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SYNTHETIC RUBBERS FROM CARBON-FLUORINE COMPOUNDS

CARL L. SANDBERG

MINNESOTA MINING AND MANUFACTURING COMPANY

NOVEMBER 1957

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WRIGHT AIR DEVELOPMENT CENTER

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CARL L. SANDBERG

MINNESOTA MINING AND MANUFACTURING COMPANY

NOVEMBER 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

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 Lt. J. M. Kelble acting as project engineer.

This report covers the period from December 15, 1956 to June 15, 1957.

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 35% of the effort involved in the contract during this period. This leaves approximately 65% of said effort as representing the actual polymerization studies and evaluation of polymers reported herein.

ABSTRACT

Further evaluation of 3(ω -chloroperfluoroethoxy)-1,1-dihydroperfluoropropyl acrylate has shown it to be comparable to other perfluoro alkoxy acrylates in low temperature properties and resistance to aromatic solvents and hot air aging, but somewhat poorer in resistance to oxygenated solvents and to diester lubricants.

Attempts to homopolymerize 1,2-epoxyperfluoroheptane with peroxide catalysts or with a ferric chloride:propylene oxide catalyst have given mainly reaction products and little evidence of polymerization. Attempts to copolymerize 1,2-epoxyperfluoroheptane with propylene oxide, using a ferric chloride:propylene oxide catalyst, have given viscous liquid products which may be copolymers.

Exploratory copolymerizations of perfluoro-2-azapropene with vinyl-type monomers have given products containing small amounts of the azapropene.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:



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

TABLE OF CONTENTS

	Page
INTRODUCTION	1
FLUORINE-CONTAINING ACRYLATES	2
FLUORINATED OLEFIN OXIDES	6
1. Polymerization of Hydrocarbon Olefin Oxides	6
2. Reaction of 1,2-Epoxyperfluoroheptane (EFH) with Free-Radical Catalysts	10
3. Reaction of 1,2-Epoxyperfluoroheptane (EFH) with FeCl ₃ :Propylene Oxide Catalyst	10
4. Copolymerization of EFH with Propylene Oxide	11
FLUOROCARBON NITROGEN MONOMERS	13
SUMMARY AND CONCLUSIONS	15
APPENDIX	16

LIST OF ABBREVIATIONS

Cl-FEFPA	3(ω -Chloroperfluoroethoxy)-1,1-dihydroperfluoropropyl acrylate, $\text{ClCF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{CH}_2\text{OCOCH}=\text{CH}_2$
H-FEFPA	3(ω -Hydroperfluoroethoxy)-1,1-dihydroperfluoropropyl acrylate, $\text{HCF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{CH}_2\text{OCOCH}=\text{CH}_2$
2F4	3M Brand Fluoro-Rubber 2F4, poly-3-perfluoromethoxy-1,1-dihydroperfluoropropyl acrylate, $\text{CF}_3\text{OCF}_2\text{CF}_2\text{CH}_2\text{OCOCH}=\text{CH}_2$
EFH	1,2-Epoxyperfluoroheptane, $\text{C}_5\text{F}_{11}-\underset{\text{O}}{\text{CF}-\text{CF}_2}$
PrO	Propylene Oxide, $\text{CH}_3-\underset{\text{O}}{\text{CH}-\text{CH}_2}$
FAP	Perfluoro-2-azapropene, $\text{CF}_3-\text{N}=\text{CF}_2$

INTRODUCTION

The research effort supported by this contract has led to new solvent-resistant and heat-resistant fluorine-containing polyacrylate rubbers. Some additional exploratory work is reported here, but the major effort has now shifted to other fluorine-containing polymers. Fluorine-containing polysiloxanes were studied during the last contract period.

A study of the polymerization of the fluorinated olefin oxide $R_f\text{CF}(\text{O})\text{CF}_2$ was initiated during the present contract. Monomers

of this type are available through the contractor's facilities, and during the past six months polymerization studies on 1,2-epoxyperfluoroheptane have constituted the major portion of the work carried out under the contract. A few additional experiments with 3(ω -chloroperfluoroethoxy)-1,1-dihydroperfluoropropyl acrylate and some copolymerization experiments with a new monomer, perfluoro-2-azapropene, $\text{CF}_3\text{-N=CF}_2$ have also been carried out.

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

FLUORINE-CONTAINING ACRYLATES

Two additional homopolymers of 3(ω)-chloroperfluoroethoxy)-1,1-dihydroperfluoropropyl acrylate (ω -Cl-FEPPA) and two copolymers with added acrylic acid were prepared in the standard emulsion recipe. (See Appendix 1 for recipe). Analyses of this lot of Cl-FEPPA monomer indicates that it contains the requisite amount of chlorine and that only 0.02% acrylic acid has been carried over from the esterification step. Polymerization data are given in Table I. The products were obtained by freezing the latexes, washing the polymer with water and then drying in vacuo at 50°C. The polymers are soft rubbers of high molecular weight.

Polymers were compounded and cured using the standard amine recipe (see Appendix 2). Properties of the vulcanizates are given in Table II, along with comparative data for some other fluorine-containing alkoxy acrylate rubbers synthesized under this contract.

The Cl-FEPPA vulcanizates are rather low in tensile strength, and no improvement was observed with the two copolymers containing additional acrylic acid. Resistance to solvents at room temperature is good and the hot turbo oil resistance is fair, considering the low initial tensile value.

The Cl-FEPPA vulcanizates show the good low temperature properties characteristic of the other fluorine-containing alkoxy acrylates, such as 3M Brand Fluoro-Rubber 2F4. Resistance to aromatic fuels is very good, but somewhat higher swelling is observed in oxygenated solvents. This behavior is also observed for the ω -hydro analog, H-FEPPA. Dry heat resistance is comparable to that of 2F4, but resistance to diester lubricants is somewhat inferior.

This additional evaluation of Cl-FEPPA rubber and the process for preparing it has not shown sufficient promise, relative to the other alkoxy acrylates, to require further study at this time. Attention has, therefore, turned to two other monomer systems described in the following sections.

TABLE I
PREPARATION OF ω -Cl-FEPPA POLYMERS

Polymer No.	Cl-FEPPA Charge, g.	Acrylic Acid Charge, g.	Reaction Conditions*	% Conversion	Inherent Viscosity** $\langle \eta \rangle$
4890-5-1	5.0	0.0010	16 hrs. at 50°C.	98	1.73
6140-5-1	5.0	0.0010	"	100	2.44
6140-5-2	5.0	0.0035	"	100	2.72
6140-5-3	5.0	0.0058	"	100	2.43

* In emulsion, using the following recipe:

Monomer	100 parts by weight
Water	180
DuPontol ME	3
Potassium persulfate	0.25

** In 2:1 acetone:methyl perfluorobutyrate

TABLE II

PROPERTIES OF SOME FLUORINE-CONTAINING
ALKOXY ACRYLATE POLYMERS

Polymer Description	2Flu	FEFPA	H-FEFPA	Cl-FEFPA	Lot I	Lot II	Lot III	Lot IV
Structure	$\begin{array}{c} \text{-CH}_2\text{-CH-} \\ \\ \text{C=O} \\ \\ \text{O} \\ \\ \text{CF}_3\text{OCF}_2\text{CF}_2\text{CH}_2 \end{array}$	$\begin{array}{c} \text{-CH}_2\text{-CH-} \\ \\ \text{C=O} \\ \\ \text{O} \\ \\ \text{CF}_3\text{CF}_2\text{OCF}_2\text{CF}_2\text{CH}_2 \end{array}$	$\begin{array}{c} \text{-CH}_2\text{-CH-} \\ \\ \text{C=O} \\ \\ \text{O} \\ \\ \text{HCF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{CH}_2 \end{array}$	$\begin{array}{c} \text{-CH}_2\text{-CH-} \\ \\ \text{C=O} \\ \\ \text{O} \\ \\ \text{ClCF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{CH}_2 \end{array}$				
% Copolymerized Acrylic Acid	0.03	?	0.05		0.02	0.02	0.075	0.115
Inherent Viscosity	1.85	0.95	3.6		1.7	2.4	2.7	2.4
Properties of Vulcanizates (Amine Cure)								
Fl ₀₀ , psi	210	280	200		190	225	105	120
Tensile Strength, psi	970	550	900		620	800	525	680
Ultimate Elongation, %	370	300	310		380	300	440	450
Set at Break, %	7.5	-	8		37	6.2	12.5	12.5
Low Temperature Properties								
Gehman T ₁₀ , °F.	-11	-12	-16		-18	-29	-29	-31
Scott Brittle Pt., °F.	-33	-42	-28		-40	-34	-40	-35
T _g of Gum, °F.	-67	-88	-88		-94	-	-	-

TABLE II - continued
 PROPERTIES OF SOME FLUORINE-CONTAINING
 ALKOXY ACRYLATE POLYMERS

Volume Swell	2F4	FEFPA	H-FEFPA	Cl-FEFPA
(70:30 Fuel	9	26	17	-
48 hrs., 77°F. (Benzene	13	21	25	-
(Acetone	41	35	220	-
70 hrs., 212°F. Water	37	38	20	-
Properties after 100 hrs. at 350°F. in Air				
Tensile Strength, psi	150	105	190	120
Ultimate Elongation, %	240	50	245	150
Weight Change, %	-3.3	-5.3	-3.7	-3.7
Properties after 100 hrs. at 400°F. in Turbo Oil #15				
Tensile Strength, psi	670	400	360	100
Ultimate Elongation, %	200	120	265	220
Volume Change, %	-6	0	-	+3.15
				90
				140
				+4.1
				110
				320
				+3.6

FLUORINATED OLEFIN OXIDES

The polymerization of partially fluorinated olefin oxides has been studied at other laboratories /1,2/ and products varying from solids to liquids have been reported. The use of acid catalysts such as BF_3 , AlCl_3 , and FeCl_3 led to fairly high molecular weight polymers. Polymers of perfluoroolefin oxides have not yet been described.

A new fluorinated olefin oxide, 1,2-epoxyperfluoroheptane, $\text{C}_5\text{F}_{11}\text{O}$, has been examined in homopolymerization and copolymerization experiments. These experiments are described in detail below and in Tables III, IV, and V. The olefin oxide was carefully fractionated through a 60-plate Todd column and a center cut (b.p. 81.5°C . uncorrected) reserved for use. Infrared spectra and gas chromatography indicate that this cut is very nearly a single, pure compound.

1. Polymerization of Hydrocarbon Olefin Oxides

In preparation for work with the fluorinated olefin oxide, the polymerization of propylene oxide and butylene oxide (straight chain isomers) was studied. Catalysts such as KOH , BF_3 etherate, and FeCl_3 were examined and yielded low molecular weight products. The FeCl_3 :propylene oxide adduct catalyst described by Pruitt and Baggett /3/ and used by Price and coworkers /4,5/ gave somewhat better results. Good yields of moderate molecular

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- /1/ Pierce, O.R., Smith, D. D., and Murch, R. M. "Fluorine-Containing Polyethers", WADC Technical Report 55-193, United States Air Force, Air Research and Development Command.
 - /2/ Jones, F. B., Lichtenwalter, C. A., Stickney, P. B., and Heilegmann, R. G., "Polymerization Studies on Monomers and Evaluation of Derivative Polymers", WADC Technical Report 57-110, United States Air Force, Air Research and Development Command.
 - /3/ Pruitt, M. E. and Baggett, J. M., "Catalysts for the Polymerization of Olefin Oxides", U.S. Patent 2,706,181.
 - /4/ Price, C. C., Osgan, M., Hughes, R. E. and Shambelan, C., "The Polymerization of L-Propylene Oxide", J.A.C.S. 78, 690 (1956).
 - /5/ Price, C. C. and Osgan, M., *ibid*, p. 4787.

TABLE III

REACTION OF EFH WITH FREE RADICAL INITIATORS

Polymer No.	Catalyst	Reaction Time, hrs. 100°C.	% Yield	Description of Product	Analysis % C % F
6135-7-1	t-butyl hydroperoxide	60	40	Gummy solid	
6135-7-2	di-isopropyl benzene hydroperoxide	60	35	" "	
6135-7-3	peracetic acid	60	60	Greasy solid, softens 70°C.	22.6 50.6
6135-7-4	azobisisobutyronitrile	160	-	-	
6135-7-5	1-isobutoxy-1-cumyl peroxyethane	110	45	Brittle	
6135-7-6	paramenthene hydroperoxide	60	20	Soft gum	
6135-7-7	2,2-bis(t-but.peroxy)butane	110	35	Viscous syrup	
6135-7-8	t-butyl perbenzoate	110	30	Soft gum	
6135-7-9	acetyl peroxide	130	20	Putty	
6135-7-11	peracetic acid	110	40	Greasy solid	
6135-7-12	di-isopropyl benzene hydroperoxide	110	15	Gum	
6554-2-1	di-t-butyl peroxide	64	24	Black syrup	
6554-2-2	di-isopropyl benzene hydroperoxide	64	11	" "	32.6
6554-2-3	peracetic acid	64	-	Tube exploded	
6554-2-4	1-isobutoxy-1-cumyl peroxyethane	64	33	Black syrup	26.2 49.9
6135-13-3	di-isopropyl benzene hydroperoxide	240	15	Brown syrup	

TABLE IV

REACTIONS OF 1,2-EPOXYPERFLUOROHEPTANE (EFH)
WITH FeCl₃:PROPYLENE OXIDE (Pro) CATALYSTS

Run No.	Catalyst Charge, g.		EFH g.	Reaction Conditions Hrs.	°C.	% Yield	Analysis		Appearance of Product
	FeCl ₃	Pro					% C	% F	
6145-51-1	0.06	-	2.0	232	90	0	no reaction		
6534-2-5	0.04	0.04	5.0	64	100	5	33.8		Black semi-solid
6534-2-6	0.07	g. FeCl ₃ :Pro adduct	5.0	620	50	40	31.7	47.7	Black syrup
6534-13-2	0.014	0.083	5.0	260	100	0	no reaction		
6534-13-4	0.056	0.33	5.0	260	100	20	30.2	49.0	Black liquid
6534-23-6	0.056	0.12	5.0	112	102	4	29.4	50.1	Black semi-solid

TABLE V

COPOLYMERIZATION OF 1,2-EPOXYPERFLUOROHEPTANE (EFH)
AND PROPYLENE OXIDE (Pro) USING FeCl_3 :Pro CATALYST

Polymer No.	Catalyst Charge		Monomer Charge		Solvent Diethyl Ether, ml.	Reaction Conditions Hrs.	°C.	% Yield	$\langle \eta \rangle$ in Benzene	Analysis		Appearance of Product
	FeCl_3 , g.	Pro, g.	EFH, g.	Pro, g.						% C	% F	
6554-13-5	0.056	0.33	2.0	2.5	-	88	100	100	0.01	-	34.0	Tan syrup
6554-23-4	0.056	0.12	2.0	2.5	-	40	102	100	-	40.6	38.0	Orange liquid
6554-23-0	0.014	-	2.0	2.5	-	40	102	100	-	42.0	36.0	Yellow liquid
6554-23-1	0.056	-	2.0	2.5	-	40	102	92	-	41.3	41.7	"
6554-23-2	0.056	-	3.0	1.7	-	112	102	100	-	37.5	41.8	Black syrup
6554-23-3	0.056	-	4.0	0.83	-	112	102	>50	-	32.9	49.0	"
6554-28-5	0.056	0.33	3.7	1.2	-	233	82	?	-	33.1	43.4	Black, tacky semi-solid
6554-37-5	0.056	0.33	3.5	1.2	-	400	50	58	-	-	-	Brown liquid
6554-37-1	0.056	0.33	5.5	0.43	-	160	84	23	-	37.5	37.5	"
6554-37-2	0.056	0.33	5.5	0.87	-	160	84	61	-	36.3	42.5	"
6554-37-7	0.014	0.083	-	4.1	-	64	78	64	0.66	-	-	Tough, waxy solid
6554-7-3	0.014	0.083	-	4.1	-	160	97	63	0.26	-	-	Gummy
6554-7-4	0.014	0.083	-	4.1	10	160	97	27	0.49	-	-	Tough solid
6554-37-11	0.014	0.083	-	4.1	10	136	80	18	0.64	-	-	Tough, waxy solid
6554-37-9	0.014	-	-	4.1	-	64	83	48	0.35	-	-	Waxy solid
6554-23-5	0.056	0.12	-	4.1	-	40	91	66	0.19	-	-	Tacky solid
6554-37-6	0.056	0.33	-	4.1	-	64	78	39	0.28	-	-	Waxy solid
6554-7-6	0.056	0.33	-	4.1	10	160	89	100	0.23	-	-	Gummy

weight polymer were obtained with propylene oxide and a FeCl_3 : propylene oxide catalyst prepared according to the patent. The best products were obtained when carefully fractionated monomer was used and when precautions were taken to exclude moisture from the catalyst.

2. Reaction of 1,2-Epoxyperfluoroheptane (EFH) with Free-Radical Catalysts

Prolonged heating of EFH with several types of free radical initiators gave small yields of dark, solid products. These were not completely identified but appear to be largely mixtures of reaction products, with possibly a small amount of low polymer. Details of the reaction are given in Table III.

The product from reaction 7-3 was examined in more detail. The product softens at about 70°C . and is soluble in acetone. Infrared analysis indicates a high concentration of fluorocarbon C=O and OH . Elemental analysis indicates loss of fluorine. (Found: 22.6% C, 50.6% F; Theory: 23.0% C, 72.7% F). Silicon tetrafluoride was the major component of the gas recovered from the glass reaction tube, also indicating that fluoride had split out from the epoxide. One of the reactions occurring appears to be ring opening followed by rearrangement to an acid fluoride. Apparently this reaction may also be accompanied by more deep-seated rearrangements involving fragmentation of the molecule.

Products obtained with alkyl peroxide and hydroperoxide catalysts indicate that ring opening and rearrangement may also occur on heating with these catalysts, but the extent of reaction is somewhat less than when acyl peroxides are used.

Neutralization of the products with KOH indicates that in some cases 25% of the reacted epoxide groups were converted to acid or acid fluoride. Under more mild reaction conditions, conversions were lower, but product distribution appeared similar.

3. Reaction of 1,2-Epoxyperfluoroheptane (EFH) with FeCl_3 : Propylene Oxide Catalyst.

In another series of homopolymerization experiments (Table IV) in glass ampoules, the ferric chloride:propylene oxide adduct^{3,4,5/} was used as a catalyst. In most of these experiments the ferric chloride:propylene oxide catalyst was prepared in the polymerization ampoule. It was thus possible to avoid the inconvenient step of weighing the syrupy catalyst into the polymerization tube. In experiment 13-4, 1.0 ml. of a 5.5% solution of FeCl_3 in anhydrous ether was pipetted into a dry, nitrogen-flushed ampoule. The tube was chilled in liquid nitrogen while continuing the nitrogen flushing. To the cold tube, 0.4 ml. of propylene oxide

was added and the tube was then evacuated and sealed. The mixture was shaken one hour at 0°C. and one hour at 25°C., opened and immediately pumped on a vacuum system to remove the volatile products. The ampoule was then filled with nitrogen and chilled, 5.0 g. EFH was added, and the tube was evacuated and sealed. It was then placed in a heated (80 to 105°C.) rocking tube assembly for reaction.

The products were separated into gas, volatile liquid, and viscous portions. Silicon tetrafluoride was the major constituent of the gas phase, again indicating loss of fluoride from the epoxide. About 50 to 90% of the charges were recovered as low-boiling liquids and consisted mainly of unreacted EFH. Non-volatile, brown, viscous syrups were obtained in 5 to 35% yields and were shown by infrared analyses to contain substantial amounts of fluorocarbon C=O and some OH. These products appear to be largely mixtures of reaction products, with possibly a small amount of low molecular weight polymer. Infrared analysis indicates that these products are similar to those prepared with peroxide catalysts. Elemental analysis and neutralization numbers also indicate this similarity.

Anhydrous ferric chloride has not appeared to be as active a catalyst as the ferric chloride:propylene oxide adduct.

The attempts to polymerize EFH at elevated temperatures, in general, gave mixed reaction products in yields up to about 50%. A small amount of low polymer appeared to have formed in some experiments. Attempts to separate the products were only partially successful and the nature of the reactions occurring are, therefore, not yet known.

4. Copolymerization of EFH with Propylene Oxide

Attempts to copolymerize EFH with approximately equal parts of propylene oxide resulted in high conversions to viscous liquid products. The ferric chloride:propylene oxide catalyst was used in these experiments and prepared as described earlier. Experimental details are given in Table V. Attempts to react charges richer in EFH gave products more closely resembling those obtained with EFH alone.

Product 6554-13-5 was obtained in 100% yield from a charge of 2.0 g. EFH and 2.5 g. propylene oxide. (Under comparable conditions, a 10% conversion would be obtained with EFH alone). Approximately 10% of the product was low molecular weight polypropylene oxide. The remainder was a tan, viscous syrup which split into two equal parts when extracted with cyclic C₆F₁₂O. The ether-soluble material contained 43.5% F (corresponding to

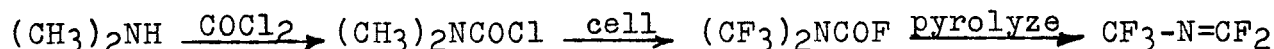
19 mole %, calculated as EFH), whereas the insoluble material contained 24.6% F (7.5 mole % EFH). Infrared analysis of the two portions shows much less of the anomolous C=O absorption in the ether-insoluble portion than in the soluble portion or the original mixture. Absorptions associated with the C-O groups of polypropylene oxide were also diminished and C-F bands were stronger. The ratio of C=O to C-F absorption is considerably lower than for reaction products obtained with EFH alone, suggesting that the undesirable rearrangement to acid fluoride may have been suppressed. The product is quite low molecular weight (inherent viscosity in benzene ~0.01) and soluble in most organic solvents. A suitable procedure for separation of the mixed product is needed to prove copolymerization, but has not been found so far. The possibility that the product is a mixture of polypropylene oxide and EFH reaction products is unlikely, but has not yet been disproved.

Experiments in which the charges were approximately equimolar EFH and propylene oxide gave products more like those obtained with EFH alone, but in better conversion. Additional experiments are needed to cover the entire range of charge compositions.

FLUOROCARBON NITROGEN MONOMERS

The preparation of some nitrogen analogs of perfluoroolefins has been described^{/6,7/} recently in the literature. The homopolymer of one member of the series, $\text{CF}_3\text{-N=CF}_2$, has been reported^{/8/} but the product had not been characterized. A small amount of $\text{CF}_3\text{-N=CF}_2$ (perfluoro-2-azapropene, FAP) has been prepared in this laboratory and was used in exploratory copolymerization with vinyl type monomers.

The FAP monomer was prepared by the procedure of Young^{/7/}, starting with dimethyl amine and involving the following series of reactions:



A total of 25 g. of product (b.p. $-34^\circ\text{C}.$) was obtained.

Comonomers used with FAP include the following: vinyl acetate, vinyl isobutyl ether, styrene, ethyl acrylate, acrylonitrile, chlorotrifluoroethylene, and vinyl 1,1-dihydroperfluorobutyl ether. Polymerizations were carried out in bulk at $50^\circ\text{C}.$, using benzoyl peroxide and t-butyl hydroperoxide initiators. Details are given in Table VI.

In most cases, the products contained small amounts of FAP, based on nitrogen analysis. Product 16-8, a crumbly solid obtained with FAP and vinyl 1,1-dihydroperfluorobutyl ether, was obtained in 28% yield and contained 17 mole % FAP. With vinyl acetate, vinyl isobutyl ether, and chlorotrifluoroethylene, small amounts of FAP entered the polymer. Products resulting from attempts to copolymerize FAP with styrene, ethyl acrylate, and acrylonitrile do not as yet appear to contain any perfluoro-2-azapropene.

-
- /6/ Barr, D. A. and Haszeldine, R. N., "Perfluoroalkyl Derivatives of Nitrogen, Part 1", J.Chem.Soc., 1881 (1955).
 - /7/ Young, J. A., Simmons, T. C. and Hoffmann, F. W., "Fluorocarbon Nitrogen Compounds. Perfluoro Carbonic Acid Derivatives", J.A.C.S. 78, 5637 (1956).
 - /8/ Brown, H. E., Dresdner, R. D., Wethington, J. A. Jr., and Young, J. A., "Preparation of Fluorine-Containing Compounds", WADC Technical Report 56-234, United States Air Force, Air Research and Development Command.

TABLE VI
COPOLYMERIZATION OF PERFLUORO-2-AZAPROPENE (FAP)
WITH VINYL-TYPE MONOMERS

Polymer No.	FAP Charged g.	Comonomer, g.	Catalyst*	Reaction Conditions Hrs.	Reaction Conditions °C.	% Yield	$\langle \eta \rangle$ in Benzene	Wt. % FAP in Product
15-1	0.66	0.50 vinyl isobutyl ether	Bz ₂ O ₂	60	50	25	0.09	3.8
16-1	0.66	0.20 "	"	90	50	22	-	2.3
16-2	0.66	0.20 "	t-BHP	90	50	20	-	3.2
16-9	0.66	0.20 "	"	30	70	20	0.18	3.9
16-7	-	0.50 "	Bz ₂ O ₂	90	50	4	-	-
16-5	-	0.50 "	t-BHP	90	50	2	-	-
15-2	0.66	0.43 vinyl acetate	Bz ₂ O ₂	60	50	32	0.20	5.7
16-6	-	0.43 "	"	90	50	95	-	-
15-3	0.66	0.52 styrene	"	60	50	41	-	-
15-4	0.66	0.50 ethyl acrylate	"	60	50	29	-	-
15-5	0.66	0.26 acrylonitrile	"	60	50	26	-	-
16-8	0.27	0.45 vinyl 1,1-dihydroperfluoro-butyl ether	t-BHP	90	50	28	-	12.5
19-2	1.0	1.0 C ₃ F ₆	"	66	50	-	-	-
19-3	1.0	1.0 CF ₂ CFCl	"	66	50	6	-	3.1

* Catalyst charged 2% by weight of monomer
Benzoyl Peroxide (Bz₂O₂); t-Butyl Hydroperoxide (t-BHP)

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.

Polymers of 3(ω -chloroperfluoroethoxy)1,1-dihydroperfluoropropyl acrylate, (ω -Cl-FEPPA) and copolymers with traces of acrylic acid have been evaluated. Vulcanizates obtained with the amine cure have the low temperature flexibility characteristic of the other fluorine-containing alkoxy acrylates previously prepared. Resistance to aromatic solvents and 70:30 fuel is also comparable, but somewhat higher swelling is observed in oxygenated solvents. Resistance to dry heat is comparable but resistance to diester lubricants, as well as tensile strengths, are somewhat inferior. Preparation of ω -Cl-FEPPA polymer does not look particularly attractive relative to other fluorine-containing alkoxy acrylates.

Major effort was directed toward polymerization of 1,2-epoxyperfluoroheptane, $C_5F_{11}\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{CF}_2$. Peroxide-catalyzed reactions at elevated temperatures gave fair conversions to products which appear to be mainly the result of ring opening and rearrangement. The products contain little, if any, polymer.

Attempts to polymerize $C_5F_{11}\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{CF}_2$ with $FeCl_3$:propylene oxide adducts led to fair yields of similar reaction products with little evidence of polymer formation.

Attempts to copolymerize $C_5F_{11}\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{CF}_2$ and propylene oxide with certain $FeCl_3$:propylene oxide adducts gave high conversions to products which appear to be copolymers. They are tan, viscous liquids. The molecular weights of the products are quite low and it has not yet been possible to prove that copolymerization occurred.

Preliminary attempts to copolymerize perfluoro-2-azapropene, $CF_3-N=CF_2$, with vinyl-type monomers have given low molecular weight products containing small amounts of the azapropene.

APPENDIX

1. Emulsion recipe for fluorine-containing acrylates

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

2. Amine Recipe

Polymer	100 parts by weight
Philblack 0	35
Sulfur	1.0
Triethylene tetramine	1.0

Cure: 30 minutes at 310°F.