Contrails

WADC TECHNICAL REPORT 52-197
PART VII
ASTIA DOCUMENT No. AD 142027

SYNTHETIC RUBBERS FROM CARBON-FLUORINE COMPOUNDS

CARL A. DAHLQUIST

MINNESOTA MINING AND MANUFACTURING COMPANY

OCTOBER 1957

MATERIALS LABORATORY
CONTRACT No. AF 33(038)-515
PROJECT No. 7340

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.
400 – November 1957

Approved for Public Release

Contrails

FOREWORD

This report was prepared by the Minnesota Mining and Manufacturing Company under USAF Contract No. AF 33(038)515. This contract was initiated under Project No. 7340, "Rubber, Plastic, and Composite Materials," Task No. 73405, "Compounding of Elastomers." It was administered under the direction of the Materials Laboratory, Directorate of Laboratories, Wright Air Development Center with Mr. E. R. Bartholomew as project engineer.

This report covers the period from November 15, 1955 to December 15, 1956.

The monomers which constitute the raw materials used in the work under the contract; viz., polymerization studies and evaluation of polymers, are available only through the use of contractor's personnel and facilities, and constitute approximately 60% of the effort involved in the contract during this period. This leaves approximately 40% of said effort as representing the actual polymerization studies and evaluation of polymers reported herein.

Approved for Public Release

Contrails

ABSTRACT

Twenty pounds of the polymer of perfluoromethoxy 1,1 dihydroperfluoropropyl acrylate were prepared for Wright Air Development Center.

A copolymer of 3(ω -chloroperfluoroethoxy) 1,1 dihydroperfluoropropyl acrylate and its ω -hydro analog has shown some promise as a heat, solvent, and low temperature resistant rubber.

Fluorine-containing silanes ($R_fCH_2CH_2Si(CH_3)(OC_2H_5)_2$) were polymerized to low molecular weight oils (probably the cyclic tetramer), but attempts to polymerize the oils to high molecular weight polymers did not succeed. Rubbery copolymers of each of these silanes and dimethyl dichlorosilane have been prepared, but no useful vulcanizates have been obtained. Fluorine-containing polysiloxane oils having $-Si(CH_3)_3$ end groups have been prepared.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

R. T. Schwartz

R. T. SCHWARTZ
Chief, Organic Materials Branch
Materials Laboratory

GALVIN LIBRARY
ILLINOIS INSTITUTE OF TECHNOLOGY
NOV 21 2005
GOVERNMENT DOCUMENTS
DEPOSITORY #0146-A

Approved for Public Release

Contrails

TABLE OF CONTENTS

	Page
INTRODUCTION	1
FLUORINE-CONTAINING POLYACRYLATES	2
1. Poly-3-Perfluoromethoxy 1,1-dihydroperfluoropropyl acrylate	2
2. Poly-3-Perfluoroethoxy 1,1-dihydroperfluoropropyl acrylate (FEFPA)	5
3. Poly-3(ω-hydroperfluoroethoxy 1,1-dihydroperfluoropropyl acrylate (H-FEFPA)	5
4. 3(ω-chloroperfluoroethoxy 1,1-dihydroperfluoropropyl acrylate	7
5. 5-Chloro-5,4,4-trifluoro-3-thiapentyl acrylate (I)	12
6. 6,6,6,5,4,4-hexafluoro-3-thiahexyl acrylate (II)	12
7. 6,6,6,5,5,4,4-heptafluorohexyl acrylate	12
FLUORINE-CONTAINING DIENE COPOLYMERS	14
1. Perfluorobutadiene:Vinyl 1,1-dihydroperfluorobutyl ether copolymer	14
2. Copolymer of perfluoropropene and vinyl 1,1-dihydroperfluorobutyl ether (VFBE)	16
3. Copolymerization of 1,4 perfluoropentadiene	16
FLUORINATED SILANES, $R_fC_2H_4Si(CH_3)(OC_2H_5)_2$	17
Hydrolysis by acid catalysis	17
Hydrolysis by base catalysis	17
Distillation of CF_3 silane hydrolysate	19
Polymerization	21
Copolymerization of $R_fC_2H_4Si(CH_3)(OC_2H_5)_2$ with dimethyl siloxane	29
Properties of the Copolymers and their vulcanizates	32
SUMMARY AND CONCLUSIONS	33
APPENDIX	35

Approved for Public Release

Contrails

LIST OF TABLES

Table		Page
I	Comparative Data on Lots of 2F4 Prepared from TFAA and Sulfan Monomer	3
II	Evaluation of 2F4 Submitted to WADC	4
III	Evaluation of H-FEFPA:Acrylic Acid Copolymers.	6
IV	Fluorine-Containing Acrylates	8
V	Vulcanization of ω-chloro FEFPA Polymers	11
VI	Evaluation of FBd:VFBE(3:1) Copolymer	15
VII	Hydrolysis of $R_fC_2H_4Si(CH_3)(OC_2H_5)_2$	18
VIII	Distillation of CF_3 Hydrolysate	20
IX	Polymerization of Silane Hydrolysates	25

Approved for Public Release

Contrails

Approved for Public Release

Contrails

INTRODUCTION

The research effort supported by this contract has led to new solvent resistant and heat resistant fluorine-containing polyacrylate rubbers. This area has now been investigated quite thoroughly, and although some exploratory work remains, major effort has shifted to other fluorine-containing polymers.

The fluorine-containing polysiloxanes have been investigated because new monomers are available through the contractor's facilities. Polymerization studies on monomers of the type $R_fC_2H_4Si(CH_3)(OC_2H_5)_2$ constitute the major effort during the past thirteen months of the contract period.

Manuscript released by author 1 August 1957 for publication as a WADC Technical Report.

Approved for Public Release

Contrails

FLUORINE-CONTAINING POLYACRYLATES

1. Poly 3-Perfluoromethoxy 1,1-dihydroperfluoropropyl acrylate*

During the period covered by this report, the preparation of 20 pounds of the subject polymer requested by WADC was completed. As pointed out in earlier reports, the fluorine-containing acrylate rubbers which have ether oxygen in the side chain have better low temperature properties than 3M Brand Fluoro-Rubber 1F4**, (hereafter designated 1F4 in this report), and equivalent solvent resistance and aging properties. The advantage in low temperature properties prompted WADC's request for sufficient material for small-scale evaluation in finished parts.

Since copolymerization of a small amount of acrylic acid is highly beneficial to the curing of 1F4 in the standard amine recipe (see Appendix 1), small amounts of acrylic acid, up to about 0.15 weight percent, were copolymerized with $CF_3OCF_2CF_2CH_2OCOCH{=}CH_2$. Duplicate series were prepared from the TFAA*** and Sulfan**** monomers. The copolymers prepared from TFAA monomer (see Appendix 2 for emulsion recipe) consistently gave slightly higher inherent viscosity measurements (see Table I) than corresponding copolymer from Sulfan monomer. Consequently the TFAA monomer was selected for scaleup, but physical properties of vulcanizates showed no significant advantage for the TFAA monomer.

The tightness of cure, as judged by elongation to break, is more sensitive to acrylic acid content in 2F4 than in 1F4. The optimum acrylic acid content in the initial small trial preparations of 2F4 appeared to fall near 0.1%, but this amount gave short cures in larger scale preparations, and the 0.03% level selected for the larger preparations proved more satisfactory.

* Now 3M Brand Fluoro-Rubber 2F4.

** Formerly known as poly-FBA (poly 1,1-dihydroperfluorobutyl acrylate).

*** TFAA - Trifluoro acetic anhydride. Used as esterification promoter.

**** Sulfan - Sulfur trioxide. Also used as esterification promoter.

Approved for Public Release

Contents

As reported previously, the most significant advantage of 2F4 over 1F4 is the improvement in low temperature flexibility, where Gehman flex data, Scott brittle point measurements, and glass temperature (-67°F. for 2F4, -22°F. for 1F4) all indicate an advantage of 30°F. to 45°F. for 2F4.

Amine cured 2F4 compares very favorably to amine cured 1F4 in resistance to solvents and hot turbo oil (see Table IV). Tensile strength after hot air aging is lower, but original tensile strength is also somewhat less than for 1F4. The mechanical properties of compounds prepared from the polymer submitted to WADC compare very favorably with the best obtained in previous experimental lots.

TABLE I

Comparative Data on Lots of 2F4 Prepared from TFAA and Sulfan Monomer

Type of Monomer	Wt. % Co-polymerized Acrylic Acid	Inherent Viscosity	Properties of Vulcanizate F_{100} psi	F_{200} psi	F_{300} psi	Tensile, psi	Elong. %	Break Set, %
Copolymers from small lots of experimental monomer								
TFAA	0.03	1.9	120	260	440	830	550	25
TFAA	0.09	1.5	230	560	960	1060	330	9
TFAA	0.15	1.8	290	680	-	1050	290	6
Sulfan	0.02	1.3	120	260	470	820	480	21
Sulfan	0.08	1.3	240	590	-	990	305	13
Sulfan	0.15	1.2	280	655	-	1010	290	6
Copolymers from larger lot of monomer								
TFAA	0.03	1.6	190	470	830	975	360	13
TFAA	0.09	1.7	290	720	-	940	255	6
TFAA	0.09	1.7	280	690	-	970	270	9
TFAA	0.15	1.3	490	-	-	830	160	3

Recipe:

2F4	100 parts by weight
Philblack O	35
Sulfur	1
TETA	1

Cure: 30 min. at 310°F. 24 hrs. after milling.

Approved for Public Release

Contrails

TABLE II

Evaluation of 2F4 Submitted to WADC

Properties of Latex* and Raw Polymer	1 First Half	2 Second Half	3 Blend of 1 & 2 Latices
Wt. % Copolymerized Acrylic Acid	0.03	0.03	0.03
Latex solids	34.5	34.7	34.6
Conversion	94.4	95.1	-
pH after polymerization	1.8	1.9	-
pH before coagulation (adjusted)	6.8	6.1	-
% ash in polymer	0.6	0.7	0.7
Inherent viscosity of polymer	1.8	1.9	-
Properties of Amine Vulcanizate Before Aging**			
Tensile Properties			
F_{100}, psi	185	250	210
F_{200}, psi	420	550	475
F_{300}, psi	725	860	785
F_{break}, psi	960	930	970
Extension at break, %	390	325	370
Break set, %	6	6	7.5
Low Temperature Flexibility			
Gehman T_{10}, °F.	-12	-11	-9
Scott brittle temp., °F.	-33	-38	-33
Compression Set (ASTM D-395-497 "B")			
Before post cure	54.5	48.5	52.5
After post cure (24 hrs. at 300°F.)	18.5	12.5	16
Hardness, Shore Durometer A-2			
Before post cure	53	54	52
After post cure (24 hrs. at 300°F.)	63	63	63
Percent Volume Swell (ASTM D-471-49T "B")			
70:30 Isooctane:toluene (48 hrs. at 77°F.)	-	-	9
Benzene (48 hrs. at 77°F.)	-	-	13
Acetone (48 hrs. at 77°F.)	-	-	41
Ethyl acetate (48 hrs. at 77°F.)	-	-	48
Ethyl alcohol (48 hrs. at 77°F.)	-	-	3
Water (70 hrs. at 212°F.)	-	-	37
Properties of Amine Vulcanizate after Aging in Penola Turbo Oil - 100 hrs. at 400°F.)			
% volume change	-	-	-6
F_{100}, psi	240	320	300
F_{200}, psi	515	-	670
F_{break}, psi	575	560	670
Elongation, %	220	170	200
Break set, %	10	0	3

* For emulsion polymerization recipe, see Appendix 2.
** For curing recipe, see Appendix 1

Approved for Public Release

Contrails

2. Poly-3-Perfluoroethoxy 1,1-Dihydroperfluoropropyl Acrylate (FEFPA) $\left[\overline{CF_3CF_2OCF_2CF_2CH_2OCOCH}\right]_n$, and

$$\begin{array}{c} \\ CH_2 \end{array}$$

3. Its ω-Hydro Analog, Poly-3(ω-Hydroperfluoroethoxy) 1,1-Dihydroperfluoropropyl Acrylate (H-FEFPA)

$$\left[\overline{HCF_2CF_2OCF_2CF_2CH_2OCOCH}\right]_n$$

$$CH_2$$

Earlier, these polymers seemed to have an economic advantage over 2F4, but a key step in the monomer preparation, which looked attractive in small scale preparations, has given very disappointing yields in larger scale runs, and it now seems unlikely that these materials will replace 2F4.

Four small polymer samples of H-FEFPA containing from 0 to 0.55% acrylic acid were evaluated in the standard polyamine recipe, with results listed in Table III. Acrylic acid increases the rate of cure, and improves solvent and dry heat resistance up to a point. Rather unexpectedly, it also seems to improve low temperature flexibility slightly. While the difference is within experimental error, the trend has been noticed quite consistently.

The perfluoroalkoxyalkyl acrylate polymers are faster curing than 1F4, and require less copolymerized acrylic acid. From the data obtained to date, it appears that poly-H-FEFPA has poorer retention of properties after aging in hot Turbo Oil than 1F4 or 2F4. It is also more sensitive to ketone and ester solvents.

Approved for Public Release

Contrails

TABLE III

Evaluation of H-FEFPA:Acrylic Acid Copolymers

	100 H-FEFPA (~0.05 AA)	99.9 H-FEFPA 0.10 AA	99.75* H-FEFPA 0.25 AA	99.45 H-FEFPA 0.55 AA
Inherent Viscosity	3.6	3.6	3.6	3.6
ORIGINAL PROPERTIES				
Modulus at 100% elongation, psi	200	320	550	720
Tensile strength, psi	900	910	780	720
Ultimate elongation, %	310	230	150	110
Set at break, %	8	6	16	6
Hardness, Shore A-2	52	58	77	71
Compression set "B" (post-cured 24 hrs. at 300°F.)	12	21	34	27
Gehman T_{10}, °F.	-16	-20	-20	-26
ASTM brittle point, °F.	-28	-29	-26	-33
Volume increase, 38 hrs. at 77°F.				
in 70:30 isooctane:toluene	17	8	6	10
benzene	25	25	21	26
acetone	220	205	150	160
ethyl acetate	280	205	170	170
water (212°F.)	20	14	11	18
AGED 100 HOURS IN AIR AT 350°F.				
Weight loss, %	3.7	4.4	5.3	6.4
Tensile strength, psi	190	320	280	290
Ultimate elongation, %	245	160	40	45
Set at break, %	37	19	12	6
AGED 100 HOURS IN PENOLA TURBO OIL #15 AT 400°F.				
Tensile strength, psi	360	330	370	470
Ultimate elongation, %	205	105	75	50
Set at break, %	11	6	11	6

* Contains about 40 parts of carbon black; others, 35 parts

Approved for Public Release

Contrails

4. 3(ω-Chloroperfluoroethoxy 1,1-dihydroperfluoropropyl acrylate

A new fluorine-containing acrylate monomer, 3(ω-chloroperfluoroethoxy 1,1-dihydroperfluoropropyl acrylate (Cl-FEFPA) was prepared by conversion of γ(β-chloro perfluoroethoxy) perfluoropropionyl fluoride to the methyl ester, reduction to the 1,1-dihydro alcohol, and conversion to the acrylic ester. It was discovered later that the monomer contained a considerable amount, approaching 50 mole percent, of 3(ω-hydroperfluoroethoxy 1,1-dihydroperfluoropropyl acrylate. The reason for this is that some of the chlorine was abstracted and replaced by hydrogen in the lithium aluminum hydride reduction of the ester to the alcohol. The monomer also contained approximately 0.2% of acrylic acid. It polymerized readily in the standard emulsion recipe (see Appendix 2) to a high molecular weight rubbery polymer. Properties of the gum rubber were as follows:

Inherent viscosity (Vistex method)	2.5
Glass transition temperature	-94°F.
General appearance: white, highly elastic, snappy, somewhat tacky	

The polymer was compounded and cured, first using the silicate recipe (see Appendix 3) for very preliminary evaluation of low temperature flexibility and solvent resistance, then using the standard amine recipe (see Appendix 1) for more complete evaluation. Properties of the vulcanizates are given in Table IV along with comparative data for other fluorine-containing acrylate rubbers which have been synthesized under this contract.

The amine vulcanizate was short and tensile strength was rather poor. The over-cure may be due to the relatively high acrylic acid content of the copolymer.

A slight improvement in properties (tensile strength 780 psi, elongation 225%) was achieved by reducing the triethylene tetramine to 0.85 parts by weight in the standard recipe (see Appendix 1).

Approved for Public Release

Approved for Public Release

TABLE IV
FLUORINE-CONTAINING ACRYLATES

Polymer Designation	1F4	2F4	FEFPA	H-FEFPA	Cl-FEFPA*
Structure	$-CH_2-CH-$ $C=O$ O $C_3F_7-CH_2$	$-CH_2-CH-$ $C=O$ O $CF_3OCF_2CF_2CH_2$	$-CH_2-CH-$ $C=O$ O $CF_3CF_2OCF_2CF_2-CH_2$	$-CH_2-CH-$ $C=O$ O $HCF_2CF_2OCF_2CF_2-CH_2$	$-CH_2-CH-$ $C=O$ O $ClCF_2CF_2OCF_2CF_2-CH_2$
% Copolymerized Acrylic Acid	0.15	0.03	?	0.05	0.2
Inherent Viscosity	2.5	1.85	0.95	3.6	2.5

Properties of Vulcanizate	Amine	Silicate	Amine	Silicate	Amine	Silicate	Amine	Silicate	Amine	Silicate
F_{100} psi	320	-	210	-	280	-	200	-	445	-
F_{200} psi	660	-	475	-	550	-	490	-	-	-
F_{300} psi	1080	-	785	-	-	-	850	-	-	-
Ultimate Strength, psi	1200	720	970	-	700	-	900	-	710	-
Elongation, %	350	200	370	-	300	-	310	-	175	-
Set at Break, %	10	-	7.5	-	-	-	8	-	6.2	-
Hardness Shore A-2	55	-	52	-	-	-	52	-	73	-
Low Temperature Properties										
Gehman T_{10}, °F	+12	-	-11	-	-12	-17	-16	-38	-31	-33
Scott Brittle Pt., °F	+ 7	-	-33	-	-42	-44	-28	-54	-44	-49
Tg of Gum, °F	-22		-67		-88		-88		-94	

*Actually a Cl-FEFPA:H-FEFPA Copolymer

TABLE IV (Continued)
FLUORINE-CONTAINING ACRYLATES

		1F4		2F4		FEFPA		H-FEFPA		Cl-FEFPA	
		Amine	Silicate	Amine	Silicate	Amine	Silicate	Amine	Silicate	Amine	Silicate
Volume Swell,%, 48 hrs. 77°F	70:30 Fuel	17	12	9	-	26	16	17	5	16	17
	benzene	26	23	13	-	21	18	25	27	27	36
	acetone	90	85	41	-	35	34	220	450	141	370
	eth. acetate	100	105	48	-	43	-	280	-	155	-
	eth. alcohol	-	0	3	-	-	-	-	-	13	-
70 hrs. 212°F, water		30	300+	37	-	38	320	20	330	12	295
Properties after 100 hrs. at 350°F in Air											
Tensile Strength, psi		350		150		105		190		365	
Ultimate Elongation, %		270		240		50		245		120	
Weight Change, %		- 4.5		- 3.3		- 5.3		- 3.7		- 6.85	
Properties after 100 Hrs. at 400°F in Turbo Oil #15											
Tensile Strength, psi		600		670		400		360		535	
Ultimate Elongation, %		160		200		120		205		60	
Volume Change, %		0		- 6		0		-		- 7.2	

Approved for Public Release

Contrails

Several high molecular weight polymers containing various amounts of copolymerized acrylic acid were prepared from the mixed monomer and cured in the standard amine recipe (see Appendix 1). As with other fluorine-containing alkoxy acrylates, the best cure was obtained with a very minor amount of copolymerized acrylic acid. However, the physical properties of the vulcanizates were only mediocre (see Table V).

The Cl-FEFPA vulcanizate shows the improved low temperature properties, relative to 1F4, characteristic of the other fluorine-containing alkoxy acrylates. Resistance to aromatic fuels and diester lubricants is excellent, but it swells somewhat more than the 1F4 vulcanizate in oxygenated solvents. Dry heat resistance is comparable to that of 1F4.

Approved for Public Release

Approved for Public Release

TABLE V

VULCANIZATION OF ω-CHLORO FEFPA POLYMERS

% Acrylic Acid in Monomer Charge	Inherent Viscosity* $\langle\eta\rangle$	Properties of Unaged Vulcanizate F_{100} PSI	F_{Break} PSI	Elongation to Break %	Remarks
0.02	2.44	225	800	300	Best mechanical properties, but tensile strength is low. Snappy rubber.
0.075	2.76	105	525	440	Weak vulcanizate.
0.115	2.43	120	680	450	Weak vulcanizate.
0.2	2.5	455	710	175	Snappy vulcanizate, but poor elongation.
1.0	2.1	95	460	360	Weak vulcanizate. Very strong odor.

* In 2:1 acetone:methyl perfluorobutyrate.

Confidential

Contrails

5. 5-Chloro-5,4,4-trifluoro-3-thiapentyl acrylate, (I), ($CFHClCF_2SCH_2CH_2O\overset{O}{\overset{\|}{C}}CH=CH_2$), and

6. 6,6,6,5,4,4-hexafluoro-3-thiahexyl acrylate, (II), ($CF_3CFHCF_2SCH_2CH_2O\overset{O}{\overset{\|}{C}}CH=CH_2$) were polymerized in a conventional emulsion recipe (see Appendix 2) to rubbery, high molecular weight polymers. Inherent viscosities and glass transition temperatures were as follows:

	I	II
$\langle \eta \rangle$ (in acetone)	3.22	1.41
T_g	-51°F.	-63°F.

After compounding and curing in the oxide recipe shown in Appendix 4, the following low temperature flexibility and volume swell properties were obtained:

	I	II
Gehman flexibility, T_{10}	+2°F.	+2°F.
ASTM Brittle Point	0° to -4°F.	-6°F.
Volume Swell, %		
Benzene	345	216
Turbo Oil	282	260
Skydrol	495	310
70:30 Fuel	25	29

It was concluded that these elastomers do not show sufficient solvent resistance to warrant further effort.

7. 6,6,6,5,5,4,4-Heptafluorohexyl acrylate was also polymerized in the emulsion recipe of Appendix 2. The inherent viscosity was 2.3 and the glass transition temperature approximately -40°F. The polymer was compounded in the amine recipe of Appendix 1 and given a 30 minute cure at 310°F. after the customary 24 hour rest period. No vulcanization occurred. After prolonged heating at 350°F. the compound became short but had no strength. Trimene base and dicumyl peroxide were also ineffective curatives at 310°F.

Approved for Public Release

Contrails

A cure was obtained using an oxide recipe (see Appendix 4) but it was short and weak. Properties were as follows:

Modulus at 100% elongation	330 psi
Tensile strength	400 "
Elongation at break, %	160
Set at break, %	28
Gehman Flexibility, T_{10}	12°F.
ASTM Brittle Point	21°F.
Volume swell, 48 hrs. at 77°F.	
70:30 fuel	6.5%
benzene	21%
acetone	111%

It is difficult to judge the resistance of the vulcanizate to high temperature air or Turbo Oil aging because the cure continues and causes embrittlement.

Approved for Public Release

Contract

FLUORINE-CONTAINING DIENE COPOLYMERS

1. Perfluorobutadiene:Vinyl 1,1-Dihydroperfluorobutyl Ether Copolymer

A comprehensive evaluation of this copolymer was begun during the preceding contract period and completed early in the period covered by this report (results are given in Table VI). The carbon filled amine vulcanizate shows good stability in air at 400°F. It is difficult to judge the performance in hot turbo oil relative to that of 1F4 or 2F4 because the initial properties are inferior to those of the acrylates. Percentage-wise, the decrease in tensile strength is somewhat greater and the decrease in elongation about the same.

All samples prepared to date have been more or less crosslinked during polymerization. Efforts to reduce crosslinking have been rewarded with only minor success, but this should not be an insurmountable obstacle. No further work is planned for the immediate future unless specifically requested by WADC.

Approved for Public Release

Contrails

TABLE VI

Evaluation of FBd:VFBE(3:1) Copolymer*

Copolymer	100
Philblack O	35
Triethylene tetramine	1.0

Cure: 60 min. at 310°F.

ORIGINAL PROPERTIES	
Tensile strength, psi	790
Ultimate elongation, %	60
Set at break, %	0
Hardness, Shore A-2	82
Compression set "B" (post-cured 24 hrs. at 300°F.)	39
Gehman T_{10}, °F.	+30
ASTM brittle point, °F.	+43
Volume increase, %, 48 hrs. at 77°F. in	
70:30 isooctane:toluene	16
benzene	20
toluene	20
acetone	87
methyl ethyl ketone	105
ethyl acetate	120
ethyl alcohol	7
water (70 hrs. at 212°F.)	18

AGING IN AIR AT 400°F.	100 Hrs.	195 Hrs.	265 Hrs.
Weight loss, %	7.8	11.3	13.4
Tensile strength, psi	820	810	670
Ultimate elongation, %	40	30	10
Set at break, %	0	0	0

AGING IN TURBO OIL #15 AT 400°F.	50 Hrs.	100 Hrs.	195 Hrs.	265 Hrs.
Volume increase, %	0	9	6	14
Tensile strength, psi	490	270	115	130
Ultimate elongation, %	50	40	0	0
Set at break, %	0	13	0	0

AGING IN CALIFORNIA RESEARCH OIL #52742 AT 400°F.	100 Hrs.
Volume increase, %	3
Tensile strength, psi	750
Ultimate elongation, %	20
Set at break, %	0

*NOTE: The monomer charge ratio has been maintained at 3 mols FBd to 1 mol VFBE. At 56% conversion, fluorine analysis indicated the copolymer composition was 0.45 mol FBd to 0.55 mol VFBE. The copolymer of this composition was used above and in most of the earlier work.

Approved for Public Release

Contrails

2. Copolymer of Perfluoropropene and Vinyl 1, 1-Dihydro-perfluorobutyl Ether, (VFBE)

This is a difficult system to control and no products of interest have been obtained. VFBE enters the copolymer preferentially, and introduction of a substantial amount of perfluoropropene into the copolymer requires a high ratio of perfluoropropene to VFBE during polymerization (see WADC Technical Report 52-197, Part 6). However, the resulting copolymers are then more plastic than rubbery.

3. Copolymerization of 1,4 Perfluoropentadiene*

Attempts were made to copolymerize 1,4 perfluoropentadiene with (1) vinyl 1,1-dihydroperfluorobutyl ether (VFBE); (2) vinyl acetate; (3) vinyl n-butyl ether; and (4) styrene. Copolymers were obtained with (1) and (2), but not with (3) and (4).

The copolymers of perfluoropentadiene and VFBE (monomer ratios 3:1 and 1:1) were plastic rather than rubbery, but it was of some interest that they did not crosslink excessively as did the perfluorobutadiene:VFBE copolymers described in the preceding Report No. 29.

*Monomer supplied by Dr. J. D. Park, University of Colorado, Boulder, Colorado.

Approved for Public Release

Contrails

FLUORINATED SILANES, $R_fC_2H_4Si(CH_3)(OC_2H_5)_2$

Hydrolysis by Acid Catalysis

Two of the subject silanes, one having $R_f = CF_3$-, the other $R_f = C_8F_{17}$-, have been prepared. Hydrolysis of either silane in refluxing 10% aqueous HCl yields 90-95% of a slightly viscous polysiloxane oil showing weak hydroxyl absorption bands in the infrared (see Table VII). When the reaction is run for 4 hours, the usual practice, the products show no ethoxy-silane bands. Room temperature acid hydrolysis of the C_8F_{17} silane produces a water swollen gel which condenses to the familiar polysiloxane oil on drying over P_2O_5 at room temperature. The solid intermediate is believed to be the silane-diol. The following reactions are probably involved:

$$C_8F_{17}C_2H_4Si(CH_3)(OC_2H_5)_2 + 2H_2O \xrightarrow{HCl} C_8F_{17}C_2H_4Si(CH_3)(OH)_2 + 2C_2H_5OH$$

$$nC_8F_{17}C_2H_4Si(CH_3)(OH)_2 \rightleftharpoons (C_8F_{17}C_2H_4Si(CH_3)O)_n + nH_2O$$

Hydrolysis by Base Catalysis

The silanes were hydrolyzed for 4 hours in refluxing 10% aqueous KOH. The CF_3 hydrolysate dissolved as the potassium silanolate salt in the aqueous medium. Acidifying the solution gave an insoluble oil which, on drying, gave a product which was distinguishable from the hydrolysate prepared with refluxing 10% HCl only in that it showed higher hydroxyl absorption. Titration of the aqueous phase for fluoride ion indicated that 0.3% of the original fluorine was lost. In the base catalyzed hydrolysis of the C_8F_{17}-silane, the starting silane was recovered almost quantitatively.

Typical results of acid and base catalyzed hydrolysis are given in Table VII.

Approved for Public Release

Approved for Public Release

TABLE VII

Hydrolysis of $R_fC_2H_4Si(CH_3)(OC_2H_5)_2$

R_f Run Number	Hydrolytic Medium	Temp.	Poly-siloxane yield (%)	$n_D^{77°F}$	Analysis Theoretical %C	Analysis Theoretical %F	Analysis Found %C	Analysis Found %F	Infrared Analysis
CF_3 #1	10% HCl	Reflux	80	1.3731	30.8	36.6	30.5	38.4	Medium OH band, no SiOEt.
#2	10% HCl	Reflux	94	1.3726			30.5	35.6	Weak OH band. No SiOEt.
#3	10% HCl	Reflux	94	1.3748			-	-	Weak OH band. No SiOEt.
#4	10% KOH	Reflux	60	1.3740			-	-	More OH than other samples. No. C=C.
C_8F_{17} #1	10% HCl	Reflux	91	1.3381	26.1	63.8	25.7	63.2	No OH, or SiOEt detected.
#2	10% KOH	Reflux	Ca. 5	-			27.8	61.1	Not run.

$n_D^{77°F}$ of CF_3 monomer = 1.3651.

$n_D^{77°F}$ of C_8F_{17} monomer = 1.3396.

Contrails

Distillation of CF_3 Silane Hydrolysate

A small sample of a CF_3 hydrolysate was distilled through a 5" column filled with Hasteloy Heli-Pak. Distillation data are given in Table VIII. No boiling point plateaus were obtained and the fractionation was undoubtedly very inefficient. Slow dehydrofluorination occurred throughout the 16 hour distillation, as evidenced by the condensation of an acid material and the etching of the liquid air-cooled pyrex trap.

Infrared curves showed trace -OH (silanol or water) absorption in all cuts and weak bands at 5.75 μ, possibly due to the following unsaturation: $(CF_2=CHCH_2\dot{S}i\ (CH_3)O\rightarrow_n$. However, carbon and fluorine analyses are so close to theoretical for all but the residue that the degree of unsaturation in the distillates must be very low. Titration with Karl Fisher reagent, which determines total water + silanol,[1] gave values close to 0.1% in all cases.

Extensive decomposition of the hydrolysate did not occur until a pot temperature of 554°F. was reached. At this point, discoloration and gas evolution (probably chiefly HF) became quite rapid. The pot residue was still soluble in ether, however, at the end of the distillation.

The best guess at this point is that the distillate is composed of cyclic trimer, tetramer and pentamer. Boiling points of 210°F./3 mm. and 288°F./3 mm., and refractive indices of 1.3658 and 1.3715 for the cyclic trimer and tetramer, respectively, have been reported.[2]

1. H. Gilman & L. S. Miller, J.A.C.S., 73, 2367 (1951)

2. G. B. Butler, R. Dunmire, G. W. Dyckes, and P. Tarrant. Paper presented at the American Chemical Society Meeting in Atlantic City, September, 1956.

Approved for Public Release

Approved for Public Release

TABLE VIII

Distillation of CF_3 Hydrolysate

Cut #	Vapor Temp. (°F./mm.)	Yield (g.)	$n_D^{73°F.}$*	Theoretical %C	Theoretical %F	Found %C	Found %F	Nature of Product	Infrared Analysis
1	208-252° /1-3 mm.	2.22	1.3700	30.8	36.6	30.8	35.5	colorless, thin oil	Trace of OH. Strong band at 9.85μ. Weak band at 5.75.
2	219-250° /1.5-2.0	5.93	1.3711			30.7	36.1	colorless, thin oil	Trace of OH. Weak band at 9.85. Weak band at 5.75.
3	252-284° /1.5-2.0	2.38	1.3749			30.7	36.5	colorless, thin oil	Similar to Cut #2.
Residue	-	3.62	1.3785			30.5	33.9	Brown, viscous, ether-soluble oil	No OH. Weak band at 9.85. Medium band at 5.75, weak one at 5.85

* $n_D^{73°F}$ = 1.3745 for the original hydrolysate.

Contrails

Polymerization

Tetramethylammonium hydroxide was the catalyst chosen for most of the polymerization studies conducted, because of its high reactivity in polymerizing octamethyl cyclotetrasiloxane (D_4) and its ready solubility in the fluorinated silane hydrolysates at room temperature. The usual method of conducting runs was to charge the catalyst in the desired amount as a 10% aqueous solution to the reaction vessel. The base was then dried to a crystalline hydrate containing about 30% water by evacuating the vessel with an oil pump for several hours at 122°F. The silane hydrolysate was then added and the mixture was stirred vigorously in an almost completely sealed system at the desired temperature. D_4 could be readily bulk polymerized to an attractive gum by this technique, using 0.1 part $(CH_3)_4NOH$ in 2 hours of reaction at 149°F. The results of some D_4 polymerizations are given below:

Monomer Conc.(%)	$(CH_3)_4NOH$ Conc.(parts)	Temp. (°F.)	Time (hrs.)	$\langle n \rangle$	Nature of Product
100	0.1	140	2.0	0.60	Attractive gum.
100	1.0	140	7.0	0.62	Gum is very short; soluble in C_6H_6.
57	0.1	176	1.5	0.52	Attractive gum.
67	1.0	176	0.3	0.12	Very viscous fluid
			1.0	0.13	Very viscous fluid
			3.0	0.14	Very viscous fluid
			18.0	0.21	Very soft gum

In the solution polymerizations the catalyst was added as a 10% aqueous solution to benzene and the monomer was added following the removal of the water by azeotropic distillation. The reactions were run with vigorous stirring at reflux. It was found by titration with standard HCl that 90% of the base was present at the end of the reaction with 0.1 part catalyst.

The product prepared in benzene solution using 0.1 part catalyst was found to give very satisfactory results as a silicone rubber base.

Samples of CF_3 silane hydrolysate, cuts #1, 2 and 3 (see Table VIII), could be polymerized to extremely viscous oils within 10 minutes by reaction with 1 part of $(CH_3)_4NOH$ at 140°F. No further polymerization occurred when the reactions

Approved for Public Release

Contrails

were continued for several days. Variation of catalyst concentration and reaction temperature were ineffective in producing products of higher molecular weight. It was found that raising the temperature from 140° to 176°F. caused an irreversible reversion to a considerably thinner oil.

The reaction of the CF_3 silane hydrolysate with 5 parts of $(CH_3)_4NOH$ was studied at 140°F. It was found by titrating an aliquot sample of the mixture that 23.9% (1.20 parts) of the base was consumed in the first 5 minutes. No further destruction of the catalyst occurred on continuing the reaction for 18 hours at 140°F.

The same CF_3 hydrolysate was used in a benzene solution polymerization similar to that used in the D_4 reactions. Three portions of $(CH_3)_4NOH$, each 1 part per 100 parts of hydrolysate, were added incrementally, spaced over 3 hour intervals, to a 50% solution of the hydrolysate. Water was removed azeotropically after each addition and benzene was replenished intermittently to maintain approximately 50% monomer concentration. The catalyst dissolved very readily at reflux temperature.

A brown precipitate was formed continuously throughout the reaction. Base was still present one hour after the final catalyst addition, but disappeared 2 hours later. The reaction was stopped at this point. The precipitate, which was water-soluble, is believed to have been tetramethylammonium fluoride.

In every hydrolysis the product was turbid, and OH absorption in the infrared indicated entrapped water or uncondensed silanol end groups. A CF_3 hydrolysate was treated with anhydrous K_2CO_3 according to a patented procedure[3] to condense completely all silanol groups, remove the water, and neutralize any possible acidic impurity. (No siloxane rearrangement occurs in this treatment.) Twelve g. of hydrolysate (n_D^{73}= 1.3741) and 1 g. of K_2CO_3 were heated at 284°F. under 3 mm. pressure. An appreciable amount of water was split out. The mixture was filtered to recover the perfectly clear siloxane (n_D^{73} = 1.3763). The compound was reacted at 140°F. with 0.1, 1 and 2 parts of $(CH_3)_4NOH$. In the latter two cases there was appreciable thickening of the oil in the first 10 minutes, but no further change occurred in 18 hours.

3. J. J. Duane, U.S. 2,744,923 (to Union Carbide), 1956.

Approved for Public Release

Contracts

The product of the reaction with 2 parts catalyst was mixed with a large volume of water. An aliquot of this was titrated and it was found that 44% (0.88 part) of the base had been neutralized. The remainder of the water extract contained only 40% of the theoretical fluoride ion expected if the consumed base had been neutralized by the splitting out of HF.

These results indicated that the initiation step for the polymerization of the CF_3 silane hydrolysate occurred very rapidly when $(CH_3)_4NOH$ was used as the catalyst. Failure to obtain higher molecular weight products was believed to be due to one or more of the following factors: (1) the existence of an unfavorable equilibrium between cyclic and linear polysiloxanes; (2) stability of silanol end groups produced during the rearrangement reaction; and (3) a rapid termination reaction involving the recombination of the active anion with the $(CH_3)_4N^+$ cation. (The fact that an acid, presumably HF, is split out during the polymerization and partially neutralizes the catalyst is a complicating, but not a limiting, factor in the reaction.) Time did not permit the investigation of these factors. It is most likely that the second factor, i.e., silanol stability, is the important one in limiting molecular weights obtained in these experiments. If that is true, it would be essential to operate under anhydrous conditions, or well above 212°F.

An attempt was made to determine whether the C_8F_{17} silane hydrolysate was subject to rearrangement with $(CH_3)_4NOH$. The classical method of preparing chain-blocked polysiloxane oils was adapted to the use of $(CH_3)_4NOH$ in these reactions.[4]

D_4 was reacted with 2.5 parts hexamethyldisiloxane and 5 parts $(CH_3)_4NOH$ for 24 hours at 176°F. in a control experiment to yield an oil which, after purification, had a viscosity of 89 cs. at 100°F. and a viscosity index of 151 (vs. η 100 = 1.8 cs. and V.I. = 107 for D_4 itself). The C_8F_{17}-hydrolysate was reacted with 5.9 parts hexamethyldisiloxane and 5.5. parts $(CH_3)_4NOH$ for 24 hours at 176°F. The purified product had a viscosity of 97.9 cs. at 100°F. and a V.I. = 59 (vs. η 100 = 119 cs. and a V.I. of 4.8 for the C_8F_{17} hydrolysate). It is believed that the reaction was successful in converting the largely cyclic C_8F_{17}-hydrolysate to a linear polymer. Since the experiment involved the use of one $(CH_3)_3Si-$ group per 2.5 C_8F_{17}-siloxane groups, it was expected that the linear product would have a higher V.I. than the starting material, but not a higher bulk viscosity. It is possible that such materials may have utility as non-flammable, thermally stable oils.

4. D. F. Wilcock and W. Patnode, J.A.C.S. 68, 358 (1946)

Approved for Public Release

Contrails

Many other catalysts were tried in attempts to polymerize the fluorinated silane hydrolysates. These included H_2SO_4, KOH, CsOH, potassium silanolates, sodium methoxide, sodium hydride, lithium aluminum hydride, benzyl trimethylammonium methoxide, trimethylamine borane salt, nitrosyl fluorosulfonate, sodium 1,1-dihydroperfluorobutoxide, trifluoromethane sulfonic acid and sodium borohydride. The reactions were carried out using vigorous agitation in partially sealed 4 ml. test tubes or 25 ml. flasks, except in a few cases where other conditions are specified. In all cases, control experiments were run using D_4. All data are given in Table IX.

The only reaction to yield a solid fluorinated polysiloxane was the one run with lithium aluminum hydride. A product, the consistency of molding clay, was formed when the reaction mixture was allowed to stand at room temperature for 6 months in a sealed tube, following a 6-hour reaction at 230°F. (The control run with D_4 failed to yield a solid product under the same conditions.) The product was highly crosslinked and insoluble. An infrared curve showed no loss of C-F absorption band intensity. The curve for the Si-O-Si absorption region (9-10μ) approximated that found for Silastic LS-53* more closely than it did the low molecular weight CF_3 siloxane oils. Subsequent attempts to polymerize samples of CF_3 hydrolysates, which had previously been dehydrated with K_2CO_3, using lithium aluminum hydride and sodium borohydride, failed to yield solid products. The CF_3 or C_8F_{17} siloxane oils could be vulcanized to soft, spongy solids by irradiation using a megavolt General Electric electron beam generator. However, dosages of 250-300 megareps were required and, as expected, the products had poor properties because of their low primary molecular weights.

*Fluorine-containing siloxane rubber produced by Dow-Corning Corporation.

Approved for Public Release

Approved for Public Release

TABLE IX

Polymerization of Silane Hydrolysates

Run No.	Monomer	Catalyst	Cat.* Conc.	Reaction Conditions (Temperatures in °F.)	Results
C_8F_{17}#1-1	C_8F_{17}Hydrolysate	conc. H_2SO_4	0.7	20.5 hrs. at 293° in sealed ampoule	No polymerization. Extensive charring. Catalyst insoluble.
C_8F_{17}#1-2	C_8F_{17}Hydrolysate	KOH	0.2	Same	No change. Catalyst insoluble.
C_8F_{17}#1-3	" plus octamethyl cyclotetra-siloxane (D4)	conc. H_2SO_4	0.4	Same	Copolymerization to a one-phase viscous oil. Monomers were immiscible orginally at 293°F.
C_8F_{17}#1-4	Same as 1-3	KOH	0.1	Same	Two liquid phases, no copolymerization. Only D4 showed any viscosity increase.
D4 #1	D4	conc. H_2SO_4	1.3	4 hrs. at room temp. in sealed ampoule	Polymerization to soft rubber.
D4 #2	D4	KOH	0.3	8 hrs. at 293° in sealed ampoule	Polymerization to a soft gum.
CF_3 #1-1	CF_3 Hydrolysate	conc. H_2SO_4	1	6 hrs. at 248°, 14 hrs. at 356°	No change. Catalyst insoluble.
D4 #3	D4	KOH	0.4	15 min. at 275°	Viscous oil used as catalyst in D4 #4.
D4 #4	D4	Product of D4 #3	5 pts.	10 min. at 320°	Polymerization to a soft rubber.
CF_3#2-1	CF_3 Hydrolysate	Product of D4 #3	10 pts.	7 hrs. at 356°	Fluid oil at 356°F, somewhat viscous at r.t.
D4 #5	D4	CsOH	2	1.3 hrs. at 356°	Polymerization to a gel.

TABLE IX (Continued)

Polymerization of Silane Hydrolysates

Run No.	Monomer	Catalyst	Cat.* Conc.	Reaction Conditions (Temperatures in °F.)	Results
CF_3 #2-2	CF_3 Hydrolysate	CsOH	2	3 hrs. at 356°	Fluid at 356°F, very viscous oil at r.t. Catalyst insoluble.
CF_3 #2-3	CF_3 Hydrolysate	KOH	2	5.3 hrs. at 356°	Fluid at 356°F, very viscous oil at r.t. Catalyst insoluble.
CF_3 #2-4	CF_3 Hydrolysate	CsOH	1	3.5 hrs. at 356°	Fluid at 356°F, viscous oil at r.t. Not as viscous as #2-2.
CF_3 #2-5	CF_3 Hydrolysate	H_2SO_4	2	6 hrs. at 356°	Fluid at 356°F, slightly viscous at r.t. Somewhat charred. Catalyst insoluble.
D4 #6	D4	Product of CF_3#2-3	5 pts.	5 min. at 356°	Polymerization to soft rubber.
CF_3#2-6	CF_3 Hydrolysate	Same	5 pts.	5.5 hrs. at 356°	Fluid at 356°F, slightly viscous oil at r.t.
D4 #7	D4	benzyl** trimethyl ammonium methoxide	2	3 hrs. at 356°	Slightly viscous. Catalyst decomposed.
CF_3#2-7	CF_3 Hydrolysate	CsOH	5	4.3 hrs. at 356°	Fluid at 356°F, viscous oil at r.t.
D4 #8	D4	$(CH_3)_3N.BH_3$***	2 pts.	1.3 hrs. at 257-275°	Polymerization to a soft rubber.
D4 #9	D4	benzyl ** trimethyl ammonium methoxide	2	2.5 hrs. at 275°	Slightly viscous oil at r.t.
D4 #10	D4	$NOSO_3F$	2 pts.	1.8 hrs. at 356°	Slightly viscous oil at r.t. Brown, flocculent ppt.

Approved for Public Release

Approved for Public Release

TABLE IX (Continued)
Polymerization of Silane Hydrolysates

Run No.	Monomer	Catalyst	Cat.* Conc.	Reaction Conditions (Temperatures in °F.)	Results
D4 #11	D4	NaH	3	3.3 hrs. at 356°	Very viscous oil at 356°F, soft gum at r.t. Catalyst is insoluble.
CF_3#2-9	CF_3 Hydrolysate	NaH	3	3.3 hrs. at 356°	Very viscous oil at r.t. NaH is insoluble.
D4 #12	D4	$NaOCH_3$	2	5.5 hrs. at 356°	Slightly viscous oil at r.t. Catalyst insoluble.
CF_3#2-10	CF_3 Hydrolysate	Na as $NaOCH_2C_3F_7$	1 pt.	4 hrs. at 230°	No change. Catalyst is soluble at 230°F.
CF_3#2-11	CF_3 Hydrolysate	Same	1 pt.	3 days at 122°, 4 days at 257°	Same.
D4 #14	D4	$C_8F_{17}SO_3H$	0.4	10 min. at 248°	Polymerization to firm gum.
CF_3#1-2	CF_3 Hydrolysate	$C_8F_{17}SO_3H$	0.4	18 hrs. at 203-257°	Slightly viscous, dark oil. Catalyst insoluble.
D4 #15	D4	$LiAlH_4$	1	6 hrs. at 230° 6 mos. at r.t.	No apparent reaction. Catalyst insoluble.
CF_3#1-3	CF_3 Hydrolysate	$LiAlH_4$	ca. 5	6 hrs. at 230° 6 mos. at r.t.	No apparent reaction at 230°F. Standing for 6 mos. at r.t. yielded a clay-like solid. Catalyst is insoluble.
D4 #16	D4	CF_3SO_3H	1	2 hrs. at r.t.	Polymerization to an attractive gum.
CF_3#3-1	CF_3 Hydrolysate	CF_3SO_3H	1	6 hrs. at 252-310°	No reaction. Catalyst was soluble.
CF_3#11-5	CF_3 Hydrolysate	$NaBH_4$	0.2	24 hrs. at 194-284°	No reaction. Catalyst insoluble.
CF_3#11-6	CF_3 Hydrolysate	$NaBH_4$	1	24 hrs. at 194-284°	No reaction. Catalyst insoluble.

TABLE IX (Continued)
Polymerization of Silane Hydrolysates

Run No.	Monomer	Catalyst	Cat.* Conc.	Reaction Conditions (Temperatures in °F.)	Results
CF_3#11-7	CF_3 Hydrolysate	$LiAlH_4$	0.2	3 days at 194°	No reaction. Catalyst insoluble.
CF_3#11-8	CF_3 Hydrolysate	$LiAlH_4$	1.0	3 days at 194°	Viscous oil produced.

* Parts per 100 parts monomer.

** Obtained as 40% methanol solution from Summer Chemical Co. Methanol pumped off prior to reaction

*** Obtained from Callery Chemical Co.

Approved for Public Release

Contrails

Copolymerization of $R_fC_2H_4Si(CH_3)(OC_2H_5)_2$ with Dimethyl Siloxane

The most common methods of copolymerizing silanes involve the polymerization of either the cohydrolysate or a mixture of the separate hydrolysates. Both methods have been tried.

a. Polymerization of Cohydrolysate

A 2:3 mixture, by weight, of $CF_3C_2H_4Si(CH_3)(OC_2H_5)_2$ and $(CH_3)_2Si(OC_2H_5)_2$ (29.9 mole % CF_3 silane) was hydrolyzed by dropwise addition to refluxing 10% HCl. After purification, a 49% yield of a somewhat viscous oil, $n_D^{77°F.} = 1.3888$, was obtained. The product contained 18.5% F (32 mole % $CF_3C_2H_4Si(CH_3)O$). It could be polymerized to the gum stage by reaction with 1% tetramethylammonium hydroxide for 3 hours at 140°F.

A mixture of equal parts by weight of $C_8F_{17}C_2H_4Si(CH_3)(OC_2H_5)_2$ and $(CH_3)_2Si(OC_2H_5)_2$ (20.4 mole % C_8F_{17} silane), was hydrolyzed in a similar manner. A 72% yield of a somewhat viscous oil was obtained, $n_D^{77°F.} = 1.3580$. The product contained 47.6% (30.0 mole % $C_8F_{17}C_2H_4Si(CH_3)O$). An attempt to polymerize this product to the gum stage with 1% $(CH_3)_4NOH$ for 24 hours at 140°F. failed.

b. Copolymerization of Mixed Hydrolysates

A mixture of 1 equivalent of $C_8F_{17}C_2H_4\dot{S}i(CH_3)O-$, in the form of its hydrolysate, and 8 equivalents of $(CH_3)_2\dot{S}iO-$, in the form of D_4 was copolymerized to a gum by reaction with 1% $(CH_3)_4NOH$ for 24 hours at 140°F. The product was separable into two soluble gum fractions containing 21.3% F (6.8 mole % C_8F_{17} siloxane) and 35.5% F (15.5 mole % C_8F_{17} siloxane). When the fluorinated siloxane charge was increased to 20 mole %, the mixture could not be polymerized using the same conditions.

These common techniques of copolymerization suffer in the compositional heterogeneity of the products formed. In the case of cohydrolysis, the dimethyl silane is far more water soluble and undoubtedly hydrolyzes at a considerably higher rate than does the fluorinated silane. Copolymerization of the mixed hydrolysates would also be expected to yield heterogeneous products due to the different reactivities of the respective hydrolysates.

Approved for Public Release

Contrails

More satisfactory results have been obtained using the method described below.

c. Condensation of Fluorinated Silanes with Dimethyldichlorosilane

This reaction involves the condensation of the fluorinated diethoxysilane with dimethyldichlorosilane in an anhydrous system to split out ethyl chloride and form an intermediate siloxane oil, capable of being polymerized further. The reaction is as follows:

$$nR_fC_2H_4Si(CH_3)(OC_2H_5)_2 + n(CH_3)_2SiCl \xrightarrow[\text{reflux}]{1\%\ FeCl_3} \left(\begin{array}{c} C_2H_4R_f \\ | \\ Si \\ | \\ CH_3 \end{array} \text{—O—} \begin{array}{c} CH_3 \\ | \\ Si \\ | \\ CH_3 \end{array} \text{-O-}\right)_n + 2nC_2H_5Cl$$

The Servais patent[1] discloses an analogous process for copolymerizing hydrocarbon silanes.

The reaction using fluorinated silanes can be carried out by using any charge ratio between 33 and 67 mole % of the fluorinated silane. When the latter is used, the principal product is the trimer terminated with ethoxy groups. Many of these reactions have been run, and a typical experiment is described.

The following charge was made into a one-neck, 100 ml. flask:

41.4 g.	$CF_3C_2H_4Si(CH_3)(OC_2H_5)_2$	(0.180 mole)
11.6 g.	$(CH_3)_2SiCl_2$	(0.090 mole)
0.5 g.	anhydrous $FeCl_3$	

The dimethyl dichlorosilane used was the General Electric Company's SC-02. It was fractionated through a 60 plate column and a heart cut was taken which was only 1/3 of the distilled material, boiling at 157°F. (uncorrected). This was a precaution to assure that only difunctional silane was present in the samples used in the condensation reactions.

1. P. C. Servais, U.S. 2,485,928 (to Dow Chemical), 1949

Approved for Public Release

Contrails

The solution was refluxed (158°F) while stirring with a magnetic bar. Evolution of ethyl chloride started shortly after the attainment of reflux and continued for 15 minutes. The pot temperature was raised to about 212°F. and stirring was continued for an additional 2 hours. 9.46 g. of ethyl chloride was collected in a dry ice trap (81.5% of theoretical). The flask was then evacuated with a water aspirator and kept at about 248°F. for 2 hours in an attempt to remove unreacted silanes. The oily product had a refractive index of 1.378 at this point. Fifty ml. of 10% HCl was added to the flask and the mixture was stirred vigorously at reflux to hydrolyze all ethoxy end groups. (Similar treatment with 5% Na_2CO_3 is effective in hydrolyzing Si-Cl end groups, but does not remove all $SiOC_2H_5$ groups.) The mixture was neutralized with dilute NH_4OH to precipitate hydrated Fe_2O_3. The product was suction filtered and the oil was separated. The water layer was extracted with xylene hexafluoride and this extract was combined with the product. The solution was then extracted with dilute NH_4OH and several portions of water until the wash water was neutral to litmus and gave a negative chloride test. The solvent was taken off on a steam bath and the product was finally dried in vacuo at 140°F. A 29.4 g. yield (85% overall yield) of a fluid, straw-colored oil, n=1.383, was obtained. The product contained 29.4% F (66.0 mole % CF_3 siloxane). The infrared curve showed a very small -OH band, but no $SiOC_2H_5$ band. In two separate 1 g. runs, this product could be polymerized to soft gums using 1% $(CH_3)_4NOH$ as catalyst by stirring for 3 days at 140°F. However, two attempts to polymerize this intermediate on 10 g. scales failed to yield gums even after 10 days reaction, possibly due to the difficulty involved in stirring the viscous masses effectively.

Intermediates of the following compositions have been made by this process:

Run No.	Molar Charge Ratio R_f Silane/ $(CH_3)_2SiCl_2$	Ethyl Chloride Evolved (% of theoretical)	% Yield	$n_D^{77°F}$ after hydrolysis)	%F Theoretical	%F Found
CF_3#6	$1CF_3/1$	87	92	1.386	24.8	25.1
CF_3#8	$2CF_3/1$	81.5	85	1.383	29.6	29.4
CF_3#10	$2CF_3/1$	91	-	1.381	29.6	28.5
C_8F_{17}#3	$1C_8F_{17}/1$	-	83	1.351	55.8	54.8
C_8F_{17}#9	$1C_8F_{17}/2$	89	78	1.354	49.5	49.4
C_8F_{17}#10	$1C_8F_{17}/2$	83.5	82	1.353	49.5	50.0

Approved for Public Release

Contracts

Both the CF_3 intermediates, #6 and #8, could be polymerized with 1% $(CH_3)_4NOH$ to satisfactory gums. The former compound required only 6 hours of reaction at 140°F., while the latter required 3 days at 140°F. When the catalyst concentration was reduced to 0.5 part, reactions failed to yield gums even after 7 days at 140°F. We speculate that this difference may be attributable to a diminution in reactivity with increased fluorine content in the intermediate.

Neither of the intermediates made from the C_8F_{17} silane could be polymerized directly. However, it was found that the addition of 2 equivalents of dimethyl siloxane in the form of D_4 to the product of run #3, or the addition of 1 equivalent to #10, permitted copolymerization to homogeneous gums, each containing 44.4% fluorine (25 mole % C_8F_{17} siloxane). These reactions were carried out for 24-30 hours at 140°F. (using 1% $(CH_3)_4NOH$). Attempts to use 1 part of either KOH or CsOH failed to yield rubbery polymers in reactions with these intermediates at 212-302°F. The use of 1 part of CF_3SO_3H was successful in polymerizations run at 248°F. but yielded crosslinked gums.

Properties of the Copolymers and their Vulcanizates

The 1:1 $CF_3:(CH_3)_2$ and 1:3 $(C_8F_{17}:(CH_3)_2$ copolymer gums have glass temperatures below -166°F. Neither of these products is flammable. A sample of 1:1 $CF_3:(CH_3)_2$ gum was aged in air at 392°F. for 91 hours. It flowed badly and suffered 20% weight loss in the first hour, but only 2% in the subsequent period. The heavy weight loss at the outset was undoubtedly due to depolymerization caused by the $(CH_3)_4NOH$ residue. The catalyst appeared to be completely decomposed after the first hour, as evidenced by the disappearance of its odor from the sample. It now seems that the catalyst can be effectively removed by several reprecipitations of the copolymer from xylene hexafluoride solutions diluted with methanol.

A sample of the 1:3 $C_8F_{17}:(CH_3)_2$ gum was crosslinked by a high energy electron dose of 8 megareps and this was found by crude tests to swell about 60% in toluene and 210% in isooctane.

The 1:3 $C_8F_{17}:(CH_3)_2$ copolymer gum was compounded and cured in the recipe shown in Appendix 5. The vulcanizate was badly cracked and very weak. Swell in 70:30 fuel was 55%, in isooctane 60%, after 48 hours at room temperature.

The 2:1 $CF_3:(CH_3)_2$ copolymer gum and the above 1:3 $C_8F_{17}:(CH_3)_2$ copolymer were each cured in the recipe shown in Appendix 6. The cured materials again were badly cracked and very weak. The CF_3- rubber showed 32% swell in 70:30 fuel while the C_8F_{17}- rubber swelled 44% (48 hours immersion at room temperature).

Approved for Public Release

Contrails

SUMMARY AND CONCLUSIONS

The object of the research described in this report is the preparation and evaluation of fluorine-containing elastomers with very wide useful temperature ranges and resistance to a wide variety of solvents, hydraulic fluids, lubricants, and other liquids.

A twenty-pound sample of 3M Brand Fluoro-Rubber 2F4 was submitted to WADC at their request. It is substantially equivalent to 3M Brand Fluoro-Rubber 1F4 (formerly poly-FBA) in resistance to heat and solvents, but is superior to 1F4 in low temperature flexibility by some 30° to 40°F. Copolymerization with trace amounts of acrylic acid increases rate of cure and improves mechanical properties of amine vulcanizates. However, tensile strengths have been somewhat lower than typical values for amine-cured 1F4.

The polymers of 3-perfluoroethoxy 1,1-dihydroperfluoropropyl acrylate (FEFPA) and its ω-hydro analog (H-FEFPA) respond to amine curing in much the same way as 2F4 above. Preparation of these polymers does not look as attractive as it once did because of disappointing monomer yields in scale up.

A new member of the class of fluorine-containing alkoxy acrylates, -chloro perfluoroethoxy 1,1-dihydroperfluoropropyl acrylate,

$$ClCF_2CF_2OCF_2CF_2CH_2OCCH=CH_2 \ ,$$

has been synthesized. However, all of the 3(ω-chloroperfluoroethoxy) 1,1-dihydroperfluoropropyl acrylate polymer prepared to date has contained substantial amounts of copolymerized ω-hydro analog. Vulcanizates have low temperature flexibility comparable to that of other fluorine-containing alkoxy acrylates mentioned above. Solvent resistance compares with that of poly H-FEFPA, i.e., good resistance to 70:30 fuel and to diester lubricants, poor resistance to ketones. The pure monomer can be prepared and the homopolymer will be characterized.

Three other polymers of new fluorine-containing acrylate monomers were evaluated:

(I) 5-chloro-5,4,4-trifluoro-3-thiapentyl acrylate
(II) 6,6,6,5,4,4-hexafluoro-3-thiahexyl acrylate
(III) 6,6,6,5,5,4,4-heptafluorohexyl acrylate

Approved for Public Release

Contrails

(I) and (II) have low temperature flexibility properties superior to 3M Brand Fluoro-Rubber 1F4, but have poor fuel and solvent resistance. (III) has not been cured satisfactorily.

Copolymers of perfluorobutadiene and 1,1-dihydroperfluoro butyl vinyl ether have good heat resistance but are highly crosslinked and give vulcanizates with poor mechanical properties. The copolymerization of perfluoropropene and 1,1-dihydroperfluorobutyl vinyl ether could not be controlled.

1,4-Perfluoropentadiene (PFP) copolymerizes with 1,1-dihydroperfluorobutyl vinyl ether to give a plastic material. A plastic copolymer of PFP and vinyl acetate was also prepared.

Major effort was directed toward polymerization of the following fluorine-containing silanes:

1. $CF_3CH_2CH_2Si(CH_3)(OC_2H_5)_2$ and

2. $C_8F_{17}CH_2CH_2Si(CH_3)(OC_2H_5)_2$

Acid and base catalyzed hydrolysis of $CF_3CH_2CH_2Si(CH_3)(OC_2H_5)_2$ has led to oils. Attempts to polymerize the oils by base catalysis were unsuccessful.

$C_8F_{17}CH_2CH_2SiCH_3(OC_2H_5)_2$ yielded an oil by acid hydrolysis, but not with base. The oil obtained by acid hydrolysis could not be polymerized.

Copolymers of $(CH_3)_2\dot{S}iO-$ and $R_fC_2H_2\dot{S}i(CH_3)O-$ (where R_f is CF_3- or $C_8F_{17}-$) were vulcanized to very weak rubbers. The products obtained did show remarkably good low temperature properties (glass transition temperatures below -166°F.) and fair solvent resistance.

Over a long period of time, the $CF_3CH_2CH_2Si(CH_3)(OC_2H_5)_2$ hydrolyzate polymerized to a solid, but not rubbery, material in the presence of lithium aluminum hydride.

$-\dot{S}i(CH_3)_3$ terminated oils were prepared from the hydrolyzate of $C_8F_{17}CH_2CH_2SiCH_3(OC_2H_5)_2$.

Approved for Public Release

Contrails

APPENDIX

1. Amine Recipe

Polymer	100 parts by weight
Philblack O	35
Sulfur	1.0
Triethylene Tetramine	1.0 (Occasionally 1.25 for tighter cure)

Cure: 30 minutes at 310°F.

2. Emulsion recipe for fluorine-containing acrylates

Monomer	100 parts by weight
Water	180
Duponol ME	3
Potassium Persulfate	0.25

3. Silicate Recipe

Polymer	100 parts by weight
$Na_2SiO_3.9H_2O$	6.72
$Ca(OH)_2$	2.72

Cure: 3 hours at 310°F.

4. Oxide Recipe

Polymer	100 parts by weight
Philblack O	40
MgO	25
Stearic Acid	3

Cure: 3 hours at 330°F.

5. First recipe for silicone rubber vulcanizate

Polymer	100 parts by weight
HiSil X303	40
Zinc Oxide	20
Dicumyl Peroxide (95%)	3

Bin age before cure - 48 hours
Cure: 60 minutes at 310°F.

Approved for Public Release

Contrails

6. Second recipe for Silicone Rubber Vulcanizate

Polymer	100	parts by weight
HiSil X303	30	
Zinc Oxide	5	
Benzoyl Peroxide	3	

Cure: 5 minutes at 260°F.
Postcure: 24 hours at 300°F.

Approved for Public Release