WADC TECHNICAL REPORT 54-213

ELASTOMERIC FLUOROALKYL SILOXANE COPOLYMERS

Roy T. Clark, Jr.,
Capt, USAF

Materials Laboratory

July 1954

RDO No. 617-11(A-B)

Wright Air Development Center
Air Research and Development Command
United States Air Force
Wright-Patterson Air Force Base, Ohio

Carpenter Litho & Prtg. Co., Springfield, O.
200 - 8 October 1954

FOREWORD

This report was prepared by the Organic Materials Branch and was initiated under Research and Development Order No. 617-11(A-B), "Synthesis and Evaluation of New Polymers". The report was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with Capt Roy T. Clark acting as project engineer.

ABSTRACT

Preparation of fluorine-containing silicone heteropolymers has been accomplished on an experimental scale. Specifically, elastomeric copolymers have been prepared of dimethyl dichlorosilane with bis 3,3,4,4,5,5,5 heptafluoropentyl diethoxysilane, 3,3,4,4,5,5,5 heptafluoropentyl methyl diethoxysilane and bis 3,3,3 trifluoropropyl dimethoxysilane. Copolymerization was realized both from the oil resulting from cohydrolysis of these compounds and by polymerizing a blend of the separately hydrolyzed materials.

These copolymers all exhibited improved resistance to the swelling action by fuels and retained other desirable physical properties to a large degree when compared to methyl silicone rubber prepared by the same method. Although these elastomers, like commercial silicone rubber, had rather low tensile strength when in the swelled condition, they had considerably greater stability in diester oil at elevated temperature than either methyl silicone rubber prepared in the same manner or the commercially available polymers; the fluorinated elastomers retain over 50% of their tensile strength after 24 hours in diester fluid at 400°F, whereas the unfluorinated materials dissolve at approximately 350°F. Attempts to prepare fluorine-containing silicone homopolymers have been unsuccessful.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

M. R. WHITMORE
Technical Director
Materials Laboratory
Directorate of Research

TABLE OF CONTENTS

I. INTRODUCTION

The research discussed herein was conducted in the Organic Materials Branch, Materials Laboratory, Directorate of Research, WADC. The proposed objective of this research was to prepare and evaluate copolymers of dimethyl dichlorosilane and fluoroalkyl difunctional silanes as fuel resistant and high temperature oil resistant elastomers.

Purdue University, under contract AF 33(038)20581, prepared the fluoroalkyl silanes which were utilized in this investigation.

II. DISCUSSION

Extremes in operating temperatures of present and future aircraft have stimulated considerable interest in the expanded utilization of silicone rubber as an aircraft material. This rubber remains flexible at -100 degrees F and can be used at +500 degrees F for many hours. No other known rubber will do this. Silicone rubber does have several short-comings, however, such as lower tensile strength than many natural and synthetic rubbers, poor abrasion resistance, complete deterioration above 380 degrees F in diester oils, and poor resistance to the swelling action caused by fuels. It is believed that all of these will be improved considerably by new compounding discoveries, however fuel resistance appears to be a problem which will require modification of the polymer as well. One possible method of modification to improve this property is through the introduction of fluorine into the basic structure of the siloxane chain.

1. Methyl Silicone Elastomers

The most easily prepared and widely used silicone rubber known is polydimethyl siloxane. Since previous attempts to prepare this material for control purposes were unsuccessful, the initial phases of this investigation were devoted to its preparation. A study of the previous work by Luck (1) and literature by Rochow (2) indicated that the primary reason for the lack of success was probably due to the use of impure dimethyl dichlorosilane. In consideration of this assumption, approximately 1.5 liters of commercial grade dimethyl dichlorosilane were distilled through a modified Todd column and the

fraction boiling at 70 degrees C at 760 mm was collected for use. Approximately 12 mls of material boiling from 68 degrees to 70 degrees C were obtained. This fraction undoubtedly contains considerable methyl trichloro silane which causes excessive crosslinking of the siloxane chains prior to curing. If this occurs, brittle non-elastomeric polymers are formed. In order to obtain elastomeric siloxane polymers, crosslinking must occur, but it should take place during the curing process with peroxide rather than during polymerization. The following are presented to support this conclusion:

Experiment C-4

Fifty ml of distilled dimethyl dichlorosilane were added dropwise to 200 ml of 10% HCl over a period of 1 hour. Stirring continued 2 additional hours. Hydrolyzed oil separated and centrifuged to remove additional water. Ten grams of oil heated to 140 degrees C in an open system and 20 drops of 5% NaOH in ethanol added. Stirring continued and temperature kept between 140 degrees - 150 degrees C for 55 minutes when a thick semi-solid polymer formed. On compounding with 75 parts of ethyl polysiloxane coated Santocel "C" filler and 6.6 parts of benzoyl peroxide, curing 20 minutes at 258 degrees F, and aging 1 hour at 300 degrees F a fairly good elastomer was obtained. Tensile Strength 450 lbs/in^2; 128% Elongation.

Experiment C-13B

Fifty ml of undistilled (commercial grade) dimethyl dichlorosilane were added dropwise with stirring to 400 ml of 10% HCl over a period of 1 hour. Stirring continued 2 additional hours. Hydrolyzed oil separated

and centrifuged to remove additional water. Ten grams of oil heated to 130 degrees C with stirring in an open system and 20 drops of 5% NaOH in ethanol were added. Stirring and heating continued for 1 1/4 hours with temperature at 130 degrees C when the material became to viscous for mechanical stirring because of clinging to the stirrer. Heating continued for 20 minutes and the material became a thick semi-solid elastomer. On compounding with 50 parts of ethyl polysiloxane coated Santocel "C" filler and 5 parts of benzoyl peroxide, curing 20 minutes at 258 degrees F and aging 1 hour at 300 degrees F, a brittle non-elastomeric sample was obtained. Tensile strength approximately 50 lbs/in^2.

When these experiments were repeated using sulfuric acid as the polymerizing agent, a fair elastomer was obtained with the distilled silane, and a brittle non-elastomeric sample was obtained with the undistilled silane. Sulfuric acid, however, seems to produce a more highly crosslinked product. It is thought that it acts as an oxidizing agent and demethylates some of the silicon atoms which results in the formation of a siloxane bridge or removes hydrogen atoms and forms methylene ether linkages. Additional evidence is that sulfuric acid causes crosslinking when used to polymerize octamethyl cyclotetrasiloxane, a material which is free from trifunctional units. Polymerization of this material with KOH produces a polymer with a tensile strength in excess of 800 lbs/in^2 on compounding.

2. Copolymers of Dimethyl Dichlorosilane and Bis 3,3,4,4,5,5,5 Heptafluoropentyl Diethoxy Silane

Since previous investigators found that bis 3,3,4,4,5,5,5 heptafluoropentyl diethoxy silane (3) could not be homopolymerized into

an elastomer, the most feasible method of introducing fluoroalkyl groups into the siloxane chain appeared to be copolymerization with a compound, such as dimethyl dichlorosilane, which is known to produce elastomeric materials. The following experiments are presented as evidence that the above can be accomplished to produce silicone elastomeric materials with improved thermalstability in diester oil as well as fuel resistance.

Experiment C-16

Twelve grams of distilled dimethyl dichlorosilane (B.P. 70 degrees C) and 3 grams of bis 3,3,4,4,5,5,5 heptafluoropentyl diethyoxy silane were placed in a separatory funnel and mixed thoroughly. Mixture added dropwise with stirring to 100 ml of 10% HCl over a period of 20 minutes and stirring continued for 2 additional hours. Solution placed in a separatory funnel and allowed to stand over night. Clear oil settled to the bottom and was separated. HCl layer extracted with diethyl ether, ether evaporated, oil layers combined and heated to drive off adhering water. Yield of oil 6.6 grams or 44% of starting material. Refractive index 1.3878 at 20 degrees C. Infrared spectrum recorded.

Six and one half grams of the oil heated to 120 degrees C in an open system on a hot plate with stirring and 20 drops of freshly prepared 5% NaOH in ethanol were added. Heating and stirring continued for 2 hours with temperature 120 degrees to 130 degrees C. Polymer became too viscous to stir because material began to cling to stirrer; therefore, only heating was continued for 40 additional minutes. A transparent solid elastomeric polymer formed. Weight 3.5 grams. Yield 54% of oil or 23% of starting material. Infrared spectrum indicated no

loss of fluorine. On compounding with 50 parts of ethyl polysiloxane coated Santocel "C" filler and 5 parts of benzoyl peroxide with curing at 258 degrees F for 15 minutes and aging for 1 hour at 300 degrees F, a rather good sample was obtained. Specimen handled well on the mill. Physical properties are listed in Table I.

Experiment C-17

A blend of three grams of bis 3,3,4,4,5,5,5 heptafluoropentyl diethoxy silane and 6.9 grams of methyl silicone oil (prepared from 10% HCl hydrolysis of distilled $(CH_3)_2 SiCl_2$)was made and mixed thoroughly. Blend heated to 120 degrees C and 20 drops of 5% NaOH in ethanol added with stirring. Heating and stirring continued for 8 hours with temperature 125 degrees to 130 degrees C with some change in viscosity. Ten additional drops of freshly prepared 5% NaOH in ethanol added and heating and stirring continued for 2 hours with temperature 140 degrees to 150 degrees C. Material began to cling to stirrer so stirring was discontinued. Temperature kept 140 degrees to 150 degrees C for 1 additional hour when a transparent solid elastomeric material formed. Weight 5.3 grams. Yield 53.5% of oil. Infrared spectrum indicated no loss of fluorine. On compounding in the same manner as C-16 a rather good sample was obtained. Physical properties are listed in Table I.

NOTE: Sodium hydroxide is dispersed in ethanol for the convenience of adding small quantities only and the ethanol is allowed to boil out of the system. Twenty drops of 5% ethanolic NaOH equals .023 gm. of NaOH.

Experiment C-25

Three grams of bis 3,3,4,4,5,5,5 heptafluoropentyl silane diol (4) and 10 grams of distilled dimethyl dichlorosilane were thoroughly mixed

and added dropwise to 100 ml of 10% HCl with stirring over a period of 20 minutes. Stirring continued 1 hour; then oil and HCl solution refluxed for 15 hours. Oil separated, HCl solution extracted twice with diethyl ether, ether evaporated, and oils combined. Oil centrifuged then heated for 5 minutes to drive off adhering water. Infrared curve almost identical to Experiment C-18. Refractive index 1.3786 at 20 degrees C. Yield of oil 5.8 gm or 44% of starting material.

Five grams of the oil placed in a closed system and 15 drops of 5% KOH in ethanol added when the temperature reached 100 degrees C. The system was then opened and the ethanol allowed to volatilize. System closed, temperature raised to 160 degrees C for 7 hours with stirring and on cooling a solid elastomeric material formed. Weight 4.5 grams. Yield 90% of oil or 44% of starting material. Infrared spectrum indicated slightly greater fluorine content in polymerized material than in the oil. This was probably due to a slight amount of volatilization of cyclic tetramer while the system was open to allow volatilization of the ethanol. Compounded with 45 parts of ethyl polysiloxane coated Santocel "C" filler and 5 parts of benzoyl peroxide with curing 15 minutes at 258 degrees F and aging 1 hour at 300 degrees F. Physical data is presented in Table I.

3. Copolymers of Dimethyl Dichlorosilane and 3,3,4,4,5,5,5 Heptafluoropentyl Methyl Diethoxysilane

Several attempts were made to homopolymerize 3,3,4,4,5,5,5 heptafluoropentyl methyl diethoxysilane into an elastomer with potassium hydroxide but none were successful. The highest degree of polymerization was obtained in the following manner:

Ten grams of 3,3,4,4,5,5,5 heptafluoropentyl methyl diethoxysilane were placed in 100 ml. of 10% HCl and refluxed for 18 hours. The resulting oil was then separated and centrifuged to remove adhering water. Four grams of the hydrolyzed oil were placed in a reflux apparatus, three drops of con. sulfuric acid were added and the mixture allowed to boil for 6 hours. Three additional drops of con. sulfuric acid were then added and heating continued for 34 hours. On cooling only a very slight increase in viscosity was noted.

Since it was not possible to prepare a homopolymer of 3,3,4,4,5,5,5 heptafluoropentyl methyl diethoxysilane, copolymerization investigations of this compound and dimethyl dichlorosilane were initiated. It was found that copolymers could be prepared by cohydrolyzing the previously mentioned types of silanes in water, dilute hydrochloric acid, sodium sulfate sclution, sodium carbonate solution, etc., then polymerizing the cohydrolysis product thus obtained by heating with well known polymerizing agents such as sodium hydroxide, potassium hydroxide, sulfuric acid, ferric chloride hexahydrate, etc., until a gel of the desired consistancy is obtained. It has been found desirable to reflux the hydrolyzed product and hydrolyzing media for several hours to effect more complete hydrolysis prior to polymerization.

An alternative method of preparing these elastomers is by blending the difunctional fluoroalkyl silanes or the hydrolyzed oil obtained from them with methyl silicone oil and using the same polymerization method described previously. The methyl silicone oil used may be the fraction boiling above 175 degrees C at 760 mm., the unfractionated oil, or the cyclic materials such as octamethylcyclotetrasiloxane.

If the high boiling material or unfractionated methyl silicone oil is used, it must be prepared from pure or substantially pure difunctional dimethyl silane. If sodium hydroxide is used as the polymerizing catalyst in a closed system, it is desirable to use methyl silicone oil from which the fraction boiling below 175 degrees C at 760 mm. has been removed. (Sodium hydroxide appears to be ineffective in polymerizing the low boiling cyclic siloxanes at a rate feasible for this application).

The copolymers may be compounded and cured by conventional methods used for silicone rubber using various fillers such as silica, titania, etc., in a quantity sufficient to form a pasty mass which can be easily handled. Vulcanizing agents such as benzoyl peroxide may be used, preferably from 2 to 6 parts of peroxide per 100 parts of polymer by weight. Vulcanization may be accomplished by heating at approximately 250 degrees F for 15 minutes and the elastomer obtained can be aged at the desired conditions to produce particular polymer characteristics.

The following experiments set forth, in detail, methods used to prepare elastomeric fluorosilicone copolymers:

Experiment C-26A

Twenty-four grams of distilled dimethyl dichlorosilane and 8 grams of 3,3,4,4,5,5,5 heptafluoropentyl methyl diethoxysilane were thoroughly mixed and added dropwise to 100 ml., of 10% HCl with stirring over a period of 40 minutes. Stirring continued for 1 hour; HCl solution and the oily hydrolysis product were placed in a reflux apparatus and allowed to reflux for 22 hours. Oil separated, centrifuged, and heated

to remove adhering water. Yield of oil 14.3 grams. Seven grams of the oil heated to 100 degrees C in an open system and .027 grams of KOH in 15 drops of ethanol were added with stirring. The temperature was raised to 130 degrees C with continued stirring and after 35 minutes a thick semi-solid elastomeric material formed. Infrared analysis indicated no loss of fluorine on polymerization. The sample was compounded with 45 parts of ethylpolysiloxane coated Santocel "C" filler and 5 parts of benzoyl peroxide with curing at 258 degrees F for 15 minutes and aging for 2 1/2 hours at 300 degrees F. Physical properties are presented in Table II.

Experiment C-26B

Seven grams of the hydrolyzed oil from Experiment C-26A and 5 mg. of $FeCl_3 \cdot 6H_2O$ were added with stirring in an open system. The temperature was raised to 130 degrees C with continued stirring and after one hour, a thick brown semi-solid elastomeric material formed. The sample was compounded with 60 parts of ethylpolysiloxane coated Santocel, "C" and 5 parts of benzoyl peroxide with curing at 258 degrees F for 15 minutes and aging 1 hour at 300° degrees F. Physical properties are presented in Table II.

Experiment C-29

Fifteen grams of 3,3,4,4,5,5,5 heptafluoropentyl methyl diethoxysilane were added to 100 ml of 10% HCl and the mixture refluxed for 24 hours. The mixture was then placed in a separatory funnel; the oil which settled to the bottom separated and the HCl layer extracted with ether. When the ether evaporated, the oils were combined and heated to remove adhering water. Four and one half grams of the hydrolyzed fluoro-

silicone oil were blended with 7 grams of methyl silicone oil from which the cyclic tetramer had been removed by distillation and the mixture heated to 110 degrees C in an open system. Thirty drops of ethanol containing .054 grams of KOH were added with stirring and the temperature raised to 160 degrees C. Heating and stirring continued for 2 hours when a semi-solid elastomeric material formed. The sample was compounded with 45 parts of ethylpolysiloxane coated Santocel "C" filler, 5 parts of benzoyl peroxide with curing at 258 degrees F for 15 minutes and aging for 1 hour at 300 degrees F. Physical properties are presented in Table II.

Experiment C-34

Six grams of 3,3,4,4,5,5,5 heptafluoropentyl methyl diethoxysilane were hydrolyzed in the same manner as Experiment C-29. Three and seven tenths grams of this oil were blended with 7.4 grams of octamethylcyclotetrasiloxane and heated to 100 degrees C in a beaker on a hot plate with stirring, then fifty drops of 5% CsOH in ethanol were added and the ethanol allowed to volatilize. The mixture was placed in a closed system and heated at 195 degrees C with stirring for 140 hours and on cooling a semi-solid elastomeric material formed. The sample was compounded with 45 parts of ethylpolysiloxane coated Santocel "C" and 5 parts of benzoyl peroxide with molding at 258 degrees F for 15 minutes and aging 1 hour at 300 degrees F. Physical properties are presented in Table II.

4. Copolymer of Dimethyl Dichlorosilane and Bis 3,3,3 Trifluoropropyl Dimethoxysilane

The following experiment sets forth a method used to prepare a copolymer of the above-named compounds:

Experiment C-36

Three grams of bis 3,3,3 trifluoropropyl dimethoxysilane and twelve grams of distilled dimethyl dichlorosilane were thoroughly mixed in a separatory funnel and added dropwise with stirring to 100 ml of 10% HCl over a period of 20 minutes. Stirring continued one additional hour. The mixture was placed in a reflux apparatus and refluxed for 72 hours. The oil was separated, the HCl solution extracted with diethyl ether, the ether evaporated and the oils combined and heated to drive off adhering water. Yield 6 grams of oil. Six grams of oil were heated to 100 degrees C in an open system on a hot plate and 15 drops of 5% KOH in ethanol added with stirring. The temperature was raised to 150 degrees C and heating and stirring continued for 30 minutes. On cooling a semi-solid elastomeric material formed which was compounded with 45 parts of ethylpolysiloxane coated Santocel "C" and 3 parts of benzoyl peroxide with curing at 258 degrees F for 15 minutes, and aging 1 hour at 300 degrees F. This sample had the following properties:

Tensile Strength	411 lbs/in^2
Elongation	95%
Swell in 70/30 fuel after 48 hours at room temp.	196%
Density	1.28
Flexible at -65 degrees F	

III. INFRARED DATA

On examination of the spectrum of the cohydrolyzed oil in experiment C-16 and comparing it with the spectrum of the same oil after polymerization with NaOH, it was found that none of the bands present in the spectrum of the hydrolyzed oil disappeared; however, a band appeared in the polymerized material which was not present in the oil, indicating a structural change. This band is located at 11.9 microns and is also found in the polymer obtained in C-17 and C-18. It is considered to be evidence of copolymerization. As expected, it is not found in the oil in these experiments prior to polymerization. A large difference between relative intensity of several bands of the hydrolyzed oils and the polymers was noted and investigated. It can be seen that the relative intensity of the band at 8.15 microns (C-F from bis 3,3,4,4,5,5,5 heptafluoropentyl diethoxy silane) to the band at 7.95 microns ($Si-CH_3$ from methyl silicone oil) is much greater in the polymer, indicating a greater concentration of fluorine in the polymer than in the monomer mixture. An increase in the relative intensity of the band at 9.8 microns and a decrease in the relative intensity of the band at 14.4 microns is also noted in the polymer. Since the spectrogram of octamethyl cyclotetrasiloxane contains a relatively low absorption at 9.8 microns and a relatively high absorption at 14.4 microns when compared to the spectrum of methyl silicone oil or the cohydrolyzed oil, it is deducted that a large portion of this material volatilizes during polymerization from the open system. Octamethyl cyclotetrasiloxane is the lowest boiling constituent (B.P. 175°C) of the silicone oil which exists in an appreciable quantity (42%). It has also been found that NaOH is

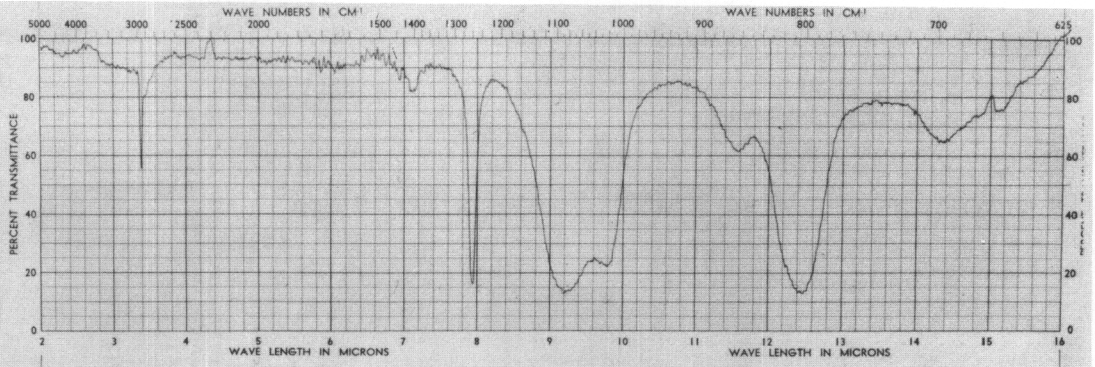
ineffective as a polymerizing agent for the cyclic tetramer at the temperature employed. This volatilization undoubtedly accounts for the yields of only 55% of the oil.

The only difference in the spectra of the blended oils and the cohydrolyzed oils is an additional band in the spectrum of the blend (C-17) before polymerization. This band occurs at 10.4 microns and disappears after polymerization. It is associated with the ethoxy group. Another band associated with this group occurs at 9.2 microns and is masked by the broad band from 9 to 10 microns. These spectra also show a larger amount of fluorine in the cohydrolyzed product than the blend which contains the calculated equivalent of oil from 12 grams of dimethyl dichlorosilane. It is assumed that this is due to the volatilization of the dimethyl dichlorosilane during cohydrolysis giving rise to a greater concentration of fluorine containing oil. A correlation between the relative intensity of the C-F absorption, density, and swell in fuel can also be noted in Table I.

I. R. SPECTROPHOTOMETER
NaCl PRISM

NO.		
DATE		INDEX
SAMPLE		
Methyl Silicone Gum from $(CH_3)_2SiCl_2$ hydrolyzed in 10% H_2O at Room Temp.		
FROM WCRTF		
SAMP. CELL: NaCl	MM	CMS.
REF. CELL NaCl	MM	CMS.
CHEM.	MG.	MG.
SOLV.		
VOL. C.C.	% C.C.	%
F.S. SOLID	C. GAS	MM

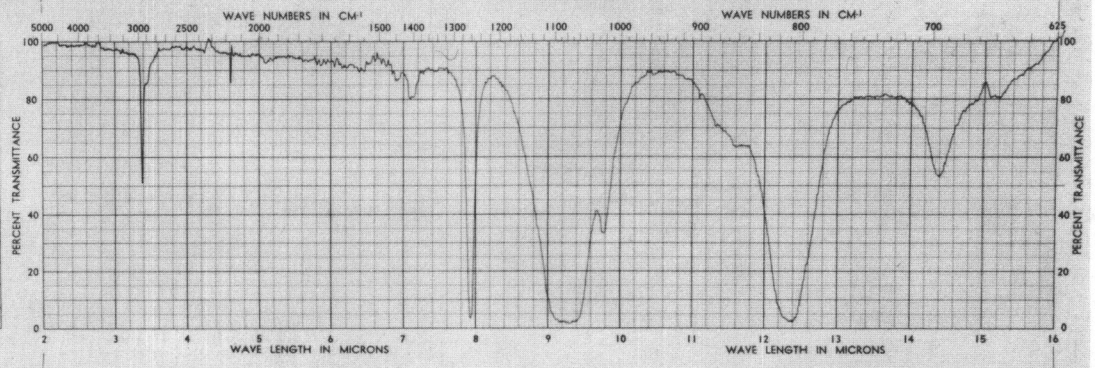
BAIRD ASSOCIATES, INC.
CAMBRIDGE, MASS., U.S.A.
1029-9



I. R. SPECTROPHOTOMETER
NaCl PRISM

NO.		
DATE		INDEX
28 Sept '53	AM 1181	
SAMPLE		
Octamethyl Cyclo-tetra siloxane		
FROM WCRTF		
SAMP. CELL: NaCl	MM	CMS.
REF. CELL NaCl	MM	CMS.
CHEM.	MG.	MG.
SOLV.		
VOL. C.C.	% C.C.	%
F.S. SOLID	C. GAS	MM

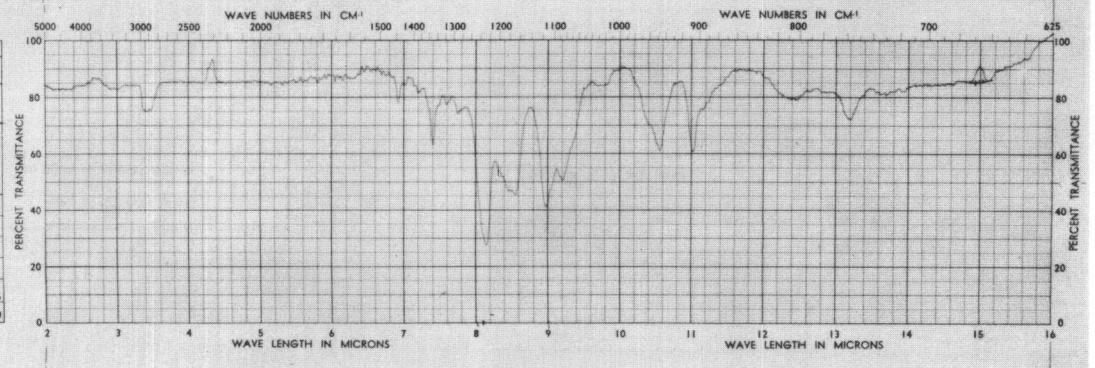
BAIRD ASSOCIATES, INC.
CAMBRIDGE, MASS., U.S.A.
1029-9



I. R. SPECTROPHOTOMETER
NaCl PRISM

NO.	1353	
DATE		INDEX
3 Sept '53	AM 1079	
SAMPLE		
$(C_3F_7CH_2CH_2)_2Si(OC_2H_5)_2$ B.P. 121°C @ 25 mm ND_{20} 1.3420		
FROM WCRTF (Swan)		
SAMP. CELL: NaCl	MM	CMS.
REF. CELL NaCl	MM	CMS.
CHEM.	MG.	MG.
SOLV.		
VOL. C.C.	% C.C.	%
F.S. SOLID	C. GAS	MM

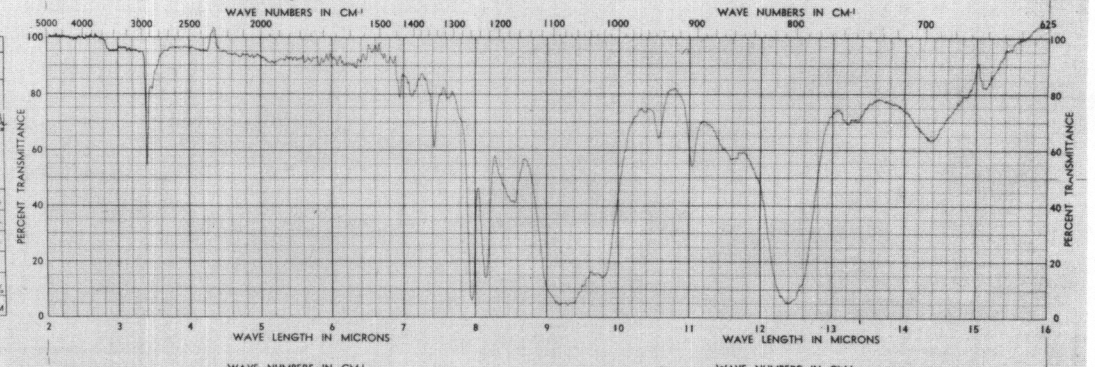
BAIRD ASSOCIATES, INC.
CAMBRIDGE, MASS., U.S.A.
1029-9



① I. R. SPECTROPHOTOMETER
NaCl PRISM

NO.		
DATE		INDEX
15 Sept. 53	AM 1124	
SAMPLE		
Condensate product of 3gm. $(C_3F_7CH_2CH_2)_2Si(OC_2H_5)_2$ + 12 gm. $(CH_3)_2SiCl_2$ (Hydrolyzed in 10% HCl at Room Temperature) ND_{20} 1.3837 C-16		
FROM WCRTF		
SAMP. CELL: NaCl	MM	CMS.
REF. CELL NaCl	MM	CMS.
CHEM.	MG.	MG.
SOLV.		
VOL. C.C.	% C.C.	%
F.S. SOLID	C. GAS	MM

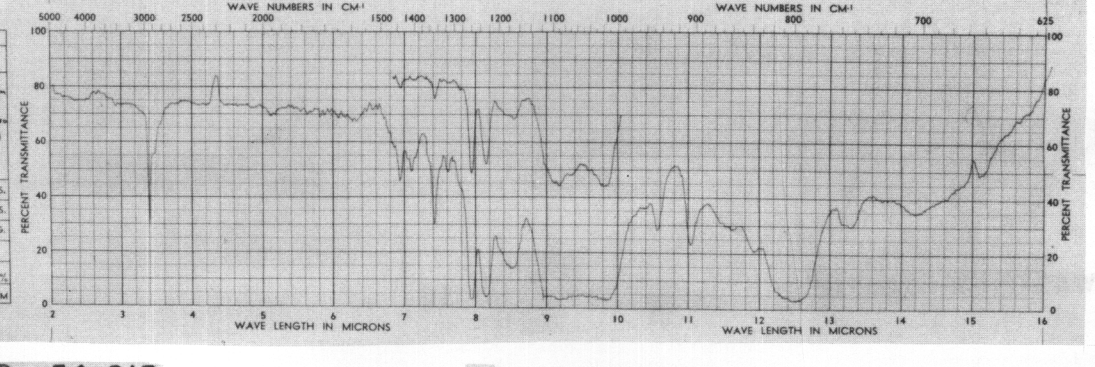
BAIRD ASSOCIATES, INC.
CAMBRIDGE, MASS., U.S.A.
1029-9



② I. R. SPECTROPHOTOMETER
NaCl PRISM

NO.		
DATE		INDEX
16 Sept. '53	AM 1139	
SAMPLE		
NaOH polymerized sample from Condensed oil of 3gm. $(C_3F_7CH_2CH_2)_2Si(OC_2H_5)_2$ + 12 gm. $(CH_3)_2SiCl_2$ (Hydrolyzed in 10% HCl at Room Temperature) C-16		
FROM WCRTF		
SAMP. CELL: NaCl	MM	CMS.
REF. CELL NaCl	MM	CMS.
CHEM.	MG.	MG.
SOLV.		
VOL. C.C.	% C.C.	%
F.S. SOLID	C. GAS	MM

BAIRD ASSOCIATES, INC.
CAMBRIDGE, MASS., U.S.A.
1029-9



(3) I. R. SPECTROPHOTOMETER
NaCl PRISM

NO.	
DATE	INDEX
16 Sept. '53	AM. 1140
SAMPLE	

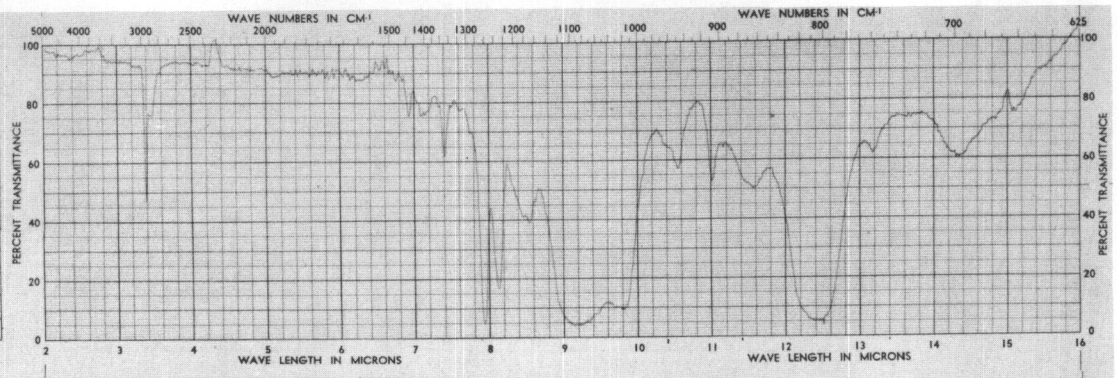
Blend of 6.9 gm. of Methyl Silicone Oil + 3 gm. of $(C_6F_5CH_2CH_2)_2Si(OC_2H_5)_2$

C-17

FROM WCRTE

SAMP. CELL:	NaCl	MM	CaF	CMS.
REF. CELL	gal.	MM		CMS.
CHEM.		MG.		MG.
SOLV.				
VOL.	C.C.	%	C.C.	%
F.S.	SOLID	C.	GAS	MM

BAIRD ASSOCIATES, INC.
CAMBRIDGE, MASS., U.S.A.
1029-9



(8) I. R. SPECTROPHOTOMETER
NaCl PRISM

NO.	
DATE	INDEX
20 Sept '53	AM. 1142
SAMPLE	

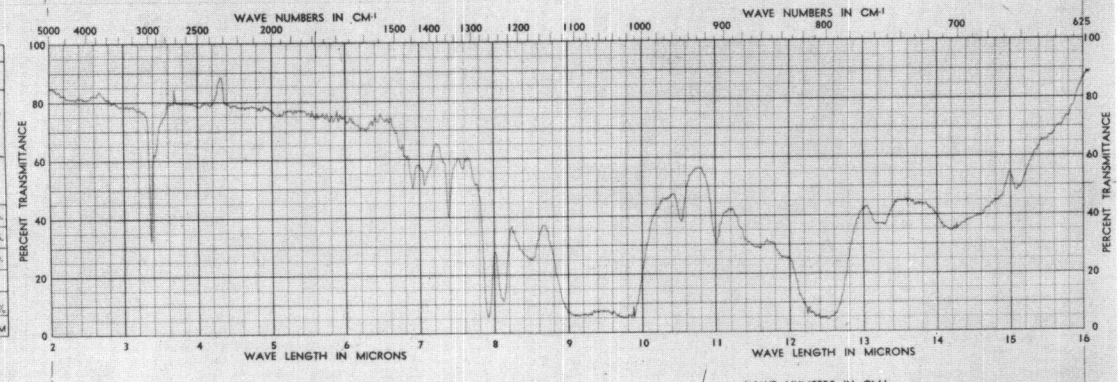
NaOH Polymerized Sample of Blend of 6.9 gms. of Methyl Silicone Oil + 3 gms. of $(C_6F_5CH_2CH_2)_2Si(OC_2H_5)_2$

C-17

FROM WCRTE

SAMP. CELL:	NaCl	MM	CaF	CMS.
REF. CELL	gal.	MM		CMS.
CHEM.		MG.		MG.
SOLV.				
VOL.	C.C.	%	C.C.	%
F.S.	SOLID	C.	GAS	MM

BAIRD ASSOCIATES, INC.
CAMBRIDGE, MASS., U.S.A.
1029-9



(5) I. R. SPECTROPHOTOMETER
NaCl PRISM

NO.	
DATE	INDEX
17 Sept. '53	AM 1141
SAMPLE	

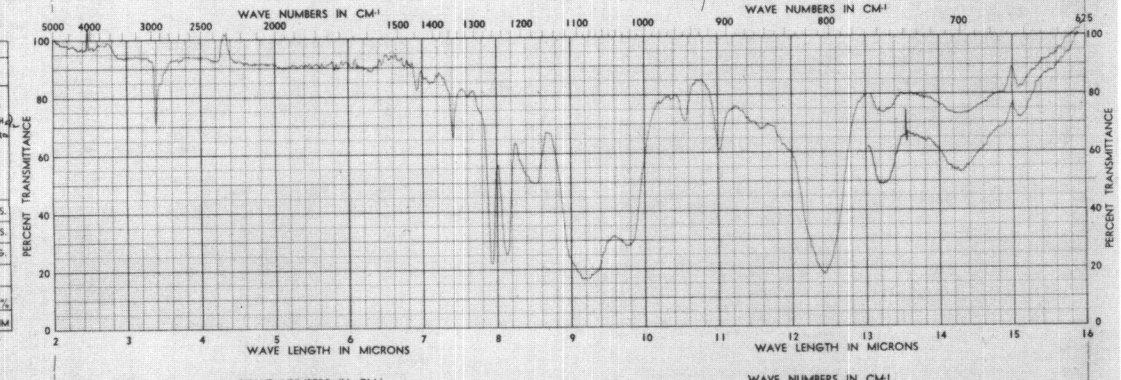
Rehydrolysis Product of 4 gm. $(C_6F_5CH_2CH_2)_2Si(OC_2H_5)_2$ + 12 gm. $(CH_3)_2SiCl_2$ Hydrolyzed in 10% HCl and Refluxed 20 hours in 10% HCl

C-18

FROM WCRTE

SAMP. CELL:	NaCl	MM	CaF	CMS.
REF. CELL	gal.	MM		CMS.
CHEM.		MG.		MG.
SOLV.				
VOL.	C.C.	%	C.C.	%
F.S.	SOLID	C.	GAS	MM

BAIRD ASSOCIATES, INC.
CAMBRIDGE, MASS., U.S.A.
1029-9



(4) I. R. SPECTROPHOTOMETER
NaCl PRISM

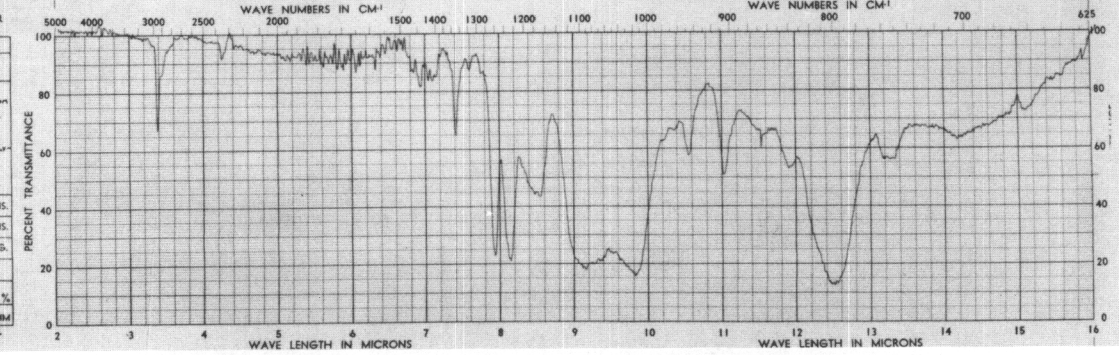
NO.	
DATE	INDEX
22 Sept. '53	AM 1143
SAMPLE	

NaOH Polymerized Sample from Copolymerized Oil of 4 gms. $(C_6F_5CH_2CH_2)_2Si(OC_2H_5)_2$ + 12 gms. $(CH_3)_2SiCl_2$ Hydrolyzed in 10% HCl in Room Temperature. C-18

FROM WCRTE

SAMP. CELL:	NaCl	MM	CaF	CMS.
REF. CELL	gal.	MM		CMS.
CHEM.		MG.		MG.
SOLV.				
VOL.	C.C.	%	C.C.	%
F.S.	SOLID	C.	GAS	MM

BAIRD ASSOCIATES, INC.
CAMBRIDGE, MASS., U.S.A.



IV. PHYSICAL PROPERTIES

TABLE I.

Data on Physical Properties of Copolymers of bis 3,3,4,4,5,5,5 heptafluoropentyl diethoxysilane and Dimethyl dichlorosilane

Exp No.	Tensile Strength lbs/in^2	% Elongation	lbs/in^2 at 100% Modulus	Set at Break	% Swell in Fuel	Density	Flex. at -65°F	Remarks
C-12	102	85	—	15%	69	1.45	OK	Compounded with 50 parts of ethyl silcxane coated Santocel "C" and 3.3 parts benzoyl peroxide
C-16	437	100	437	2%	148	1.34	OK	Swell less than 10% and tensile remained good after 24 hours in diester oil at 400°F. Good tensile after 6 hrs at 480°F in air
C-17	455	150	324	3%	166	1.27	OK	Same as C-16
C-18	440	125	384	3%	141	1.36	OK	Tensile after 48 hrs in 70/30 fuel and fuel evaporated - 466 lbs/in^2
C-20	289	65	—	12%	108	1.43	OK	Retained considerable tensile after 6 hrs. at 480°F in air.
C-25	367	75	—	11%	140	1.39	OK	Retained most of tensile after 6 hrs. at 480°F in air.

* All fuel swell tests run in 70/30 isoctane - toluene at room temperature for 48 hrs. Commercial samples swelled over 250% in fuel at room temperature in 48 hours when compounded in the same manner as the copolymers.

TABLE II.

Data on Physical Properties of Copolymers of 3,3,4,4,5,5,5 heptafluoropentyl methyl diethoxysilane and Dimethyl dichlorosilane

Exp No.	Tensile Strength lbs/in^2	% Elongation	lbs/in^2 at 100% Modulus	Set at Break	% Swell in Fuel	Density	Flex. at -65°F	Remarks
C-26A	585	137	239	7%	149	1.30	OK	Good tensile after 24 hrs. at 400°F in diester oil. Swell of less than 10%
C-26B	554	60	---	---	134	1.37	OK	
C-29	553	140	464	4%	166	1.29	OK	Tensile strength after 24 hrs. in diester oil at 400°F was 323 lbs/in^2; elongation - 130%; swell of less than 10%
C-34	483	95	---	---	151	1.32	OK	

IV. BIBLIOGRAPHY

1. Luck, Russell M., Technical Note WCRT 53-151, Polymerization and Evaluation of Fluorine Containing Silanes, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio, May 1953.

2. Rochow, E. G., Chemistry of Silicones, John Wiley and Sons, Inc., New York, 1951, p. 94.

3. Pierce, O. R., and McBee, E. T., WADC Technical Report 52-191, Part 1, Fluorine Containing Elastomers, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio, October 1952.

4. Pierce, O. R., and McBee, E. T., Summary Report, 11 June 1952 to 11 June 1953, Contract No. AF 33(038)20581.