. 263-265°C. Anal. Calcd. for $C_{22}H_{18}Br_2O_2$: Br, 36.44%. Found: Br, 36.13%.

Preparation of 3,3'-(dimethylchlorosilyl)-di-β-naphtholdimethylether

A solution of 3,3'-dibromo-di-β-naphtholdimethylether (24.6 g., 0,05 mole) in 200 ml. of THF was added dropwise to a stirred mixture of Mg. (2.7 g., 0.11 g. atom) and dimethyldichlorosilane (32 g., 0.25 mole) in THF (100 ml.). The rate of addition was such that the exothermic reaction was self-sustaining and did not require the application of external heat. When addition was complete, the solution was heated at reflux for 1-1/2 hours, allowed to cool to room temperature, and then evaporated to dryness *in vacuo*. The resulting mixture was exhaustively extracted with cyclohexane in a Soxhlet apparatus. The extracts were concentrated in vacuo to a pale yellow colored oil which decomposed upon attempted distillation *in vacuo*.

Preparation of 1,3-Bis(p-bromophenyl)hexafluoropropane (XX)

The 1,3-didodohexafluoropropane for this reaction was prepared by the method of Krespan (Ref. 4) by iodination of hexafluoroglutaryl chloride under pressure. The diiodide was fractionated at 100°C/350 torr, (literature b.p. 130-131°C/760 torr). Compound (XX) was prepared by a modification of the method of McLoughlin et al. (Ref. 3). A mixture of 1,3-diiodohexafluoropropane, 8.08 g. (0.02 mole), and *p*-iodobromobenzene, 22.6 g. (0.08 mole) was dissolved in 50 ml. of anhydrous dimethylformamide and activated copper-bronze, 11.2 g. (0.18 g.-atom) was slurried in the solution with stirring. The copper was previously activated according to the procedure of Vogel (Ref. 10). The mixture was stirred for 16 hours at 27°C, after which the temperature was increased over a three-hour period to 117-120°C, where it was held for 6 hours. The mixture was then washed with 300 ml. of water and 75. ml. of methylene chloride. The organic layer was dried with anhydrous $MgSO_4$ and the residue, after removal of solvent, was heated at 100°C/1 torr to remove excess *p*-iodobromobenzene. The crude product was recrystallized from isopropyl alcohol/water in 53% yield, m.p. 125-126°C. Anal. Calcd. for $C_{15}H_8Br_2F_6$: C, 38.99%; H, 1.75%; Br, 34.59%. Found: C, 38.2%; H, 2.2%; Br, 33.85%.

Preparation of Poly(1,4-bis(oxydimethylsilyl)benzenemethyl-3,3,3-trifluoropropylsilane)

1,4-bis(dimethylhydroxysilyl)benzene (11.32 g., 0.05 mole) was added to a solution of 3,3,3-(trifluoropropyl)methyl-bis(N,N-dimethylamino)silane (11.99 g., 0.0525 mole) in 30 ml. of dry toluene. The reaction mixture was stirred and heated, by means of an oil bath, under a nitrogen atmosphere. At approximately 70°C complete solution of the diol was obtained, and at approximately 85°C the evolution of dimethylamine commenced. The resulting solution was heated at reflux (110°C) for four hours at the end of which time five ml. of water was added and the two-phase system heated at reflux for two hours. Excess water was then removed through azeotropic distillation and the polymer solution analyzed for percent solids. Found: 38%.

Preparation of Poly(1,4-bis(oxydimethylsilyl)benzene methyl 3-(heptafluoroisopropoxy)propylsilane)

1,4-bis(dimethylhydroxysilyl)benzene (11.32 g., 0.05 mole) was added to a solution of 3-(heptafluoroisopropoxy)propylmethyl-bis(N,N-dimethylamino)silane (18.811 g., 0.0525 mole) in 30 ml. of dry toluene. Upon heating the mixture under a nitrogen atmosphere, solution of the diol occurred at 80°C and evolution of dimethylamine started at 90°C. The solution was heated at reflux for four hours, then treated with 5 ml. of H_2O, refluxed an additional two hours, freed of excess water through azeotropic distillation, and then centrifuged to remove traces of suspended particles. Analysis for percent solids was 30%.

Preparation of Poly(1,4-bis(oxydimethylsilyl)benzene phenyl-3,5-di-(trifluoromethyl)phenylsilane)

1,4-bis(dimethylhydroxysilyl)benzene (11.32 g., 0.05 mole) was added to a solution of 3,5-di(trifluoromethyl)phenyl-bis-(N,N-dimethylamino)phenylsilane (21.34 g., 0.052 mole) in 30 ml. of dry toluene. The stirred reaction mixture was heated by means of an oil bath under a nitrogen atmosphere. Evolution of dimethylamine did not occur until reflux of the toluene had been in progress for some time. At the end of six hours of heating, 5 ml. of water was added and the heterogeneous system refluxed for two hours. Excess water was then removed through azeotropic distillation and the polymer solution analyzed for percent solids. Found: 36%.

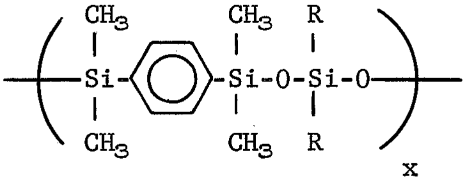
Preparation of Poly(1,4-bis(oxydimethylsilyl)benzene methyl-bis(3,5-ditrifluoromethyl)phenylsilane)

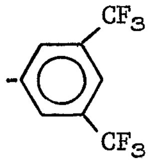
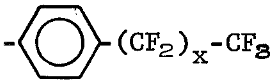
1,4-bis(dimethylhydroxysilyl)benzene (5.66 g., 0.025 mole) was added to a solution of (3,5-di(trifluoromethyl)phenyl)methyl-bis(N,N-dimethylamino)silane (8.680 g., 0.0252 mole) in 15 ml. of dry toluene. The reaction flask was immersed in an oil bath and the mixture heated with stirring under a nitrogen atmosphere. At about 85°C a homogeneous solution was obtained, and at 95°C the evolution of dimethylamine occurred. After heating the solution at toluene reflux for four hours, five ml.

of water was added and the two-phase system heated at reflux for two hours. The excess water was removed through azeotropic distillation and the polymer solution analyzed for percent solids. Found: 32%.

CONCLUSIONS

The evaluation of polymers which have been prepared thus far containing varying proportions of fluorine has pointed to the need for increased fluorine substitution, preferably in the form of fluoroaromatic groups. Thus, structures of the type



where R is  or 

shall be studied in the course of the program. It is expected that fuel resistance will be enhanced further by fluorocarbon or fused ring aromatic moieties incorporated in the diol monomer.

The molecular weight of the linear polymers critically affected the mechanical strength of the resulting elastomers. In most cases the fluorinated silphenylenesiloxane polymers have molecular weights below that required for high strength sealants. The critical nature of the monomer purity in attaining acceptable molecular weights is emphasized by these results. More purification procedures are currently being employed to yield polymers of higher molecular weights.

The processability and application characteristics of the silphenylenesiloxane sealant formulations are equivalent to the commercial fluorosilicone and the inherent thermo-oxidative stability of the experimental materials appears somewhat better than the fluorosilicone. The tensile strength and elongation of the experimental polymers are equivalent in some cases to either the commercial fluorocarbon or the fluorosilicone. While the polymers developed to date have not contained sufficient fluorination or aromatic character to confer desirable fuel resistance, the current efforts of the program are concentrating on this problem. The fluorinated groups utilized in these polymers are structured to minimize titanium stress corrosion resulting from HF elimination, and as such should constitute a more desirable alternative to the Viton fluorocarbon sealant. Efforts within the related contracted effort will continue to emphasize the definition of the stress corrosion mechanism in fluorinated sealants, so that the fluorinated structures discussed in this report can be modified or optimized as required to result in reliable sealant materials.

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APPROVAL

DEVELOPMENT OF POLYMERIC FUEL TANK SEALANTS FOR ADVANCED AEROSPACE VEHICLES

By William J. Patterson and Lawrence R. Moffett, Jr.

The information in this report has been reviewed for security classification. Review of any information concerning Department of Defense or Atomic Energy Commission programs has been made by the MSFC Security Classification Officer. This report, in its entirety, has been determined to be unclassified.

This document has also been reviewed and approved for technical accuracy.

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