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PART 1

SYNTHETIC RUBBERS FROM CARBON-FLUORINE COMPOUNDS

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FOREWORD

This report is presented in two sections, each of which is essentially an annual progress report as prepared by Minnesota Mining and Manufacturing Company under research and development Contract AF 33(038)-515. It covers the period 15 May 1949 to 15 May 1951 and is one of a series to be issued on the project; other reports will be published as research progresses.

The Materials Laboratory, Directorate of Research, Wright Air Development Center initiated this research project under Research and Development Order No. 602-192, "Fuel and Oil Resistant Polymer Research," with Mr. J. C. Mosteller as Project Engineer; Major W. H. Ebelke functioned in this capacity for the last six months of the referenced period. Research and Development Order No. 617-11, "Synthesis and Evaluation of New Polymers," superseded RDO No. 602-192 during the course of the work covered herein.

ABSTRACT

Exploratory investigation into the preparation and properties of fluorinated polymers is described. New polymeric compositions of matter have been synthesized and screened with respect to their potentialities as suitable elastomers for use under extreme conditions of temperature in contact with various fuels and oils. The esters of unsaturated hydrocarbon acids with 1,1-dihydroperfluoroalkyl alcohols represent the most promising class of monomers investigated so far; certain of their polymers have received considerable attention because of their rubbery properties and exceptional resistance to swelling by non-fluorinated solvents, although their low temperature flexibility will probably require extension by plasticization. Fluorinated condensation-type polymers such as polyesters and polyamides do not appear promising as elastomers but may have potentialities as fibres, films or structural plastics. Extensive structure versus property correlations are not attempted but it is concluded that either side-chain or backbone fluorine in polymeric structures promotes resistance to swelling by common solvents; the former does not appear to affect low temperature properties as adversely as sketal attachment. The possibility of constructing a better monomer than a fluoro-alkyl acrylate for development into a superior elastomer for specialized Air Force applications is still conceded for the field is relatively new and the number of known compounds small.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDING GENERAL:

M. E. SORTE
Colonel, USAF
Chief, Materials Laboratory
Directorate of Research

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SECTION I

Contract Period 15 May 1949 to 15 May 1950

INTRODUCTION

As the requirements of modern industrial and military usage become more stringent, it has become necessary to develop materials capable of withstanding increasingly severe extremes of temperature and conditions of chemical attack. Since the replacement of a major portion of the carbon-bonded hydrogen atoms in organic compounds by fluorine atoms produces compounds having profoundly different physical and chemical properties with greatly increased stability to chemical attack, decreased solubility in ordinary solvents, and markedly improved thermal stability, the development of fluorinated liquids and solids appears to be one method of satisfying these requirements.

In particular, it would be extremely desirable to develop highly fluorinated rubber-like materials that could be used in various applications under extreme conditions of temperature and exposure to solvents.

The Minnesota Mining & Manufacturing Company has been developing an electrochemical fluorination process invented by Professor J. H. Simons of the Pennsylvania State College, (J. Electrochem. Soc. 95, 47 (1949)). This process, involving essentially the electrolysis of a solution of an appropriate organic compound in anhydrous hydrogen fluoride, provides a source of many previously unobtainable fluorochemicals which may be converted into new types of polymers.

The Minnesota Mining & Manufacturing Company therefore entered into Contract No. AF 33(038)-515 with the United States Air Force, represented by **Wright Air Development Center**, to study the development of highly fluorinated rubber-like polymers of possible utility in the Air Force program.

The chemistry of this type of compound is largely unknown. It is, therefore, necessary to prepare new monomers, to develop processes of polymerization, and to evaluate many different types of polymers before satisfactory elastomers can be designed.

Two factors appear to be of primary importance in determining the elastomeric properties of solids. First, any flexible rubber-like polymer must contain long chain molecules capable of readily coiling and uncoiling. This requires fairly free rotation about some of the bonds in the chain. Secondly, the long chain molecules must not be so firmly bonded together in the polymer that coiling and uncoiling is restricted by the neighboring molecules. That is, the polymer should not approach the crystalline state when unstretched. For optimum properties, stretching should induce crystallization. As far as is known from the physical properties of the fluorocarbons, rotation about the carbon-carbon bonds within the chain is highly restricted. However, this can be overcome by the insertion of suitable spacing groups within the molecule. The only two commercially developed highly fluorinated polymers, polytetrafluoroethylene and polytrifluorochloroethylene, do show promising low temperature flexibility.

Therefore, there appears to be a sound basis for expecting that suitable fluorinated monomers can be obtained which will lead to polymers having superior low temperature properties.

There are four general types of polymers to be examined;

1. Fluorocarbon Unsaturates - These include the mono- and diolefinic and acetylenic fluorocarbons. Polyethylene is not a rubbery polymer; polyisobutylene, differing only in the presence of methyl side-chains, is an elastomer. Although polytetrafluoroethylene and polytrifluorochloroethylene do not have rubbery properties, fluorinated side chains may impart flexibility to the macro-molecule. The use of polyolefinic or acetylenic monomers will permit retention of unsaturation in the polymer and should allow vulcanization of the elastomer.

2. Hydrocarbon-Fluorocarbon Unsaturates - Compounds such as $CF_3-CF_2-C(CH_3)=CH_2$, $C_3F_7CO_2CH=CH_2$, etc., which when polymerized will lead to hydrocarbon polymeric units containing fluorocarbon side chains, offer the possibility of a flexible molecule with substantial inertness and a low inter-chain attraction. Copolymers of unsaturated fluorocarbons and unsaturated hydrocarbons might also be included in this class.

3. Hetero-Chain Type - For the flexibility characteristic of rubbery polymers, relatively free rotation of at least some of the bonds in a polymer unit seems to be necessary. The excellent low temperature characteristics of the silicone lubricating oils are apparently due to the oxygen atoms interpolated in the main chain of the polymer. Through the inclusion of atoms

such as oxygen, sulfur, silicon, phosphorus or nitrogen in the chain, it should be possible to vary the stiffness of the polymer at low temperature.

4. Condensation Type - In this group fall the polyesters, polyamides, etc. Several non-fluorinated polymers of this class have rubbery properties; the low inter-chain attraction of the fluorocarbons makes it necessary to explore this realm to determine whether the fluorocarbon analogues are suitable elastomers.

POLYMERIZATION STUDIES

Most of the fluorocarbon monomers investigated in this program are new materials. Many of them have been prepared by arduous procedures which have allowed the production of only small amounts. In order that the polymerization work would not have to await the development of more suitable methods of production, polymerization experiments have been adapted to a semi-micro scale.

In general, the procedure involves the addition of about 0.250 g. of the monomer and an appropriate quantity of polymerization initiator to a short ampoule of 7 mm. glass tubing. If copolymerization is being studied, the second monomer is also added. For emulsion polymerization the medium and emulsifier are included. Low-boiling monomers are handled in a vacuum system.

The ampoule is then frozen in Dry Ice or liquid air, evacuated, and sealed. The polymerization is carried out by tumbling the ampoule in a thermostat at the desired temperature. Experimental polymerizations of standard hydrocarbon monomers indicate that the results of this small-scale work can be satisfactorily correlated with those obtained on a larger scale.

By proceeding at this level, it has been possible to carry on extensive polymerization studies utilizing only a few grams of material. Meanwhile, other sections have been engaged in developing methods of producing the monomers so that the materials

will be available on a sufficiently large scale by the time promising conditions of polymerization have been developed.

Because of the lengthy names of the monomers, abbreviations have been used in several places, particularly in the tables. The names of the monomers and their abbreviations are listed here for convenience.

FEA	1,1-Dihydroperfluoroethyl acrylate
FPA	1,1-Dihydroperfluoropropyl acrylate
FBA	1,1-Dihydroperfluorobutyl acrylate
FBMA	1,1-Dihydroperfluorobutyl methacrylate
VFB	Vinyl perfluorobutyrate

Perfluoroolefins

The ultimate in resistance to chemical attack and solvent action in rubbery polymers can be expected from the completely fluorinated materials. For this reason, an extensive effort has been made to polymerize C_3F_6(CF_2=CF-CF_3) and its homologs. Although C_2F_4 and C_2F_3Cl are subject to free-radical emulsion polymerization, C_3F_6 has been found to be quite inert toward this type of initiation.

Numerous experiments have been carried out with various peroxides, acids and bases. In most cases little or no reaction was observed. Some tars containing more or less fluorine were produced, but in no case was any very promising polymer obtained. A summary of these experiments is given in Table I.

TABLE I

Polymerization Studies - C_3F_6

Catalyst	Recipe	Conditions	Remarks
(Peroxides)			
Benzoyl peroxide	2 g. C_3F_6, 1.5% cat.	Sealed glass tube, 65°, 16 hrs. shaking	No polym.
Peracetic acid	2 g. C_3F_6, 2.0% cat.	Same	No polym.
t-Butyl hydroperoxide	2 g. C_3F_6, 1.5% cat.	Same	No polym.
Diethyl dipercarbonate	2 g. C_3F_6 2.0% cat.	Same	No polym.
H_2O_2	3 g. C_3F_6 3 ml. 5% H_2O_2	Same	No polym.
Cumene hydroperoxide	2 g. C_3F_6 1.5% cat.	Same	No polym.
Cumene hydroperoxide + p-toluene sulfinic acid	2 g. C_3F_6 1.5% cat.	Same	No polym.
Cumene hydroperoxide	20.2 g. C_3F_6, 0.35 g. cat.	Bomb, 125° 120 psig., 8 hrs. 150°, 130 psig., 13 hrs. shaking	No polym.
$Na_2S_2O_3$	25 g. C_3F_6, 0.5 g. cat., 0.5 g. $NaHSO_3$ 75 g. H_2O	750 psig. 125°C., 42 hrs.	No polym.
Lauroyl peroxide	35 g. C_3F_6, 0.35 g. cat., 75 g. H_2O	3950 psig. 200°, 36 hrs.	No polym.
(Basic Catalysts)			
ϕ_3CNa			Dark oil forms
Na	0.41 g. Na, 68.9 g. NH_3 8.3 g. C_3F_6	Stirred 2 hrs. at -60°	Dark oil forms

TABLE I (Continued)

Catalyst	Recipe	Conditions	Remarks
$NaNH_2$	100 ml. NH_3, 0.1 g. $Fe(NO_3)_3$, 10.9 g. C_3F_6	Stirred together at -75° to -50°	Vigorous reaction, dark oil containing 47% F is formed
CH_3MgI	2 ml. dihexyl ether, 0.5 g. CH_3MgI, 3 g. C_3F_6	Sealed tube, 65° for 72 hrs.	No polym.
CH_3MgI	10 g. CH_3MgI 100 ml. di-n-butyl ether, 5.8 g. C_3F_6	C_3F_6 bubbled through original sol. at 50°	No polym.
(Lewis Acids)			
$H_3PO_4 \cdot BF_3$	1.52 g. C_3F_6, 3.3% cat.	Sealed tube at 60°, 20 hrs. shaking	No polym.
$2CH_3OH \cdot BF_3$	3.42 g. C_3F_6 1.9% cat.	Sealed tube at 60°, 20 hrs. shaking	No polym.
$H_3PO_4 \cdot BF_3$	3.30 g. C_3F_6, 5% cat.	Sealed tube at 75°, 47 hrs. shaking	No polym.
H_3PO_4 (100%)	2.87 g. C_3F_6 10% cat.	Sealed tube at 75°, 47 hrs. shaking	No polym.
$TiCl_4$	2.59 g. C_3F_6, 5% cat.	Sealed tube at 75°, 47 hrs. shaking	No polym.
$2CH_3OH \cdot BF_3 + PF_3$	2.5 g. C_3F_6, 0.2 g. cat. + 0.2 g. BF_3	Sealed tube at 75°, 47 hrs. shaking	No polym.
$(C_6H_5)_4Sn$	1.0 g. C_3F_6, 0.02 g. cat.	55°, 24 hrs.	No polym.
(Emulsion Polym.)			
$K_2S_2O_8$ $NaHSO_3$	1.67 g. $K_2S_2O_8$ 1.67 g. $NaHSO_3$ 3 g. H_2O, 3 g. C_3F_6	Sealed tube, 65°, 14 hrs.	No polym.

TABLE I (Continued)

Catalyst	Recipe	Conditions	Remarks
$K_2S_2O_8$, $NaHSO_3$	0.4 g. $K_2S_2O_8$ 0.4 g. $NaHSO_3$ 5 g. H_2O 23.8 g. C_3F_6	Bomb, 300 psig. 85°, 14 hrs. shaking	No polym.
$K_2S_2O_8$, $NaHSO_3$	0.7 g. $K_2S_2O_8$ 0.7 g. $NaHSO_3$ 40 g. H_2O 49.6 g. C_3F_6	Bomb, 400 psig. 100°, 16 hrs. shaking	No polym.
$K_2S_2O_8$	0.1 g. $K_2S_2O_8$ 0.2 g. borax, 20 g. H_2O 10.5 g. C_3F_6	Bomb, 350 psig., 80°, 23 hrs. shaking	No polym.
$K_2S_2O_8$	0.1 g. $K_2S_2O_8$ 0.25 g. borax 2.5 g. Duponol 1 g. H_2O 11.0 g. C_3F_6	Bomb, 400 psig. 100°, 16 hrs. shaking	No polym.
U.V. Light)			
	3 g. C_3F_6 0.54 g. biacetyl	Sealed tube in weather-ometer	Tube exploded
	1.5 g. C_3F_6 0.35 g. biacetyl	Sealed tube in weather-ometer	Tube exploded

It is not unusual to find that a material which polymerizes with difficulty can be induced to enter into a copolymer. Considerable experimentation on C_3F_6 in combination with standard, readily polymerizable, olefins such as styrene, acrylonitrile, etc., was without significant success. It was finally discovered that C_3F_6 could be incorporated into copolymers with vinyl monomers, such as vinyl chloride, vinyl acetate, or vinyl ethers, when free radicals were used as a polymerization catalyst. The experiments are summarized in Table II.

TABLE II

Vinyl Copolymerization of C_3F_6

Components	Condition	Polymer
0.5 g. C_3F_6 0.5 g. styrene 0.05 g. t-C_4H_9OOH	Sealed tube 70°, 16 hrs.	Polystyrene
0.5 g. C_3F_6 0.5 g. C_2H_3Cl 0.5 g. t-C_4H_9OOH	Sealed tube 70°, 16 hrs.	Polyvinyl chloride
0.5 g. C_3F_6 0.5 g. $C_2H_3O_2CCH_3$ 0.05 g. t-C_4H_9OOH	Sealed tube 70°, 16 hrs.	No polymer
0.5 g. C_3F_6 0.5 g. $C_2H_3O_2CCH_3$ 0.05 g. t-C_4H_9OOH	Sealed tube 125°, 16 hrs.	Tacky polymer 13% F 17% C_3F_6
1.0 g. C_3F_6 1.0 g. $C_2H_3O_2CCH_3$ 0.02 g. $(CH_3CO_2)_2$	Sealed tube 50°, 18 hrs.	Clear, flexible 15% C_3F_6
1.0 g. C_3F_6 2.0 g. $C_2H_3O_2CCH_3$ 0.3 g. $(CH_3CO_2)_2$	Sealed tube 50°, 18 hrs.	Clear, flexible 20% C_3F_6
1.0 g. C_3F_6 0.5 g. $C_2H_3O_2CCH_3$ 0.015 g. $(CH_3CO_2)_2$	Sealed tube 50°, 18 hrs.	Clear, flexible 11% C_3F_6
1 g. C_3F_6 1 g. $C_2H_3O_2CCH_3$ 0.05 g. t-C_4H_9OOH	Sealed tube 138°, 16 hrs.	Dark, soft
0.5 g. C_3F_6 1.0 g. $C_2H_3O_2CCH_3$ 0.05 g. t-C_4H_9OOH	Sealed tube 138°, 16 hrs.	Dark, soft 32% C_3F_6
52 g. C_3F_6 6 g. $C_2H_3O_2CCH_3$ 0.3 g. $(CH_3CO_2)_2$	Sealed tube 50°, 53 hrs.	Slightly brittle 47% C_3F_6
2 g. C_3F_6 0.5 g. $C_2H_3O_2CCH_3$ 0.25 g. $(BzO)_2$	Sealed tube 70°, 48 hrs.	26% C_3F_6

TABLE II (Continued)

Components	Condition	Polymer
0.5 g. C_3F_6 0.5 g. $C_2H_3O_2CCH_3$ 1.8 cc. H_2O 0.002 g. $K_2S_2O_8$ 0.002 g. $NaHSO_3$	Sealed tube 75°C.	Good latex 10% C_3F_6
3 g. C_3F_6 0.2 g. C_2H_3Cl 0.005 g. $(CH_3CO_2)_2$	Sealed tube 50°, 48 hrs.	White powder 18% C_3F_6
1 g. C_3F_6 1 g. $i\text{-}C_3F_7OC_2H_3$ 0.02 g. $(CH_3CO_2)_2$	50°, 16 hrs.	Colorless, tacky 57% C_3F_6

The vinyl ethers appear to be particularly promising. As is the case with C_3F_6, these compounds are normally inert toward polymerization by free radicals although they can be polymerized in the presence of acids, such as boron trifluoride, aluminum chloride, etc. Mixtures of perfluoropropene and vinyl ethers polymerize readily in the presence of free radical initiators to form copolymers containing, in some cases, a slight excess of C_3F_6, indicating the possibility that relatively highly fluorinated polymers can be obtained from this type of reaction.

General methods have been developed for the production of terminal olefins, such as perfluoropentene-1, perfluorobutene-1, etc. The polymerization of these compounds is now under investigation.

Perfluoroalkyl-Substituted Hydrocarbon Olefins

Considerable time has been spent in an attempt to prepare polymers containing perfluoroalkyl side chains, typified by poly-2-perfluoropropylpropylene. Some of the experiments are listed in Table III.

TABLE III

Polymerization Studies of 2-Perfluoropropylpropylene (FPP)

Catalyst	Recipe	Conditions	Results
BF_3	0.2 g. FPP + BF_3	BF_3 passed through at -80°	No polymer
ϕ_3CNa	3-4 drops FPP 2 ml. ether sol. ϕ_3CNa	-80°	No polymer
Diethyl diper-carbonate	0.5 g. FPP 0.5 g. cat.	Sealed tube 106°, 16 hrs.	No polymer
Na	3 drops FPP 2 ml. NH_3 sol. of Na	<-40°	No polymer
$K_2S_2O_8$ $NaHSO_3$	1.3 g. FPP, 2.5 g. H_2O 0.015 g. $K_2S_2O_8$ 0.015 g. $NaHSO_3$ 0.05 g. Duponol ME	Sealed tube 75°, 20 hrs.	No polymer
$K_2S_2O_8$ $NaHSO_3$	1.3 g. FPP, 2.5 g. H_2O 0.015 g. $K_2S_2O_8$ 0.015 g. $NaHSO_3$ 0.05 g. Duponol ME	Sealed tube 125°, 18 hrs. 75°, 18 hrs.	No polymer
$K_2S_2O_8$ $NaHSO_3$	0.5 g. FPP, 2.0 g. acrylo-nitrile, 2.0 g. H_2O, 0.015 g. $K_2S_2O_8$, 0.015 g. $NaHSO_3$ .05 g. Duponol ME	Sealed tubes (2) 75°, 18 hrs.	Polyacrylonitrile with 1% F
$K_2S_2O_8$ $NaHSO_3$	0.5 g. FPP, 2.0 g. styrene 2.0 g. H_2O, 0.015 g. $K_2S_2O_8$ 0.015 g. $NaHSO_3$, 0.05 g. Duponol ME	Sealed tubes (2) 75° 18 hrs.	Polystyrene with <1% F
$Na_2S_2O_8$	0.5 g. FPP, 1 g. H_2O 0.1 g. cat.	Sealed tubes (2) 50°, 16 hrs.	No polymer
Cumene Hydroper-oxide	0.5 g. FPP, 0.007 g. CHP	Sealed tubes (2) 50°, 16 hrs.	No polymer

TABLE III (Continued)

Catalyst	Recipe	Conditions	Results
$InCl_3$	0.5 g. FPP, 0.001 g. $InCl_3$	Sealed tubes (2) 50°, 16 hrs.	No polymer
$Na_2S_2O_8$	0.5 g. FPP, 0.1 g. styrene 0.05 g. $Na_2S_2O_8$, 1.0 g. H_2O	Sealed tubes (2) 50°, 16 hrs.	Polystyrene with <1% F
$Na_2S_2O_8$	0.5 g. FPP, 0.1 g. acrylonitrile, 0.05 g. $Na_2S_2O_8$ 1.0 g. H_2O	Sealed tubes (2) 50°, 16 hrs.	Polyacrylonitrile with <1% F
Cumene hydroperoxide	0.5 g. FPP 0.1 g. vinyl acetate	Sealed tubes (2) 50°, 16 hrs.	No polymer
Cumene hydroperoxide	1.0 g. FPP 0.2 g. vinyl acetate .015 g. CHP	Sealed tubes (2) 125°, 16 hrs.	No polymer
Acetyl peroxide	1.0 g. FPP 0.25 g. cat.	Sealed tube 55°, 48 hrs.	No polymer
t-butyl hydroperoxide	1.0 g. FPP 0.2 g. vinyl acetate 0.05 g. cat.	Sealed tubes (2) 125°	No polymer; tube with vinyl acetate alone shows polymer
t-butyl hydroperoxide	1.0 g. FPP 0.2 g. vinyl acetate 0.05 g. cat.	Sealed tubes (2) 125°	No polymer; tube with vinyl acetate alone shows polymer

As can be seen, most of these experiments were not particularly encouraging. The last two in the table are interesting in that they show the monomer to be reactive with free radicals, since it is able to inhibit the polymerization of otherwise active vinyl acetate. Work on the polymerization of this monomer, which has been inactive for some time, will be resumed in the light of knowledge gained more recently in the copolymerization of C_3F_6 with the vinyl compounds.

Perfluoroimines

A novel class of nitrogen-containing "olefins" has been developed. These are typified by the formula

$$C_nF_{2n+1}N{=}CF_2.$$

Members of this series with n = 2, 3 and 4 have been prepared in sufficiently large amounts for exploratory polymerization work.

Since these compounds hydrolyze rather rapidly in aqueous basic solution and at an appreciable rate in neutral solution, non-aqueous conditions are being examined.

The desired product,

$$\left[\begin{array}{c} F \\ | \\ -C- \\ | \\ F \end{array} \begin{array}{c} C_nF_{2n+1} \\ | \\ N \\ | \end{array}\right]_x$$

corresponds to a saturated tertiary fluorocarbon polyamine. The low molecular weight perfluoro tertiary amines, such as $(C_2F_5)_3N$, are unique in that they possess no apparent basic properties. The compounds do not dissolve in aqueous acid solution, nor do they form salts. They are inert toward oxidizing

agents and are not affected by conditions less stringent than those necessary to destroy the perfluorocarbons themselves. The polymer might therefore be expected to have all of the stability of a fluorocarbon. Insertion of the nitrogen atoms in the chain should provide increased flexibility, so that the low temperature properties desired may be found in this class of polymer.

Polymerization of the imines has been studied using benzoyl peroxide, t-butyl hydroperoxide, cumene hydroperoxide, boron trifluoride-phosphoric acid, and boron trifluoride-ether as initiators. There was no significant reaction except with the etherate, where a gummy white solid was produced. This appears to be an imine-boron trifluoride complex.

Bulk copolymerization with acrylonitrile, styrene, vinyl acetate, C_3F_6 and $C_3F_7C(CH_3)=CH_2$ has been tried, using benzoyl peroxide as initiator at 75°. No reaction was observed with the fluorinated olefins. Although polymers were obtained in experiments with acrylonitrile, styrene, and vinyl acetate, in each case analysis showed the presence of little or no fluorine in the polymer. Further work on the imines is contemplated because their polymers, if obtainable, ought to have interesting properties.

Perfluoro Acrylonitrile

The polymers of acrylonitrile have proven extremely useful in the hydrocarbon field. Experiments have been started toward the preparation of polymers from $CF_2=CF-CN$ and its

derivatives. The perfluoro compound is far more readily hydrolyzed than its hydrocarbon analog and emulsion polymerization in water is difficult because of the rapidity of hydrolysis. Experiments using the standard $K_2S_2O_8$-sulfinic acid-Duponol ME recipes produced a small amount of granular precipitate with a fluorine content of 50-60%, corresponding to the theoretical value for poly-C_3F_3N of 53.1% fluorine. Since the initial monomer layer disappeared, it is assumed the hydrolysis is more rapid than polymerization under the conditions used.

Copolymerization with styrene and with acrylonitrile gave similar results, polymers being obtained in low yield with 5-10% fluorine content, corresponding to 10-15% perfluoroacrylonitrile in the copolymer. Work is continuing with more active initiators at low temperatures and with non-aqueous media.

Bulk polymerization of perfluoroacrylonitrile and copolymerization with styrene and with acrylonitrile, in the presence of cumene hydroperoxide as initiator, yielded polymer only in the case of styrene and then in very small amounts. The activity of the fluorinated monomer toward free radicals is evidenced by its ability to impede the polymerization under conditions in which the hydrocarbon olefin would normally be polymerized completely. In the case of the copolymerization with styrene, the solid contained 20-30% fluorine, corresponding roughly to a 1:1 copolymer.

Further experiments along these lines are planned.

Vinyl Perfluorobutyrate (VFB)

The esters of hydrocarbon alcohols with completely fluorinated acids are characterized by very ready hydrolysis. Exploratory kinetic studies indicate that in aqueous solution at a pH lower than about 6, the rate is first order with respect to ester and independent of hydrogen ion concentration. The rate of hydrolysis is about 10,000 times faster than that of ethyl acetate under similar conditions. However, the stability of polymeric esters is satisfactory, the high molecular weight, with correspondingly low solubility, having decreased the rate of hydrolysis to the point where poly-VFB is stable to boiling water for several hours.

Polymers of $C_3F_7CO_2CH{=}CH_2$ have been obtained from bulk polymerization with a peroxide catalyst. Both water and formamide have been used as a dispersion medium for emulsion polymerization. In no case so far has a latex been produced, although with water and a persulfate-sulfinic acid initiator system, polymer is produced in coagulum form. Activated aqueous recipes using iron-sugar or ascorbic acid result in very low yields of a weak polymer. In many cases the solid obtained had a relatively low fluorine value. Copolymerization with vinyl acetate in formamide resulted in a polymer containing only 4.5% fluorine.

The difficulty of obtaining a stable emulsion of fluorinated monomer in aqueous or hydrocarbon type solvent may be overcome

with long-chain fluorinated acids as emulsifiers. An experiment in which sodium perfluorocaprate was tried yielded a viscous residue of undetermined composition. Further studies are contemplated using initiators active at low temperature, so that the rate of hydrolysis will not play too large a role, and using nonaqueous suspending media.

1,1-Dihydroperfluoroalkyl Acrylates

The perfluoro acids can be reduced in satisfactory yield to the 1,1-dihydroperfluoro alcohols. The esters of these alcohols with hydrocarbon acids have essentially the same hydrolytic stability as is shown by the normal hydrocarbon esters. The first three members of the series, 1,1-dihydroperfluoroethyl, propyl and butyl alcohols, have been converted to the acrylates which have been found to polymerize.

The hydrocarbon acrylates form polymers that are essentially rubbery in nature. The polyacrylates of the fluorocarbon alcohols are very similar in properties. Polymers have been produced on the 250 mg. level that merit extensive further investigation. In a few cases larger scale preparations have already been tried. The polymerizations in general were carried out as previously described. Approximately 0.25 grams of monomer, 0.5 grams of water and corresponding quantities of initiator, activator or emulsifier were sealed in a glass tube of about 2 cc. capacity and agitated in a water bath. All runs were made in duplicate or triplicate; they are summarized in Table IV.

TABLE IV

Polymerization Studies of 1,1-Dihydroperfluoroalkyl Acrylates

Monomers	Appearance of Latex	Appearance of Polymer	Solubility of Polymer	Analysis of Polymer	Remarks
FBA	Pale, Translucent	Rubbery, good adhesion to glass			Monomer layer gone at 2 hrs.
FBA·vinyl acetate	Stable, slight precoagulum	Rubbery, but stiffer than above. 27.4% F			Complete conv. in 40 hrs.
FBA·acrylonitrile	Stable	Hard powder			Complete conv. in 8-10 hrs.
FBA·styrene	Stable	Hard powder			Complete conv. in 8 hrs.
FBA·VFB	None	May be only poly-FBA; not yet analyzed			50% conv. in 8 hrs.
FBA·isoprene	Rather poor latex; particles separate on standing	Rubbery but very tacky; probably of low mol. wt.			Substantially complete conv. in 24 hrs., rel. slow
FBA·butadiene	Rather poor latex; better in appearance than above	Rubbery, snappy, probably of rel. low mol. wt.			High conversion only after 70 hrs.
FBA·C_2F_4	Fair, of normal opacity, some precoagulum	Strong and rubbery			Pressure even after 20 hrs., conv. high but not complete
FBA·C_3F_6	None				All tubes exploded after varying intervals
FBA·C_2F_3Cl	Almost as transparent as water	Strong, less rubbery than previous latex			Conversion high at 20 hrs., some pressure

TABLE IV (Continued)

Monomers	Appearance of Latex	Appearance of Polymer	Solubility of Polymer	Analysis of Polymer	Remarks
FPA:FPP	Clear liquid phase, slimy coag.		Sol. MIBK, C_3F_7COOH	46% F; calc. for FPA: 46.5% F	Maybe slight copolymer, F analyses usually low
FBA:FPP	"		Insol. MIBK, sol. C_3F_7COOH	50.5% F, calc. for FBA: 52.3% F	Probably no copolymer
FEA:styrene	Good latex	Hard powder	Sol. MIBK	59.5% FEA by F det.	Probably copolymer, not proved
FEA:acrylo-nitrile	Good latex	Hard powder	Sol. MIBK, MEK insol. benzene	60% FEA by F det. 35.6% acrylo. by N det.	Sol'y. and analysis indicate copolymer
FEA	Translucent latex, more turbid than FBA	Strong, not rubbery	Sol. MIBK, MEK	34.3% F calc. for FEA: 37.0% F	
FEA-butadiene	Fair latex, precoag.	Soft, tacky, low yield	Disperses in MIBK	44.6% FEA by F det.	
FEA-C_2F_4	Translucent latex, precoag.		Sol. MIBK	37.6% F 37.0% F calc. for FEA	Very little copolymer
FEA-C_2F_3Cl	Precoag. fair latex		Sol. MIBK	10.5% C_2F_3Cl by Cl. det. 74.2% FEA by F det.	Probably not copolymer
FPA-C_2F_4	Translucent latex, precoag.	Rubbery	Sol. MEK	Not completed	
FPA-C_2F_3Cl	Translucent latex, precoag.	---	---	Not completed	
FPA-butadiene	Coarse dispersion	Soft, tacky	Swells, but insol. in MIBK	Not completed	Low yield, darkens in vac. oven

TABLE IV (Continued)

Monomers	Appearance of Latex	Appearance of Polymer	Solubility of Polymer	Analysis of Polymer	Remarks
FBA (control)	Translucent latex, some precoag.	---	---	---	Latex kept for reference
FBA:C_2F_3Cl	Translucent latex, sl. precoag.	---	Disperses in C_3F_7COOH	42% C_2F_3Cl by Cl det.	To be used to confirm previous results
FBA:C_3F_6	Clear liquid phase, precoag.	Rubbery	Sol. C_3F_7COOH No gel	61.3% F 52.3% calc. for FBA	C_3F_6 contained 6% C_2F_4 which may have polymer
FBA-C_2F_4	Clear latex, precoag.	---	Forms viscous gel in C_3F_7COOH, small insol. fraction	Not complete	---
FBA-C_2F_3Cl 25:75	Clear latex, precoag.	---	Disperses in C_3F_7COOH; sol and gel phases	Not complete	---
FBA-butadiene	Translucent latex, slimy precoag.	Soft but rubbery, snappy, not tacky.	Sol. Benz. C_3F_7COOH, 1-Cl-1-NO_2 propane gel present	Infrared indicates copolymer; % F indicates 59.5% FBA	A good copolymer; promising properties
FBA-C_2F_3Cl	Clear latex very sl. precoag.	---	Turbid dispersion in C_3F_7COOH	12.7% Cl, 42.0% C_2F_3Cl 49.2% F	Will be fractionated and analyzed if possible
FBMA	Sol'n. in $C_3F_7CO_2H$	Brittle, weak			
FBMA-FBA	Sol'n. in $C_3F_7CO_2H$	Soft, flexible			

Examination of the polymers obtained from these experiments showed that most of them are true copolymers. Some, however, can be separated into sol and gel fractions of different composition by their solubility in perfluorobutyric acid. The trifluorochloroethylene-FBA polymer was separated into a sol fraction of negligible fluorine content and a gel fraction which had the same analysis as polymerized trifluorochloroethylene, indicating that the two monomers had polymerized separately.

Polymers from the C_2F_4-heptafluorobutylacrylate reaction could be separated into a sol fraction which contained a negligible amount of C_2F_4 and a gel fraction which contained 61.5% fluorine. Polytetrafluoroethylene has 72% fluorine, poly-FBA, 52%.

Modification of Haloethylene Polymers

The two highly fluorinated commercially available plastics, polytetrafluoroethylene and polytrifluorochloroethylene, present many desirable properties. If their less desirable characteristics could be modified by polymerization under somewhat different conditions than have been used in the past, materials of wider applicability might be produced. Some experiments in this direction have been initiated.

It would be desirable, for example, to prepare a stable latex from these olefins instead of the usual coarse, granular precipitate. One method would be to carry out the polymerization in the presence of fluorinated material as dispersing agent or

as a modifier. Polymerization in the presence of 1,1-dihydroheptafluorobutyl acetate or butyl perfluoroproprionate produced polymer suspensions that settle but which are redispersible. The trifluorochloroethylene polymers are soft and pasty, those from C_2F_4 somewhat tougher. Because of the small scale, the yields were quite poor and the resulting solid was seriously contaminated with emulsifier. The fact that the usual granular precipitates were not obtained indicates that further work is justified.

Attempted copolymerization of C_2F_4 with acrylonitrile or with styrene resulted in the formation of material which could be separated almost completely into two polymer fractions. Under the conditions used, little or no copolymer was formed.

THE PROPERTIES OF 1,1-DIHYDROPERFLUOROALKYL ACRYLATE POLYMERS

The only polymers that have yet been obtained on a sufficient scale to merit further examination are those of the acrylates. Even in this case the quantities prepared were so small that only preliminary examination is possible. Nevertheless, these polymers are adequate to establish some guideposts in the previously unexplored field.

In the series of homopolymers FEA, FPA and FBA, the turbidity of the latex decreases as the fluorocarbon radical increases in size; the direction expected, because of decreased refractive index, as the number of CF_2 groups is increased. The aqueous latices are remarkable for their transparency. The refractive index of the particle is so close to that of water that even those with 30% solid content are transparent.

The rubbery nature of the polymer increases as the fluorocarbon chain length increases. In the case of hydrocarbon acrylates, the minimum brittle point is reached with the eight carbon alcohol.

The polymers are relatively stable toward combustion. While poly-FEA, with 37% fluorine, burns, poly-FPA with 47% fluorine burns only when adequate precautions have not been taken to remove the hydrocarbon emulsifier. Poly-FBA, with

52% fluorine, is self-extinguishing when removed from the flame.

The polyethyl derivative, FEA, is moderately soluble in hydrocarbon solvents. The polypropyl derivative, FPA, is soluble in methyl isobutyl ketone and in heptafluorobutyric acid. The polybutyl derivative, FBA, is insoluble in methyl isobutyl ketone or any other non-fluorinated organic solvents. The copolymers, on the other hand, acquire a solubility in hydrocarbon solvents corresponding to the amount of hydrocarbon introduced into the polymer. The butadiene-FPA copolymer was insoluble in methyl isobutyl ketone, but exhibited considerable swelling. The copolymers of FBA and butadiene or isoprene showed negligible swelling and no solubility in toluene or in methyl isobutyl ketone.

The butadiene and isoprene copolymers with the heptafluorobutyl acrylate are particularly interesting in that they form rubbery elastomers even with the relatively low molecular weight so far achieved. A few exploratory experiments have been made in which these copolymers were compounded in essentially a tread stock recipe to produce material resembling the corresponding product from natural or GRS rubber. The resistance to solvents is exceptionally good. The fact that these particular recipes result in a material of low tensile strength probably arises from the low molecular weight of the present polymer. Because of the relatively high fluorine content of these elastomers,

it would not be expected that the standard compounding conditions would be optimum; the compounding and curing of the polymers is being studied further, for the very small scale samples thus far prepared have not been adequate for extensive evaluation.

SUMMARY

Conditions for the copolymerization of highly fluorinated olefins have been developed. Unlike tetrafluoroethylene, completely fluorinated olefins have proven to be extremely reluctant to homopolymerize.

Vinyl esters of fluorocarbon acids have been polymerized to elastomeric materials; the monomers hydrolyze readily in water, however, and their satisfactory emulsion polymerization is therefore complicated.

The 1,1-dihydroperfluoroalkyl esters of acrylic acid are sufficiently stable to be polymerized under conditions approaching those normally used. Some of the polymers obtained are believed to be high molecular weight elastomers. Copolymers incorporating butadiene and isoprene have been prepared which, after compounding and curing according to standard tread stock recipes, have yielded apparently cross-linked vulcanizates comparable to those obtained from natural or GRS synthetic rubbers - except that the former exhibit considerably increased solvent and fire resistance and have relatively low tensile strength. Such copolymer vulcanizates of 1,1-dihydroperfluorobutyl acrylate show particularly promising properties.

Preliminary experiments have indicated that perfluoroacrylonitrile can be both homopolymerized and copolymerized. A novel class of unsaturates, the perfluoroimines, has also been prepared and is under investigation.

CONCLUSIONS

In order to make a start in the field of highly fluorinated elastomers with desirable low temperature properties, a great deal of auxiliary work has been necessary. Facilities for the preparation of the basic fluorocarbons had to be expanded and developed. New personnel had to be acquired and trained in the specialized techniques of fluorocarbon chemistry. Syntheses had to be devised for the monomers, many of which had not been previously prepared. It has been possible to carry all of these at the same time that the techniques of polymerization of these fluorinated materials were being developed.

Several basic assumptions were necessary to justify the initiation of this work:

1. That monomers containing a high fluorine content suitable for polymerization could be prepared.

2. That these monomers when prepared could be polymerized.

3. That the resulting polymers would have desirable low temperature flexibility.

The first two assumptions have been proven correct. Several classes of monomers, including completely fluorinated olefins, mixed fluorocarbon-hydrocarbon olefins, the vinyl esters of fluorocarbon acids, the acrylate esters of fluorocarbon alcohols, perfluoroacrylonitrile, and perfluoroimines, have been prepared in quantities suitable for initiating polymerization work. As was anticipated, the polymerization of these new classes

of material required the development of new techniques of polymerization. In some cases, at least, these difficulties have been overcome and polymers have been produced. Undoubtedly the optimum conditions have not been attained, but the value of work in this direction has been established.

The validity of the third assumption remains to be proven. The properties of the acrylate polymers and copolymers prepared up to this time are sufficiently interesting to fortify the hope of eventual success. Copolymers which are capable of vulcanization have been obtained and vulcanized. The major effort during the coming year will be directed toward the preparation of more satisfactory fluorinated polymers and more extensive investigation of the structural features necessary to foster low temperature flexibility in this class of material. In addition, the preparation of new classes of monomers and the extension of the known members of the classes already prepared will be intensified.

APPENDIX I

Properties of Fluorochemical Intermediates

Formula	b.p. °C.	n_D^{20}	d_4^{20}
$C_3F_7CH_2I$	91-91.5/740		
$C_3F_7COCH(CO_2C_2H_5)_2$	121-126/27		
CF_3CH_2NCO	55-57/748		
$C_3F_7CH_2NCO$	87-90/737		
$C_3F_7CO_2(CH_2)_4OH$	141-143/737	1.3269*	1.395*
$CF_3CO_2CH_3$	41-43		
$C_3F_7CO_2CH_3$	79.5 - 80.5	1.293	1.483
$C_3F_7CO_2CH=CH_2$	78-79/748		
$CH_2=CHCO_2CH_2CF_3$	92/742	1.3492*	1.216*
$CH_2=CHCO_2CH_2C_3F_7$	31-32/22		
$C_2H_3CO_2CH_2CF_3$	92.0	1.3492*	1.216*
$C_2H_3CO_2CH_2C_2F_5$	102-103	1.3375	1.312
$C2H3CO_2CH_2C_3F_7$	122.0	1.3279	1.455
CF_3CONH_2	75**		
$C_3F_7CONH_2$	105**		
$CF_3CH_2NH_2$	39-40		
$C_3F_7CH_2NH_2$	68/743	1.298	1.493
$C_3F_7CH_2OH$	95/749	1.2942	1.601
C_3F_6	-30		
C_3F_7H	-16 to -18		
C_2F_5H	-49		

* 26°
** Melting Point

APPENDIX I (Continued)

Formula	b.p. °C.	n_D^{20}	d_4^{20}
(Perfluoroimines)			
$C_2F_5N = CF_2$	-13.2		
$C_3F_7N = CF_2$	+12.3 - 12.5		
$C_4F_9N = CF_2$	39.0		
(Perfluoroacrylonitrile)			
$CF_2 = CF-CN$	+16.2 - 16.7		

SECTION II

Contract Period 15 May 1950 to 15 May 1951

INTRODUCTION

Elastomers make up only a very small fraction of the weight of modern aircraft. Nevertheless the correct functioning of these small rubbery parts is vital to the operation of the entire mass of machine. As the requirements of modern design become increasingly stringent, the lack of suitable elastomeric materials begins to be a limiting factor. Although great progress has been made in the past two decades in the development of synthetic rubbers, no material has yet been found which satisfies the combined requirements of freedom from swelling in the presence of hydrocarbon fluids, of freedom from permanent deformation under stress, and ability to operate satisfactorily at the very low temperature frequently encountered at high altitude as well as at polar bases. In view of the major effort that has already gone into such studies, it has become evident that a radically improved rubber can be obtained only through a radically new approach.

One such approach is the development of an elastomer based not upon hydrocarbons but upon fluorocarbons. These compounds, which have only recently become of commercial interest, comprise the analogues of the well-known hydrocarbon families in which hydrogen bonded to carbon has been substituted by fluorine. This exchange confers upon the molecule greatly increased thermal stability and resistance to attack by most chemicals and solvents.

Despite these alterations, the carbon skeletons permit reactions, if not identical with, at least in many cases similar to those familiar to the organic chemist. The Minnesota Mining & Manufacturing Company has been engaged in the development of an electrochemical fluorination process invented by Dr. J. H. Simons at the Pennsylvania State College. This process, which is described in the J. Electrochem. Soc. 95, 47 (1949), involves the electrolysis of a solution of an organic compound in anhydrous hydrogen fluoride. Through its use a great variety of previously unobtainable fluorochemicals can be prepared. Study of the reactions of these compounds has been under way for several years at 3M.

In May of 1949 the Company and the Air Materiel Command of the United States Air Force entered into Contract AF 33(038)-515 to study the preparation and properties of highly fluorinated, rubber-like polymers of potential value in the Air Force program. During the first year the work was primarily exploratory in nature. Most of the emphasis had of necessity to be on the preparation of new types of monomers, the development of techniques of polymerization, and the obtaining of preliminary data on the nature of this type of monomer. During this period, it was possible to demonstrate the desirability of further study of the preparation of fluorinated polymers. Rubber-like materials were prepared on a milligram scale and several classes of interesting polymers were given preliminary evaluation.

During the second contract year, the period covered by the present report, it was possible to put a greater emphasis on the

development of the more promising elastomers, in particular, the 1, 1-dihydroperfluoroalkyl acrylates. Some of the types of polymers which at first appeared promising were found on more extensive study to lack one or more of the properties necessary to meet the stringent requirements of the Air Force.

Because of the novelty of this whole field of chemistry the possibility of obtaining still more suitable monomers and polymers is very high. Several new compounds have been developed and the study of their polymerization characteristics initiated. Exploratory polymerization studies have been valuable even when the product was unsatisfactory. So little work has been done in this field that there were no signposts. Even at present there are too few data to support firm generalizations, but at least there are some. A stiffening effect of fluorine on the polymer backbone has been observed in several cases, particularly in the diene series. Fluorine on the side chain has not produced so much of an effect. On the other hand, backbone fluorine seems to be more effective in improving solvent resistance. Until a sufficient variety of polymer types has been prepared, this exploratory work will have to be continued. It also appears desirable to develop a satisfactory polymer, even though it may not be the eventual optimum. For this reason much emphasis has been placed on further studies of the more promising polymers. Many interesting and potentially important avenues have been passed over for the present and certain promising leads have not yet been followed up, with the understanding that more time will be available for such work in the future.

POLYMERIZATION STUDIES

The conventional polymerization techniques require the use of rather large amounts of monomer. Since this program involves preparations which are frequently tedious and very expensive in terms of material and manpower, as can be expected in the development of new materials, rapid progress has been possible only by reducing exploratory studies to a very small scale. In the study of a new monomer, quantities of the order of 250 milligrams are sealed with a corresponding amount of comonomer, with the emulsion medium and emulsifier in the case of emulsion polymerization, and with the promoter, in short ampoules of 7 millimeters glass tubing. The ampoule is frozen, evacuated, and sealed. Polymerization is carried out by tumbling the ampoule in a thermostat at the desired temperature.

In this manner it has been possible to make the most efficient use of the facilities and manpower. If the preliminary results are encouraging, more effective methods of preparing the monomer are developed and larger scale work initiated.

The chemical names of the fluorinated monomers are frequently lengthy and involved. It has been found convenient to use abbreviations. A table of the monomers, their names and abbreviation will be found at the end of the Experimental section of this report.

CONDENSATION POLYMERS

POLYAMIDES

The familiar polyamides are somewhat crystalline in nature and therefore do not make particularly satisfactory rubbers. The effect of fluorine substitution cannot be reliably predicted, although it may be expected to reduce the interchain attraction of the alkyl portion. It was, therefore, felt desirable to carry on a few preliminary experiments in this class of compounds.

Polyethylene perfluorosuccinamide has been prepared by condensation both in bulk and in solvent. In one experiment, 2.2 g. of diethyl perfluorosuccinate and 0.49 g. of ethylene diamine were dissolved in 25 cc. of dioxane cooled to 0°C. The solution was then heated to refluxing and maintained there for 6 hours. The white crystals that formed were filtered from the solution. When heated, no melting point was observed but the material gradually darkened, as a result of decomposition, between 200-290°C.

Polyhexamethylene perfluorosuccinamide was similarly prepared. Diethyl perfluorosuccinate, 2.5 g., and polyhexamethylene diamine, 1.2 g., were dissolved in 25 cc. of cooled dioxane. Reaction at room temperature was rapid to form a white insoluble product. As first formed, this material melted at 205-210°C. At this temperature further polymerization took place, as evidenced by the increase in viscosity and the liberation of ethanol. Extended heating resulted in no evident cross-linking, the material remaining thermoplastic.

The polyamide appears to be a hard solid with a high degree of internal strength. Fibers, which can be cold-drawn, are formed from the melt.

A third polyamide was prepared from 6 g. of diethyl perfluoro-adipate and 2.4 g. of hexamethylene diamine dissolved in 25 cc. of diethyl ether. After the solution had been refluxed for 1 hour, a white crystalline product was obtained. This material melted and further polymerization proceeded at slightly above the melting point. Unfortunately a final product was obtained which was infusible, suggesting that cross-linking had occurred. This may have been due to the presence of impurities in the starting material.

These results are not particularly encouraging, but the product of an α-α-ω-ω-tetrahydroperfluorodiamine and a perfluoro dibasic acid should be studied.

POLYESTERS

Several of the known high molecular weight polyesters of the hydrocarbon series have somewhat rubbery properties. For this reason, the product of fluorinated glycols and diesters have been given a preliminary investigation. The ready hydrolyzability of the monomer esters of the fluorocarbon acids is well known. However, the polyesters, such as ethylene glycol diperfluorobutyrate, glycerol triperfluorobutyrate, and pentaerythritol tetraperfluorobutyrate, when adequately purified, have been found to be only very slowly hydrolyzed by prolonged refluxing with water. It seems evident

that a polyester of sufficiently high molecular weight to be an elastomer would also have adequate hydrolytic stability.

A preliminary direct esterification of ethylene glycol by perfluorosuccinic acid resulted in a viscous liquid which did not appear rubbery, although it may have applications as a hydraulic fluid or as a plasticizer.

An attempt to obtain a polymer by ester interchange with diethyl perfluorosuccinate in ethylene glycol was unsuccessful. Even in the presence of zinc oxide, as catalyst, the interchange was prohibitively slow and discoloration was evident. Condensation was carried out by mixing 2.5 g. of diethyl perfluorosuccinate, 0.6 g. of ethylene glycol, and 0.0016 g. of zinc oxide. The mixture was refluxed at 170°C. in an oxygen free atmosphere for 16 hours, followed by heating at 0.5 millimeters for 4 days. Only a viscous yellow liquid was obtained.

The condensation of perfluoroadipic acid and 1,1,6,6-tetrahydroperfluorohexanediol-1,6 was accomplished by dissolving 0.29 g. of perfluoroadipic acid and 0.26 g. of tetrahydroperfluorohexanediol-1,6 in 5 cc. of toluene and refluxing until water was no longer liberated. The toluene was then distilled and the residue heated for 2 days at approximately 170°C./1 mm. pressure. A small amount of a dark, rubbery polymer was found. This material became brittle after several weeks at room temperature.

The esterification becomes slow at a relatively early stage, and considerable difficulty has been encountered in the preparation of polyesters of sufficiently high molecular weight. The condensation of 0.2 g. of perfluorosebacic acid and 0.3 g. of ethylene glycol at 125°C. for 22 hours, followed by 4.5 hours at 150°C./0.5 mm., produced a wax-like polyester with a melting point of about 130°C. The direct esterification of perfluoroadipic acid with ethylene glycol and diethylene glycol proceeded only to the stages of a viscous liquid. An equimolar mixture of tetrahydroperfluorohexamethylene glycol, $HOCH_2(CF_2)_4CH_2OH$, and perfluoroadipyl chloride, heated under anhydrous conditions without solvent for 96 hours at 100°C., formed a viscous liquid which could be converted to a waxy material by further heating for 48 hours at 120°C./0.5 mm. None of these compounds is of sufficiently high molecular weight to exhibit rubbery properties. The viscous liquids are substantially non-volatile and insoluble in hydrocarbon solvents. They may be of value as plasticizers for some of the fluorinated rubbers.

PERFLUOROOLEFINS

An extensive investigation of the polymerization properties of the higher perfluoroolefins indicated that they are much more resistant to free radical activation than is C_2F_4. Polymerization was not initiated by acids or bases. Copolymers could be obtained with the vinyl ethers, vinyl esters, or vinyl chlorides, in the

presence of a free-radical polymerization initiator. A more thorough study of these systems was therefore made.

C_2F_4

The simplest of the perfluoroolefins copolymerizes with the vinyl ethers. A mixture of 0.54 g. of C_2F_4, 1.0 g. of vinyl isopropyl ether, and 0.015 g. of acetyl peroxide was allowed to react for 20 hours at 60°C. in an ampoule. Analysis of the polymer formed showed the presence of 27% by weight of fluorine, corresponding to 35% copolymerized C_2F_4.

C_3F_6

This olefin has been given the most thorough study with the vinyl ethers. It was soon found that anomalous results were obtained unless very special precautions were taken to purify the olefin. The vinyl ethers are particularly sensitive to homopolymerization in the presence of even traces of acid. Passage of C_3F_6 through aqueous base followed by drying over calcium sulfate results in a material which, when sealed with vinyl isopropyl ether in the absence of peroxide, forms no polymer after 16 hours at 65°C.

A series of experiments was carried out to compare the efficiency of acetyl peroxide with benzoyl peroxide as the initiator. Polymerization was carried out in small sealed tubes at 50, 70, and 85°C. for 48 hours, with a mixture of 10 parts by weight of C_3F_6, 1 part vinyl acetate, and 0.1 part of initiator. Polymers were

obtained in 70-80% yield with acetyl peroxide. The fluorine content varied from 23-30%, corresponding to 30-40% C_3F_6. Higher temperatures resulted in higher yields of polymer but the product contained less fluorine. The use of benzoyl peroxide resulted in only 35-45% yields of polymer containing 30-40% of C_3F_6. Acetyl peroxide appears to be considerably more satisfactory, particularly at lower temperature.

The effect of varying vinyl acetate:C_3F_6 ratios was studied. With benzoyl peroxide at a temperature of 70°C., a 48-hour reaction period resulted in the formation of 50% polymer from a 5:1 olefin: acetate ratio. A 15:1 ratio resulted in 70% yield. In the first case, 25% C_3F_6 was found in the polymer and in the second, 33%. The use of acetyl peroxide at 50°C. with a 10:1 C_3F_6:vinyl acetate ratio resulted in a polymer containing 50% of copolymerized C_3F_6. Again acetyl peroxide appeared to be superior.

In an effort to avoid homopolymerization, the emulsion polymerization with vinyl acetate was studied. The basic recipe consisted of:

Vinyl Acetate	1 g.
C_3F_6	10 g.
Water	20 g.
$K_2S_2O_8$	0.1 g.

To this was added 0.1, 0.2, 0.3, and 0.4 g. of Duponol ME. Polymerization was carried out at 70°. No pronounced variation between the various tubes was observed, the fluorine content of

the polymers being 11-13%, corresponding to 15-17% C_3F_6. This was substantially less than had been found in bulk polymerization. The decrease can be accounted for by the low solubility of C_3F_6 in the medium and in the micelles of the emulsifier.

Attempted emulsion copolymerization with vinyl isopropyl ether in the presence of Duponol ME and $K_2S_2O_8$-$NaHSO_3$ was unsuccessful. With $K_2S_2O_8$ and sodium stearate, a latex was not obtained but instead a lump of polymer containing 48% fluorine, corresponding to 54% C_3F_6. The results are similar to those in bulk polymerization and evidently no true emulsion was obtained.

Basic recipes were also studied. In the presence of borax a polymer containing 58% copolymerized C_3F_6 resulted. In a series of experiments with vinyl isopropyl ether, a recipe of:

C_3F_6	0.5 g.
VIPE	0.5 g.
H_2O	1.8 g.
$K_2S_2O_8$	0.05 g.
Borax	0.01 g.

was used. From 0.005 to 0.030 g. of sodium stearate was added to the various tubes. Agitation at 65° for 64 hours resulted in 70-80% yields of approximately 1:1 copolymers, although no latex was formed in any case.

The vinyl butyl ethers are apparently less sensitive to acid polymerization. In experiments with vinyl n-butyl ether and vinyl isobutyl ether, polymers were obtained with 37% fluorine, corresponding to 48% copolymerized C_3F_6. A 1:1 mole ratio would result in 46% fluorine.

Attempts to find additional monomers which would successfully copolymerize with C_3F_6 were unsuccessful. From bulk experiments with vinyl chloride, acrylonitrile, styrene, isoprene, and isobutylene, polymers were obtained in each case with only relatively small amounts of fluorine. Maleic anhydride, dibutyl maleate, dimethyl maleate, allyl glycidyl ether, and propylene oxide were also tried with C_3F_6. Acetyl peroxide was used as initiator. After 50-80 hours at temperatures ranging from 50-70°C., no polymer was obtained.

C_4F_8

The acid catalyzed homopolymerization of vinyl ethers has been found to be even more pronounced with the C_4 olefins than with C_3F_6. Preliminary experiments with C_4F_8-1 and vinyl isopropyl ether, in which equal weights of the two were reacted at 60° in the presence of 1% acetyl peroxide, resulted in a product which consisted of two layers: an upper viscous liquid containing 15% fluorine (20% C_4F_8) and a lower layer of white, brittle polymer containing 60% fluorine (76% copolymerized C_4F_8). A 1:1 mole ratio in this case would correspond to only 68% C_4F_8. The lower layer therefore appears to contain some C_4F_8 units joined together in the polymer.

However, an attempt to repeat this experiment on a larger scale resulted in a polymer containing only 27% fluorine.

A series of tubes were prepared containing

Perfluorobutene-1	0.5 g.
VIPE	0.5 g.
$K_2S_2O_8$	0.005 g.
H_2O	1.8 g.

and either sodium stearate or Aerosol OT to the extent of 0.02 to 0.08 g. In addition some of the tubes contained 0.1 g. of borax. The tubes were agitated for 60 hours at 75°C. In most cases no polymer was obtained. In a few a very small amount of polymer analyzing 30-50% fluorine was formed. Similar results were obtained when i-C_4F_8, $(CF_3)_2C=CF_2$, was used in place of the perfluorobutene-1. Both of these olefins were somewhat less reactive than C_3F_6.

The more promising conditions were examined in another series of runs.

TABLE I

Vinyl Ethers - C_4F_8-1

Tube No.	Monomers	Catalyst	Buffer & Water	Emulsifier	Results
1	0.5 g. VIPE	0.005 g. $K_2S_2O_8$ 0.005 g. $NaHSO_3$	0.01 g. borax 2.0 g. water	0.02 g. Na stearate	Ampoule broke
2	0.5 g. VIBE 1.0 g. C_4F_8-1	0.005 g. $K_2S_2O_8$	0.01 g. borax 2.0 g. water	0.02 g. Na stearate	Two liq. layers; small amt. white powder, 31% F

TABLE I (Cont.)

Tube No.	Monomers	Catalyst	Buffer & Water	Emulsifier	Results
3	0.3 g. VME 1.0 g. C_4F_8-1	0.005 g. $K_2S_2O_8$	0.01 g. borax 2.0 g. water	0.02 g. Na stearate	Two liq. layers; small amt. white powder, 17% F
4	0.5 g. VIPE 1.0 g. C_4F_8-1	0.005 g. $K_2S_2O_8$	0.01 g. borax 2.0 g. water 0.01 g. 30% NH_4OH	0.02 g. Na stearate	Small amt. reddish brown polymer, 13% F

This type of recipe does not appear to be particularly effective for emulsion polymerization of the perfluoroolefin-vinyl ether system.

Two attempts were made to prepare olefin-ether copolymers of low enough molecular weight to be fluid. Three grams of C_4F_8-1, 1 g. of isopropyl ether, and 6 g. of chloroform or carbon tetrachloride were allowed to react for 18 hours at 75° in the presence of 0.05 g. of benzoyl peroxide. In both cases the residue after removal of solvent and excess monomer was a black rubbery polymer containing only a small percentage of fluorine. Apparently the major reaction was a homopolymerization of vinyl isopropyl ether.

Attempted polymerization with propylene oxide in a tube containing 1 g. n-C_4F_8-1, 1 g. propylene oxide and 0.01 g. of acetyl peroxide at 55°C. for 48 hours was unsuccessful. A mixture containing 1 g. of C_4F_8-1, 1 g. of vinyl isopropyl ether, and 0.02 g. of acetyl peroxide in 2 g. of methyl perfluorobutyrate produced only

a tacky polymer of very low fluorine content, after 18 hours heating at 55°.

C_9F_{18}-1

Attempts have been made to prepare polymers from the nine-carbon terminally unsaturated olefin, C_9F_{18}-1. Three small scale sealed tubes were used with 0.02 g. of acetyl peroxide as the initiator. In one tube, 1 g. of C_9F_{18}-1 was sealed; in the second, 0.5 g. of C_9F_{18}-1 and 0.05 g. of vinyl acetate; in the third, 0.5 g. of C_9F_{18}-1 and 0.05 g. of vinyl isopropyl ether.

The results were similar to those observed for the lower members of the series. No homopolymerization was observed. The vinyl acetate copolymer, with a fluorine content of only 20% (26% olefin), was a tough, white material. The vinyl isopropyl ether copolymer contained 26% fluorine, corresponding to 34 weight % of olefin. It is obvious that considerable homopolymerization of the vinyl ether occurs since the 1:1 copolymer would contain 66% fluorine. Efforts are continuing to prepare the 1:1 copolymer, which would contain 87% perfluoroolefin by weight and would be indicative of the ultimate results to be obtained from this class.

Perfluoroalkyl Olefins

A polymer from the perfluoroolefin just described would contain fluorine both on the side-chains and on the backbone. Another type of polymer, one containing a hydrocarbon backbone with fluorocarbon

side-chains, would be obtained from the perfluoroalkyl olefins 2-perfluoropropylpropene, 2-perfluorobutylpropene, and 2-perfluoroamylpropene. This polymer might be characterized by the superior flexibility of the hydrocarbon backbone and still maintain the solvent resistance of the perfluoroalkyl groups.

Perfluoropropylpropene did not yield a homopolymer in the presence of either peroxide or boron trifluoride, nor was polymerization observed with vinyl isopropyl ether and acetyl peroxide. When a mixture of 1 g. of the olefin, 1 g. of vinyl acetate, and 0.02 g. of acetyl peroxide was heated for 60 hours at 60° in the small tube set up, a 73% yield of a polymer containing 36.4% fluorine (57.3% perfluoropropylpropene) was obtained. A 1:1 mole ratio copolymer would contain 45% fluorine.

The perfluorobutyl and perfluoroamyl homologues also failed to polymerize in the presence of acetyl peroxide. Copolymerization with vinyl acetate under conditions similar to those successful with the perfluoropropylpropene were unsuccessful in both cases.

Although polymerization of the perfluoroalkyl olefins cannot be given high priority, it is hoped to resume work on this type of compound at a later date.

Fluorinated Acrylonitriles

Perfluoroacrylonitrile, CF_2=CFCN, hydrolyzes quite rapidly in water solution and hydrolysis has been the predominant reaction under

the conditions of emulsion polymerization so far studied. Most of the exploratory experiments have therefore been in bulk.

Homopolymerization in the presence of boron trifluoride or acetyl peroxide has been essentially unsuccessful. Under moderate conditions very small quantities of a very low molecular weight material was produced. Under more stringent conditions the polymerization tube exploded. Methyl magnesium iodide in ether can be used as an ionic polymerization initiator with acrylonitrile. An experiment with Grignard reagent as initiator for the polymerization of perfluoroacrylonitrile resulted in the formation of fluorine-containing, methanol-soluble, highly colored material. The product appeared to be a result of the addition of the Grignard reagent rather than polymerization.

Several bulk copolymer systems were investigated. The experiments involved equal weights of the two substances in the presence of approximately 1% acetyl peroxide. The tubes were maintained at 80°C. for 2 weeks. The reactions with vinyl isobutyl ether, perfluorobutyl acrylate, C_3F_6, and i-C_4F_8 yielded either no polymer or one which was essentially fluorine free. With isobutylene a resinous polymer containing 30% fluorine was obtained. Vinyl chloride yielded a polymer containing 15% fluorine and 36% chlorine.

Copolymerization with vinyl acetate was more successful. The reaction was carried out in a small tube with acetyl peroxide as catalyst at 50°. In a series of experiments the weight ratio of

nitrile to vinyl acetate was varied from 1:1 to 12:1. Over this range, the fluorine content of the polymer varied from 20% in the 1:1 ratio to 28% in the 12:1 ratio. The latter represents nearly a 1:1 mole ratio. No rubber-like properties were observed in the polymers.

The copolymerization reactivity of perfluoroacrylonitrile is similar to that of the perfluoroolefins. All of the materials that have formed copolymers lie in the "low Q", non-conjugated region of the Price-Alfrey diagram. Further study of this region may be profitable.

A related nitrile, α-perfluoropropyl acrylonitrile, $C_3F_7C(CN)=CH_2$, showed somewhat higher reactivity. Homopolymerization was not observed in a standard recipe of:

α-FPAN	0.125 g.
Copolymer	0.125 g.
Water	0.45 g.
Duponol ME	0.0075 g.
$Na_2S_2O_8$	0.0025 g.
Borax	0.0025 g.

With styrene a copolymer containing 31.1% fluorine (52.5% α-FPAN) was obtained. With acrylonitrile a polymer containing 13.2% fluorine (22.3% α-FPAN) was found. In neither case was there evident hydrolysis of the nitrile. Neither copolymer shows elastomeric properties.

Much more encouraging results were obtained with butadiene as a comonomer in the above recipe. The materials were sealed in tubes containing respectively 0, 0.00025, 0.00075, and 0.00150 g. of tertiary dodecyl mercaptan. Polymerization was carried out for 48 hours at 55°C.

The polymer prepared in the absence of mercaptan was quite rubbery. It contained 61% by weight of the nitrile. Examination showed an ASTM brittle point of -40 to -50°C. and a swelling volume of 600% in 70:30 isooctane:toluene solvent. The polymers prepared in the presence of mercaptan appeared to be over-modified. They contained 57% nitrile by weight, showed a brittle point of -40 to -50°C. and 200% swelling in isooctane:toluene.

FLUORINATED DIENES

Although elastomeric polymers have been, in a few cases, prepared without the use of conjugated diene monomers, most of the presently known rubbers contain a butadiene derivative as one component. Several members of this class have been studied in homo- and copolymer systems.

Perfluorobutadiene

This monomer has been obtained, with the cooperation of the Air Force, from two outside sources: Purdue Research Foundation which is also engaged in a contract with the Air Force, and the M. W. Kellogg Company, which is engaged in work leading to fluorinated polymers under the sponsorship of the Quartermaster Corps.

Homopolymerization was studied in three recipes.

TABLE II

Homopolymerization of Perfluorobutadiene

	A	B	C
FB	100	100	100
Water	180	180	180
Duponol ME	1.6	--	3.0
Na Perfluorocaprate	3.2	7.2	--
$Na_2S_2O_8$	0.56	2.0	--
$K_2S_2O_8$	--	--	5.0
Borax	0.56	1.0	--
Time	6 days	6 days	4 days, 50°
Temperature	50°	50°	2 days, 60°

From recipes A and B, small yields of hard, resinous polymers were obtained, which contained 63% of the theoretical fluorine content of poly-FB in the case of the polymer from A, and 82% in the case of the polymer from B. Some polymer formed in C, but these tubes exploded prematurely.

Copolymers with styrene and acrylonitrile were prepared in the following recipe:

Perfluorobutadiene	0.250 g.
Comonomer	0.25 g.
Water	0.45 g.
Duponol ME	0.0075 g.
$Na_2S_2O_8$	0.0025 g.
Borax	0.0025 g.

Latices were obtained from both styrene and acrylonitrile. In the former case the copolymer contained 16.8% perfluorobutadiene and with the acrylonitrile only 2.3%. Neither polymer was particularly promising. Further work is in progress with other comonomers.

2-Chloroperfluorobutadiene

This perhalobutadiene was obtained from the Purdue Research Foundation. It appears to be capable of both homo- and copolymerization. Bulk polymerization in a sealed tube in the presence of 1% acetyl peroxide proceeded slowly. After two weeks at 80°, a brown, tacky polymer had been formed in poor yield. Emulsion polymerization using a standard Duponol ME-$K_2S_2O_8$ recipe was allowed to proceed for 24 hours at 55° and then was heated for 48 hours at 100°. A rubbery polymer was obtained in poor yield. Analysis showed the presence of 17% chlorine, rather close to the theoretical 19%.

Copolymers with butadiene and 1,1-dihydroperfluorobutyl acrylate are described subsequently.

1-Perfluoropropylbutadiene

Substitution of a terminal hydrogen by a perfluoropropyl group does not seem to seriously decrease the polymerization reactivity. In a recipe consisting of

FPB	0.25 g.
Water	0.45 g.
Duponol ME	0.0075 g.
$K_2S_2O_8$	0.0025 g.
Borax	0.0025 g.

a good latex was formed after 5 days agitation at 50°C. The polymer, after coagulation, was light colored and strong, but showed only limited rubbery character, undoubtedly due to excessive cross-linking. The 58.4% fluorine content markedly affected solvent properties. Swelling was very slight in benzene and somewhat greater in methyl isobutyl ketone, diperfluorobutyl ether, and triperfluorobutylamine. Perfluorobutyric acid softened and swelled the polymer, while methyl perfluorobutyrate resulted in a cloudy dispersion.

The experiment was repeated with the persulfate reduced to 0.05 parts per 100 parts of monomer and with 3 concentrations of tertiary dodecyl mercaptan varying from 0.12 to 0.60 parts per 100 parts of monomer. All of the polymers were leathery and showed marked permanent set. The brittle temperature varied from -10, in the absence of mercaptan, to 0 to +10 in the presence of the modifier.

Copolymerization with butadiene was studied in the case of several of these fluorinated dienes in modifications of the basic emulsion recipe:

Fluorinated Diene	0.125 g.
Butadiene	0.125 g.
Water	0.45 g.
Duponol ME	0.0075 g.
$Na_2S_2O_8$	0.0025 g.
Borax	0.0025 g.

The reaction was carried out in the small sealed tubes for 48 hours at 55°. Small amounts of tertiary dodecyl mercaptan were added to

several of the reactions. In no case was any great change from the unmodified polymer observed. The table below shows a few of the properties of the uncured polymers.

TABLE III

Butadiene-Fluorinated Butadiene Copolymers

Comonomer	% Comonomer by Wt.	Brittle Point	Stiffening Point	% Swelling in 70:30 Isooctane:Toluene
1-FPB	57	-55	-45	2000
CFB	56	-30 to -35	-25 to -30	300
CFB	56	-30 to -35	-25 to -30	230
FB	40.5	Not sufficient sample		~ 300
FB	41.8	Not sufficient sample		~ 300
FB	33.8	Not sufficient sample		~ 300

A comparison of the effect of fluorine on the side-chain and fluorine on the backbone of the polymer may be obtained from the fluoropropylbutadiene and chloroperfluorobutadiene copolymers, although it must be recognized that the structural characteristics are not identical. With perfluoropropylbutadiene, the copolymer contained 34.2% fluorine located on the side-chain. 2000% swelling was observed in the isooctane:toluene mixture. In the case of chloroperfluorobutadiene, with 29.8% fluorine located on the backbone, the swelling was only 300%. Comparison of the brittle temperatures favors the side-chain location somewhat. In both instances the properties are considerably less desirable than those obtained with 1,1-dihydroperfluoroalkyl polymers of comparable fluorine content.

The copolymer of FPB with butadiene is firm, rubbery, and very tough. Its mechanical properties as judged from the uncured sample are appreciably better than those of any rubbery polymers so far prepared in this program. While its swelling volume is too high to satisfy the present rigorous requirements without serious modification, it may be of value in some applications.

The chloroperfluorobutadiene and the perfluorobutadiene copolymers were somewhat weak, although elastic. An effort is being made to prepare the butadiene copolymers with the highest possible proportion of the fluorinated diene.

UNSATURATED PERFLUOROALKYL ESTERS

Bis-1,1-Dihydroperfluorobutyl Fumarate

Preliminary studies have been made of the polymerization tendencies of the new ester, $C_3F_7CH_2O_2CCH=CHCO_2CH_2C_3F_7$. No polymer was obtained from an attempted bulk polymerization of FBF in the presence of 2% acetyl peroxide at 75°C. A sodium stearate-$K_2S_2O_8$ emulsion recipe failed to produce polymer. However, from an experiment in which

FBF	0.5 g.
VIPE	0.5 g.
H_2O	2.0 g.
$C_{17}H_{35}CO_2Na$	0.03 g.
$K_2S_2O_8$	0.05 g.

were sealed in a small glass tube at 75° for 24 hours, 0.5 g. of a clear, colorless polymer containing 46% fluorine was found. This approximates the fluorine content expected for a 1:1 copolymer.

The reactivity of the fluorinated fumarate appears to be similar to that of the hydrocarbon ester, in that it shows little tendency to homopolymerize but does enter into copolymers.

Several attempts were made to copolymerize FBF with C_4F_8-1 in bulk and emulsion recipes. No polymer was obtained. The non-fluorinated di-n-butyl fumarate similarly did not copolymerize with C_4F_8-1. The reactivity of the fluorinated fumarate with other monomers will be studied.

1,1-Dihydroperfluorobutyl Sorbate

This is one of the monomers studied in an effort to prepare polymers with a hydrocarbon backbone and a fluorinated side-chain. It was found to homopolymerize and copolymerize readily in the standard Duponol ME-persulfate recipe, a good latex being formed in 4 days at 50°C. Copolymers with styrene and acrylonitrile were also prepared.

The homopolymer, which contained 41.7% fluorine, 92.3% of the theoretical, was a soft elastic material of relatively low molecular weight. The copolymer with styrene, containing 57.5 weight % FBS, and with acrylonitrile, containing 64.5 weight % FBS, both showed limited rubbery characteristics. Severe cross-linking did not appear

to have taken place despite the absence of modifier and the extended reaction period.

The homopolymer was prepared on a somewhat larger scale in a recipe consisting of:

FBS	1.00 g.
Water	1.80 g.
Duponol ME	0.03 g.
$Na_2S_2O_8$	0.003 g.
Borax	0.001 g.

Probably as the result of the lower persulfate concentration, the polymer was firmer and had good rubbery properties. Solvent resistance was promising. The brittle temperature of the uncured polymer was unexpectedly high, appearing to be above 0°C.

1,1-Dihydroperfluorobutyl Crotonate

The reactivity of this unsaturated ester, $CH_3CH{=}CHCO_2CH_2C_3F_7$, appears to be quite low. No homopolymer was obtained with the standard recipe after 1 week at 50°C. Under these same conditions copolymers were obtained with styrene and acrylonitrile, latices being formed in both cases. Analysis indicated the presence of 4% FBC in the acrylonitrile copolymer and 14% FBC with the styrene. Butadiene copolymers were prepared in the presence of tertiary dodecyl mercaptan varying from 0 to 0.330 parts of mercaptan per 100 parts of monomer. While an increasing quantity of mercaptan softened the polymer in the expected manner, no more than 12% FBC was incorporated even at the highest mercaptan concentrations.

Vinyl Perfluoroacyl Esters

Preliminary studies during the first period indicated the possibilities of the vinyl perfluoroacyl esters. Although the monomers hydrolyze very rapidly in water, the polymers were sufficiently insoluble to be classed as water stable, no sign of hydrolysis being observed in boiling water after several hours. A series of microscale experiments was carried out to determine the copolymerization characteristics of vinyl perfluorobutyrate. Experiments described in Table IV were obtained from standard sealed tube experiments with 18 hours agitation at 55°C. The catalyst consisted of 1% of acetyl peroxide.

TABLE IV

Bulk Copolymers of Vinyl Perfluorobutyrate

Monomers	Results % Yield	% F	% VFB	Nature of Product
1.0 g. VFB 1.0 g. Acrylonitrile	45.0	7.2	13.0	Light yellow powder
1.0 g. VFB 1.0 g. Vinyl Acetate	67.0	26.8	46.6	Clear, tough, hard
1.0 g. VFB 1.0 g. Styrene	30.0	1.6	2.9	Clear, hard
1.0 g. VFB 1.0 g. Methyl Methacrylate	65.0	24.9	45.0	White, opaque, hard
1.0 g. VFB 1.0 g. Vinyl Acetate +2.0 g. Me Perfluorobutyrate (solvent)	60.0	28.2	52.8	Clear, colorless, brittle
2.25 g. VFB 0.5 g. Acrylonitrile	25.8	14.5	26.2	Cream-colored powder

TABLE IV (Cont.)

Monomers	Results % Yield	% F	% VFB	Nature of Product
1.4 g. VFB 0.5 g. Vinyl Acetate	67.9	35.1	63.5	Clear, colorless, flexible
1.65 g. VFB 0.5 g. Styrene	37.2	30.8	55.6	Opaque, yellow, flexible
1.20 g. VFB 0.5 g. Methyl Methacrylate	100.0	30.0	54.3	Opaque, white, hard

Vinyl perfluorovalerate and vinyl perfluorocaproate were also polymerized in solution. The tubes, containing 3 g. of the vinyl esters, 6 g. of methyl perfluorobutyrate, and 0.02 g. of acetyl peroxide, were shaken at 55°C. for 20 hours. Clear, extremely viscous solutions were obtained from which colorless, flexible films could be cast.

The valerate and caproate were also subjected to polymerization in aqueous medium. An emulsion recipe consisting of:

Vinyl Ester	0.25 g.
Water	0.45 g.
$K_2S_2O_8$	0.0025 g.
Duponol ME	0.0075 g.

was used with agitation for 48 hours at 45°C. In neither was a latex formed, although a precoagulum containing more than 50% fluorine was recovered. Under the conditions of the experiments, the ester was hydrolyzed before it could polymerize.

Suspension polymerization was attempted in a recipe consisting of:

Monomer	0.20 g.
Water	2.00 g.
Bentonite	0.02 g.
Diisopropylbenzene hydroperoxide	0.01 g.

Mixtures were agitated at 80°C. for 24 hours. With the valerate, a solid of less than 5% fluorine was obtained. In the case of the caproate, a low yield of polymer containing 25% fluorine was recovered.

Very considerable improvement in techniques is necessary before systems involving water can be used with these readily hydrolyzed monomers. It may be desirable to further develop polymerization in non-aqueous media.

Since the most successful results were obtained in solution polymerization, a number of experiments were tried in which a variety of vinyl esters were evaluated. Benzotrifluoride and methyl perfluorobutyrate were indicated by preliminary experiments to be the most promising solvents. The results are summarized in Table V.

TABLE V

Solution Polymerization of Vinyl Perfluoroacyl Esters

Monomer	Solvent	Catalyst	Temp.	Reaction Time, Hrs.	Comment
1.0 g. VFA	3.0 g. MFB	0.01 g. Ac_2O_2	45	18	Polymer is white powder; melts to clear, tough film; yield 45%
1.0 g. VFP	3.0 g. MFB	0.01 g. Ac_2O_2	45	18	Light tan, brittle, clear solid; yield 58%
			60	44	Solution gelled

TABLE V

Monomer	Solvent	Catalyst	Temp.	Reaction Time, Hrs.	Comment
1.0 g. VFV	3.0 g. MFB	0.01 g. Ac_2O_2	45	18	Light tan, brittle, clear solid; yield 62%;
			60	44	Solution gelled
1.0 g. VFC_6	3.0 g. MFB	0.01 g. Ac_2O_2	45	18	Light tan, brittle, clear solid;
			60	44	Solution gelled. Yield 60%
2.0 g. VFB	6.0 g. BTF	0.01 g. Ac_2O_2	55	36	White, granular solid, 78% yield
1.0 g. VFB	9.0 g. MFB	0.1 g. Ac_2O_2	50	24	White, granular, brittle; melts to clear film; 62% yield
2.0 g. VFB	6.0 g. BTF	0.01 g. Ac_2O_2	50	24	Similar to 6, 7, 65% yield
1.0 g. VFB	1.0 g. BTF	0.02 g. Bz_2O_2	55	24	Low yield of white, brittle solid which melts to clear film
2.0 g. VFB	5.0 g. MFB	0.02 g. Bz_2O_2	55	24	Low yield of slightly discolored, brittle solid
0.5 g. VFB 0.5 g. VFA	3.0 g. MFB	0.01 g. Ac_2O_2	50	18	Clear, colorless, brittle solid, fair yield
20 g. VFB	80 g. BTF	0.2 g. Ac_2O_2	50	30	10% yield of clear, very light tan solid
1.0 g. VFA	1.0 g. BTF	0.02 g. Ac_2O_2	50	24	White powder which melts to a clear, tough film
1.0 g. VFC_6	1.0 g. BTF	0.02 g. Ac_2O_2	50	24	Poor yield of clear, colorless brittle solid
1.0 g. VFC_{10}	None	0.01 g. Ac_2O_2	45	16	Clear, brown semi-liquid
1.0 g. VFC_{10}	None	0.01 g. Ac_2O_2	45-55	16 3	Clear, tan, waxy solid
1.0 g. VFC_{10}	1.0 g. MFB	0.01 g. Ac_2O_2	45-15	16 3	Clear, white powder

A cyclic ester, vinyl perfluorocyclohexyl carboxylate, was also studied. A homopolymer was prepared from a bulk mixture of 1 g. of ester and 0.1 g. of acetyl peroxide, sealed in a tube for 16 hours at 50°C. Solution polymerization was studied in a sealed tube experiment in which 1 g. of ester, 3 g. of methyl perfluorobutyrate, and 0.02 g. of acetyl peroxide were agitated for 16 hours at 50°C. The polymer in both cases was similar, being a hard, clear solid softening above 100°.

These polymers are extremely insoluble in most materials. Benzotrifluoride is an adequate solvent for polymerization but the purified, dried polymer cannot be redissolved in it. Methyl perfluorobutyrate dissolves the polyvinyl esters of the higher perfluoro acids but will not redissolve the trifluoroacetate. Aliphatic or aromatic hydrocarbons, non-fluorinated esters, ethers, etc. are not solvents.

Allyl Perfluorobutyrate

An attempt was made to decrease the brittle point of the polyvinyl esters by interposing a methylene group between the carboxyl radical and the chain. Allyl perfluorobutyrate, $C_3F_7CO_2CH_2CH=CH_2$, was found to polymerize and copolymerize, in some cases in excellent yield. Rubbery polymers have not yet been obtained; in some cases the materials are relatively soft or even viscous liquids. This compound may be of interest from the point of view of copolymers with the acrylate esters or in the preparation of polymeric plasticizers.

The results of the initial studies are summarized in Table VI.

TABLE VI

Allyl Perfluorobutyrate Polymerization

Emulsion Recipe

Monomer	0.25 g.
Water	0.45 g.
Duponol ME	0.0075 g.
$K_2S_2O_8$	0.0025 g.

(Samples agitated for 5 days at 50°C.)

Polymer

Comonomer	% F	% AFB	Comment
None			No polymer
Styrene, 0.125 g.	1.4	2.7	Hard, resinous
Acrylonitrile, 0.125 g.	1.0	1.9	Hard, resinous

Bulk Recipe

1% Ac_2O_2 as catalyst

0.5 g. total monomers

(Samples agitated for 5 days at 50°C.)

Polymer

Comonomer	% F	% AFB	Comment
VIBE, 0.125 g.	37.0	71.0	Theor. for 1:1, 37.6% F oily liquid
VIBE, 0.125 g.			No polymer
Styrene, 0.25 g.	8.2	15.7	Hard, resinous
Vinyl acetate, 0.25 g.	28.1	56.0	2 moles vinyl acetate per 1 VFB in polymer

TABLE VI (Cont.)

Comonomer	% F	% AFB	Comment
Allyl acetate, 0.25 g.			No polymer
Maleic anhydride, 0.25 g.	31.6		Viscous liquid
None	47.8	(theory, 52.3)	Viscous liquid
Allyl acetate (control) 0.5 g.			Viscous liquid

Perfluoroalkyl Acrylates

By far the greatest progress toward a low temperature solvent-resistant rubber has been made with the class of compounds obtained from the esterification of acrylic acid with the 1,1-dihydroperfluoro alcohols, such as $CF_3CF_2CF_2CH_2OH$. These alcohols are derived from the perfluoro acids by reduction of the methyl esters. The monomers polymerize rapidly in an essentially standard emulsion recipe. In most cases, an induction period of variable length, due to traces of oxygen, is experienced. Once polymerization is started, it proceeds rapidly and exothermally even at an initial temperature of 30°. It is therefore difficult to maintain a constant temperature. The presently used recipe is illustrated by Table VII. Five separate reactions were carried out under what were intended to be identical conditions.

(See table on following page)

TABLE VII

Polymerization of FBA

(FBA:100; Water:180; Luponol ME:3)

$K_2S_2O_8$ parts	Induction Period, Min.	Temperature Initial	Max.	% Conversion at 2.5 hours
0.40	90	52	67	97.1
0.40	120	45	63	97.3
0.35	170	46	62	96.5
0.35	145	46	64	98.3
0.35	130	46	63	95.1

The combined latices were coagulated by freezing and the polymer was washed and dried. The white, tough, somewhat tacky polymer had an intrinsic viscosity, as measured in methyl perfluorobutyrate solution, of 2.95. The yield was 478 g., 96%. A 440 g. sample of this material was submitted to Wright Field for evaluation (PO 156, Lot 1).

The polymerization is retarded by the presence of mercaptans. With the standard recipe, 90% conversion is reached in 15 to 20 minutes; the presence of 0.025 parts of tertiary hexadecyl mercaptan per 100 parts of monomer necessitates 60 minutes for 90% conversion. The final yields in both cases were essentially quantitative. The addition of the mercaptan also causes the expected decrease in chain length. Where unmodified material has a viscosity above 2.35, the material prepared in the presence of the t-C_{16}

mercaptan has an intrinsic viscosity of only 1.45. These results are very similar to those found for the unfluorinated polymer.

The studies of compounding, curing, and evaluation are included in a subsequent section.

While the solvent resistance of the unmodified 1,1-dihydroheptafluorobutyl acrylate polymer is more than satisfactory, its brittle point appears to be inherently too high occurring at about -20°C. in the uncured polymer.

A study of various copolymer possibilities is in progress, aiming toward decreasing the brittle point without seriously decreasing solvent resistance. Copolymers were prepared with 1,1-dihydroperfluorocapryl and 1,1-dihydroperfluorohexyl acrylate. The former gave material which had very poor properties, apparently from impurities in the capryl ester used as starting material. This reaction will be restudied. Results of the hexyl ester are reported in the section on curing and compounding.

The use of n-octyl acrylate as an FBA comonomer was studied in three experiments, one using a 75:25, one using 50:50, and one using 25:75 mole ratios of the two acrylates. Except in the case of the 75% n-octyl acrylate polymer, where the fluorine content was almost double that expected of the copolymer formed in ratios of the reactants, the polymer appeared to have about the same composition as the monomer mixture.

A methacrylate ester was prepared from 1,1-dihydroperfluorobutyl alcohol and polymerized. The polymer turned out to be a white powder which was plastic rather than rubbery. It was soluble in methyl perfluorobutyrate and benzotrifluoride, but insoluble in acetone, methyl isobutyl ketone, dioxane, and chloronitropropane. Copolymers with FBA have not yet been made.

A number of small scale attempts were made to copolymerize FBA with isoprene, dihydrodicyclopentadienyl acrylate, 2-chloroethyl vinyl ether, 2-chloroperfluorobutadiene, 2-chloroethyl acrylate, and divinyl ether in order to prepare polymers with a double bond or chlorine atom that would be available for subsequent vulcanization. The copolymers of isoprene and 2-chloroperfluorobutadiene were particularly promising. Additional work has been done on these two comonomers. The others will be studied in more detail when time permits.

The system, butadiene:FBA, has been studied extensively. Initial efforts were very promising. An attempt to prepare the copolymers on a larger scale was less successful. It was extremely difficult to reproduce results even under apparently identical conditions. A series of polymerizations was carried out, in which 250 milligrams of FBA was prepared in each of the following recipes and agitated in sealed tubes at 50°C. for 140 hours. Table VIII summarizes the results.

(See table on following page)

TABLE VIII

Butadiene:FBA Copolymers

Butadiene mg.	Water g.	Duponol ME mg.	$K_2S_2O_8$ mg.	t.C_{12} Mercaptan g.	Yield %	Nature of Polymer
125	0.45	7.5	2.5	0	50	Soft, tacky
100	0.45	7.5	2.5	0	50	Firm, tacky
50	0.45	7.5	2.5	0	50	Firm, rubbery
125	0.45	7.5	2.5	0.001	0	--
*125	0.45	7.5	2.5	0	0	--
125	0.45	7.5	1.5	0	50	Firm, rubbery
**125	0.45	7.5	2.5	0	0	--
**125	0.45	7.5	2.5	0.001	0	--

* FHA instead of FBA

** Isoprene instead of butadiene

It seems possible that this lack of reproducibility arises from a competing Diels-Alder condensation of the butadiene and acrylate, to form a cyclohexenyl ester. Not only would this consume the reagent but it is possible that the product would act as a polymerization retarder. The decrease in molecular weight in the low yield experiments and the presence of an ester odor which is absent from those experiments in which rubbery polymers were obtained tend to confirm the hypothesis.

Recently a compound believed to be this adduct has been prepared by reacting 5 g. of 1,1-dihydroperfluoro acrylate with 1 g. of butadiene in a sealed tube without catalyst for 60 hours

at 85°. Fractionation of the resulting liquid under vacuum resulted in the isolation of a small fraction boiling at 47-58°C./ 3 mm. This material analyzed for 42% fluorine, corresponding to about 47 mole % FBA, and had a refractive index of 1.3780. The effect of its addition during the copolymerization of FBA and butadiene will be checked.

A series of small scale experiments in sealed tubes was carried out to determine the most suitable conditions for the consistent preparation of the copolymer. The recipes and results are summarized in Table IX.

TABLE IX

Butadiene-Acrylate Copolymerization

	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7
H_2O g.	0.45	0.45	0.45	0.45	0.45	0.45
FBA g.	0.200	0.125	0.125	0.125	0.125	0.125
BD	0.050	0.125	0.125	0.125	0.125	0.125
Emulsifier g.	Dupohol ME 0.0075	Duponol ME 0.0075	Duponol ME 0.0075	Na stearate 0.0075	Na stearate 0.0075	Na stearate 0.0075
$Na_2S_2O_8$ g.	.0025	.0025	.0025	.0025	.0025	.0025
$NaHSO_3$ g.	.0025	--	.0025	--	.0025	.0025
Borax g.	--	.0025	.0050	.0025	.005	.005
Temp. °C.	40°	45°	40°	45°	40°	40°
Reaction Time, Hrs.	16	44	16	44	16	16
Results	Yield 38% fair latex, rubbery polymer 31.5% F	Yield 20% poor polymer and latex	Yield 65% good latex, strong snappy polymer, 28.0% F	No reaction	No reaction	Poor yield, soft polymer

The trials involving borax in the persulfate:bisulfite recipe appeared to give better results than did the others. Sodium stearate was quite ineffective as an emulsifier for this system. Recipes No. 3 and 4 were therefore further investigated on a larger scale, as summarized in Table X.

TABLE X

Butadiene:FBA Copolymers

	Run 8	Run 9	Run 10
H_2O g.	3.6	3.6	3.6
FBA g.	1.0	1.0	1.0
BD g.	1.0	1.0	1.0
Emulsifier g.	Duponol ME 0.06	Duponol ME 0.06	Duponol ME 0.06
$Na_2S_2O_8$ g.	0.02	0.02	0.02
$NaHSO_3$ g.	0.02	0.02	--
Borax g.	0.04	0.04	0.04
t.-C_{12} Mercaptan g.	0.001	--	--
Temp. °C.	45°	45°	45°
Reaction Time, Hrs.	16	16	16
Results	Av. yield (two ampoules): 36% Av. %F: 24.6 Rubbery polymer of fair prop.	Av. yield (two ampoules): 61% Av. % F: 25.0 Rubbery polymer tougher than 8	Av. yield (two ampoules): 70% Av. %F: 26.4 Good rubbery polymer

The copolymers obtained from experiments 8, 9, and 10 were compounded in a sulfur-Captax-zinc oxide recipe. Cures of 30 and 60 minutes at 300°F. appeared to be inadequate; the polymers showed

little change in physical properties and had a swelling volume in 70:30 isooctane:toluene mixture of 650-750%. Additional curing for 90 minutes at 300°F. produced vulcanizates with a swelling volume of 450% and ASTM brittle temperatures of -60 to -70°C.

To determine the best conditions for a larger run, in which varying ratios of monomers could be studied, three emulsion recipes were tested.

TABLE XI

Butadiene:FBA Copolymerization Recipes

	1	2	3
H_2O	3.6 g.	3.6 g.	3.6 g.
FBA	1.0 g.	1.0 g.	1.0 g.
Butadiene	1.0 g.	1.0 g.	1.0 g.
Luponol ME	0.06 g.	0.06 g.	0.06 g.
$Na_2S_2O_8$	0.02 g.	0.02 g.	0.02 g.
$NaHSO_3$	0.02 g.	0.02 g.	--
Borax	0.04 g.	--	0.04 g.

Polymer had formed in all three recipes after 24 hours at 42°C. The products from the first two were soft, tacky and apparently not homogeneous, but that from No. 3 was a firm, rubbery product which, after curing with sodium silicate for 1 hour at 150°C., produced a vulcanizate with a brittle point of -55°C. and a swelling volume of 95% in a 70:30 isooctane:toluene mixture.

Experiments were then run using recipe No. 3 with FBA:butadiene ratios of 1:1 to 5:1. The products were isolated and cured in a silicate recipe (see next section). The polymers which contained 24 to 35% fluorine were strong and rubbery. The vulcanizates had brittle temperatures of -60 to -70°C. but increased in volume in the isooctane:toluene mixture by 114-180%. The copolymer with 37% fluorine had a brittle temperature of -55° and a swelling volume of only 90%. This material, however, was weak and apparently too highly cross-linked. The 40% fluorine polymer was so weak that its properties could not be measured.

The use of a mercaptan modifier introduces further complication. It apparently retards the reaction sufficiently to allow the Diels-Alder condensation to gain headway. In a recipe which gave high yields of a good rubber in the absence of mercaptan, the addition of 100 ppm. of t.-dodecyl mercaptan reduced the yield to only 5% after 12 hours; 33 ppm. of mercaptan resulted in an 80% yield in 10 hours. The rubbery quality of both polymers was poor. In another case the following recipes were compared.

	1	2
Water	16.2	16.2
FBA	7.5	7.5
Butadiene	1.5	1.5
Duponol ME	0.27	0.27
$Na_2S_2O_8$	0.09	0.09
Borax	0.18	0.18
t.-C_{12} mercaptan	--	0.05

The tubes were agitated at 45° for 5 hours. Conversion in the first case was 82% and the second 85%. The polymer prepared in the absence of mercaptan was a white, firm, snappy material which, when cured in a silicate recipe, showed a brittle temperature of -40 to -50°C. and a swelling volume in the isooctane:toluene solvent of only 70%. The product from Run 2 was so crumbly that it could not be evaluated.

An attempt to study the properties of the 1:1 mole ratio copolymer as the function of conversion produced erratic results. Four identical tubes were prepared. Three of these produced soft, cheesy polymers and the fourth a considerably better polymer, for no obvious reason.

Assuming the Diels-Alder reaction to be uncatalyzed, a series of tubes was prepared for testing with higher persulfate concentration and lower operating temperature. The recipe consisted of:

Water (boiled; distilled)	180
FBA	83.3
Butadiene	16.7
Duponol ME	3.0
$Na_2S_2O_8$	4.0
$Na_2B_4O_7$	2.0

Tubes were agitated at a temperature of 35°. Induction periods varied from 4 to 4-1/2 hours. In one case a 47% yield was obtained at the end of 9 hours and in another only a 10% yield at the end of 14 hours. The polymers contained from 30 to 34 mole % FBA. Despite

the erratic yields and variable and excessive induction periods, the polymers obtained were of fairly high quality, indicating some promise for this approach.

Two additional tubes were prepared with this same recipe except that every precaution was taken to exclude air. Induction periods of only 1/2 hour were observed. The yield was 83.5 and 81.8%. The two polymers differed somewhat in mechanical properties, one, containing 41.8% fluorine, was rubbery and the other, containing 44.4% fluorine, was cheesy. There appears to be no reason for the observed difference, both tubes being charged and run in the same manner. Some of the variables controlling the polymerization of these monomers remain to be discovered. Experiments involving the addition of various amounts of the "Diels-Alder adduct" whose isolation was described above may help in unravelling some of these variables.

It appears probable that the addition of sufficient butadiene to the 1,1-dihydroperfluorobutyl acrylate polymer to lower the brittle point satisfactorily will simultaneously result in too great a decrease in solvent resistance. This may be overcome by the use of other monomers either with or without butadiene. Fluorinated monomers would be particularly desirable since there seems to be a good correlation between the fluorine content and the resistance to swell. 2-Chloroperfluorobutadiene was studied with this in mind.

A series of small scale experiments was carried out using a standard recipe:

Monomer	0.25 g.
H_2O	0.45 g.
Duponol ME	0.0075 g.
$K_2S_2O_8$	0.0025 g.

Mixtures were sealed and agitated in the water bath under the conditions indicated in the table below.

TABLE XII

CFB:FBA Copolymers

Monomers CFB	Monomers FBA	Reaction Conditions Time Hrs.	Reaction Conditions Temp. °C.	Analysis % F	Analysis % Cl	Infrared	Nature of Polymer
0.25	0	23 plus 42	at 55 at 100	not enough sample	17.0	--	Rubbery polymer; theo.: 19.0% Cl; yield poor
0.125	0.125	23 plus 65	at 55 at 100	45.0	4.0	appears to be copolymer	Cl analysis corresponds to 21% CFB
0.188	0.063	23 plus 42	at 55 at 100	--	9.0	--	Cl analysis corresponds to 47.4% CFB
0.063	0.188	23 plus 65	at 55 at 100	45.0	1.6	appears to be copolymer	Cl analysis corresponds to 84% CFB
0	0.25	23	at 55	--	--	--	Control; polymerization is much faster than with CFB present

Two polymer fractions were obtained. One was essentially a precoagulum, for which the analyses are shown. The other was a harder product, presumably highly cross-linked. These contained 0 to 4% chlorine, 30 to 35% fluorine. For comparison, CFB contains 53.2% fluorine and FBA 52.3% fluorine.

Poly-CFB as isolated in the first experiment is moderately rubbery, presumably because of early precipitation from the emulsion. The copolymers with FBA are more resinous and cross-linked. However, it was felt that the recipe could be revised to give higher yields and more rubbery polymers. Further exploratory experiments were therefore tried. These are summarized in Table XIII.

TABLE XIII

Polymerization of 2-Chloroperfluoro Butadiene

Monomers	Ratio	Polym. Method	% Cl	% F	% CFB by Wt.	Comments
CFB		Emulsion	17	--	85.5	Low yield, rubbery polymer
CFB		Bulk	12	--	60	Very low yield
CFB + Trace FBA		Emulsion	1.9	46.0	9.5	
CFB:FBA	1:1	Emulsion	4.0	45.4	20	
CFB:FBA	1:1	Emulsion	0.4	30-35	0-20	Very small sample
CFB:FBA	3:1	Emulsion	5.6	--	28	
CFB:FBA	1:3	Emulsion	1.6	45.7	8.0	
CFB:FBA		Bulk	4.0	49.5	20	1 mole CFB to 3 FBA in polymer
CFB: acrylonitrile		Emulsion borax				
CFB: acrylonitrile		Bulk	2.5	3.2	12	Poor check between F and Cl analyses
CFB:FBA: isoprene	48:48: 4	Bulk	3.6	--	19	Soft, tacky
CFB:FBA: isoprene	43:43: 14	Emulsion borax	7.7	--	41	Clear, rubbery

TABLE XIII (Cont.)

Monomers	Ratio	Polym. Method	% Cl	% F	% CFB by Wt.	Comments
CFB:vinyl ether	1:1	Bulk	--	7	13	Tacky, soft polymer
CFB:vinyl acetate	1:1	Bulk	--	23.2	43.5	Soft, brown polymer

The bulk experiments were carried out at 60° for 5 days, in the presence of 1% acetyl peroxide. Emulsion polymerizations were made with 1% persulfate and 3% Duponol ME, with borax where indicated.

Of particular interest are the two runs in which isoprene was present. These indicated that under the proper conditions chloroperfluorobutadiene was quite reactive and that it could be incorporated up to 40% in a copolymer. This was explored further in a reaction in which was used

CFB	0.25 g.
FBA	0.25 g.
C_5H_8	0.25 g.
Water	0.45 g.
Duponol ME	0.075 g.
$Na_2S_2O_8$	0.0025 g.
Borax	0.0025 g.

In this case only 20% chloroperfluorobutadiene was found in the polymer, which analyzed 63% FBA, 17% isoprene, and 20% CFB. An attempt to determine the brittle temperature was unsuccessful, but the polymer appeared to be quite resistant to swelling in aromatic solvents.

Under similar conditions a polymer was prepared containing 64% FBA, 22% CFB and 13% BD. The unvulcanized polymer appeared dead and inelastic; elongation was poor and the brittle point was in the region of +5 to +12°C. The value of chloroperfluorobutadiene for use in low-temperature polymers appears questionable.

The fluorinated butadiene, 1-perfluoropropyl butadeine, has been studied as a copolymer with styrene but not yet with a perfluoroalkyl acrylate.

Another substituted butadiene, CH_2=CHCH=CHCN, is reported to confer oil resistance when copolymerized with butadiene, without impairing low temperature properties. A small sample was obtained from Dr. C. S. Marvel of the University of Illinois. In preliminary experiments it was found to homopolymerize and copolymerize with FBA and with an FBA: isoprene mixture. In each case the material was resinous rather than rubbery, indicating that too high a proportion of the diene had been incorporated. The FBA copolymer, containing 31% fluorine (corresponding to 60% FBA), showed very slight swelling. The diene was considerably more reactive than had been anticipated. Further experiments are in progress to determine whether the incorporation of a very small amount of 1-cyanobutadiene will improve fuel resistance without sacrifice of low temperature flexibility.

Several of the FBA-BD copolymers became brittle after prolonged standing in air at room temperature. This is presumably due to oxidation of residual olefin linkages; the addition of antioxidants will be studied.

POLYMER EVALUATION

COMPOUNDING AND CURING

The properties of a cured polymer are largely determined by the characteristics of the uncured material. Tensile strengths and solvent resistance can be increased by cross-linking. Brittle points can be decreased to some extent by plasticization. A serious study of the compounding and curing techniques will be undertaken only when a base polymer which seems to approach satisfactory performance has been developed. However, a certain amount of work at the present time is necessary in this field, in order to give some idea of what the finished product will be like. Although one could hardly expect conventional curing agents to be the most satisfactory in the fluorinated system, they provide a logical starting point for the work. Only the acrylate polymers have been studied.

A recipe consisting of:

Polymer	4 g.
Triethylene tetramine	0.2 g.
PbO	0.4 g.

produced a rubbery cure of polybutyl acrylate in 2 hours at 312°. Polyperfluorobutyl acrylate treated according to this recipe was found to cure in 15 minutes to a hard, crumbly mass and in 60 minutes to a very hard, waxy solid. The fluorinated acrylates apparently cured a great deal faster than the non-fluorinated analogues. The time was cut down drastically; a 2-minute cure resulted in a product

which was flexible, had little permanent set, a tensile strength of 360 psi and an elongation of 1000%. A 5-minute cure gave a tensile strength of 350 psi and an elongation of 200%.

A second recipe,

Polymer	4 g.
Dichloroquinone chlorimine	0.2 g.
Pb_3O_4	4.0 g.
SRS Black	1.2 g.

produced a rubbery cure of butyl acrylate in 2 hours. An attempt to cure the polyperfluorobutyl acrylate was a failure.

Rather promising results were obtained from a recipe consisting of:

Polymer	100 parts
Red Lead	10 parts
p-quinone dioxime	2 parts
Triethylene tetramine	2 parts
Magnesium Oxide	15 parts
Ferric Oxide	1 part

At 300°F., the tensile strength increased with curing time to 90 minutes, beyond which time flexibility was lost. A 90-minute cure resulted in a material with the following properties:

Tensile	1240 psi
Elongation	125%
Brittle Point	5°C.
Permanent set	96% recovery from 75% ultimate elongation
Swelling in iso-octane:toluene	Scarcely measurable

On the basis of these results, a 6" test slab of polyperfluorobutyl acrylate was prepared and cured in the recipe for 105 minutes at 300°F. The material was submitted to Wright Field for further evaluation. The following data concerning this sample were abstracted from a report of E. R. Bartholomew, MCREXM-M5488, 15 October 1950.

Immersion Tests

Solvent	Temperature °F.	Duration Days	% Volume Increase	Brittle Point °F.
None				32
Toluene	ca. 75	2.9	6	
Isooctane	ca. 75	2.9	2	
Acetone	ca. 75	2.9	54	
Bromochloromethane			11	
AN-O-366 Hydraulic Oil	158	2.9	-3	
Di-sec-amyl sebacate	158	2.9	-3	
Water	158	2.9	11	
"Silicone" Hydraulic Oil	300	2.9	-3	
Perfluoro (diethylcyclohexane)	120	1	38	
Perfluoro (diethylcyclohexane)	120	5	41	-61
Perfluoro (methyldecalin)	120	1	42	
Perfluoro (methyldecalin)	120	5	53	-61
Fluorolube	120	1	19	
Fluorolube	120	5	26	-38
Bis-perfluorobutyl Ether	120	1	22	
Bis-perfluorobutyl Ether	120	5	21	-31
Tris-perfluorobutylamine	120	1	4	
Tris-perfluorobutylamine	120	5	12	-8

A 10% elongated sample of the polymer was unaffected by exposure to 0.015% ozone for 1 hour. Swelling but no disintegration was observed after 1 week's immersion in red fuming nitric acid at room temperature. One week's aging at 150°F. in air did not appreciably affect the material, causing only a slight shrinkage and a small apparent increase in tensile strength.

The particular polymer sample used was of relatively low molecular weight and extensive curing was necessary to give satisfactory tensile strength. Because of this, the brittle temperature was raised from approximately -20 to +20°C. Somewhat more satisfactory results were obtained with a recipe using a smaller proportion of compounding ingredients and a shorter curing time on a polymer of higher molecular weight. In Table XIV are described the results with poly-FBA, poly-FHA, copolymers of FBA and n-octyl acrylate, and an FBA-FHA copolymer.

TABLE XIV

Curing of Acrylate Polymers

Polymer	FBA	FHA	FBA:50 FHA:50	FBA:25 n-OA:75	FBA:50 n-OA:50	FBA:75 n-OA:25
Red Lead	5	4	5	7	5	5
Paraquinone dioxime	1	0.8	1	1.4	1	1
Triethylene tetramine	1	0.8	1	1.4	1	1
MgO	7.5	6	7.5	11	7.5	7.5
Fe_2O_3	0.5	0.4	0.5	0.7	0.5	0.5
T_b, ASTM brittle temp. °C.	-20	-21	-26	-70	-66	-51
% Swelling in 70:30 isooctane:toluene	0	0	0	158	175	95

Quantities were adjusted for the various polymers so that they would be approximately equivalent on a molar basis. All batches were cured for 90 minutes at 300°F.

The brittle temperature of -20°C. found for the poly-FBA is essentially the same in this case as that found with the uncompounded, uncured stock. Poly-FHA itself has about the same brittle temperature as poly-FBA but the 50:50 mixture of the two appears to be somewhat lower. The expected decrease in brittle temperature with the inclusion of n-octyl acrylate was found. However, the inclusion of even 25% showed a drastic increase in swelling.

Two silicate cures were tried on the acrylate polymer, the first consisted of:

Polymer	1.00 g.
Philblack A	0.45 g.
Lanolin	0.04 g.
Calcium Hydroxide	0.04 g.
Sodium Silicate Pentahydrate	0.10 g.

Curing for 45 minutes at 154°C. produced a vulcanizate which was hard and inelastic. Apparently poly-FBA, because of its high density, cannot tolerate so large a proportion of carbon black as the non-fluorinated polyacrylate. A modified recipe

Polymer	1.00 g.
Calcium Hydroxide	0.04 g.
Sodium Silicate Pentahydrate	0.10 g.

was quite successful. After 45 minutes cure at 154°C. a vulcanizate was obtained which showed 200% elongation and far greater flexibility at room temperature than did the polyamide cure. The brittle point was -25°C. and the tensile strength about 720 psi. A larger sample of this material was prepared and submitted to Wright Field.

Some preliminary studies have been made on the compounding of butadiene copolymers. The sodium silicate system produced a gum vulcanizate with an elongation of 150% and a tensile strength of 870 psi. A sulfur-zinc oxide-tetramethylthiuram disulfide system similar to that which is used in the vulcanizing of butyl rubber produced unexpected difficulties. The polymer broke down very rapidly when milled with the compounding ingredients, so that at the end of 15-20 minutes the original firm polymer was pasty and sticky. The vulcanizate was very weak, with a tensile strength of less than 150 psi, indicating again a badly degraded polymer.

Neither the silicate nor the polyamide cure is entirely satisfactory. The silicate cure introduces a water sensitivity that is undesirable for many applications. Further study of compounding systems is being continued.

PLASTICIZATION OF POLY-FBA

While it would be desirable to obtain a pure cured polymer which had the desired brittle point, it may not be possible to reach this objective. Plasticization offers a means of decreasing the brittle

point perhaps 10 to 20° with relatively little effort. Useful compounds must be compatible with the polymer and the curing system and must be insoluble in common solvents. It is probable that these requirements can not be met with low molecular weight compounds. However, in order to determine some of the characteristics of the new polymers, an evaluation of several low molecular weight materials was undertaken. Poly-FBA was cured according to the following recipe:

Polymer	100 parts
Red Lead	10 parts
MgO	15 parts
GMF	2 parts
Fe_2O_3	1 part
Triethylene tetramine	2 parts
Plasticizer	20 parts

The raw materials were mixed on the mill and the mass cured at 150°C. for 35-40 minutes. Plasticizers tried were

Tris(1,1-dihydroperfluorobutyl)phosphate

Triperfluorohexylamine

Ethylene Glycol Perfluorobutyrate

Glycerol Triperfluorobutyrate

Triperfluorobutylamine Distillation Residues

The unplasticized FBA had a brittle temperature of -11°C. The plasticized materials varied from +4 to -18 in brittle point, with the phosphate the only plasticizer showing a significant lowering. The glycol and glycerol esters appeared to have a stiffening, cross-linking effect. Since the above recipe appeared to lead to over-curing, it was modified to:

Polymer	100 parts
Red Lead	5 parts
MgO	7.5 parts
GMF	1.0 part
Triethylene tetramine	1.0 part
Fe_2O_3	0.5 part

The polymer was compounded and cured for 90 minutes at 150°C., then immersed in the plasticizers until the sample had reached constant weight or had absorbed the desired amount of plasticizer. They were then removed, weighed, and the brittle temperature determined. The results are shown in the following table.

TABLE XV

Plasticization of Poly-FBA

Plasticizer	Conc. of Plasticizer Wt. %	Brittle Temp. °C.	Tensile Strength psi	Solubility of Plasticizer in 70:30 Isooctane:toluene
Tris-1,1-dihydroperfluorobutyl phosphate	15	-25	--	No
	27	-35	--	
Triperfluorohexylamine	1	-18	--	No
	10	-34	--	
	20	-31	--	
Ethylene glycol diperfluorobutyrate	11	-25	600	Yes
	20	-55	450	
Glycerol triperfluorobutyrate	15	-22	--	Probably slightly soluble
	28	-25	--	
Triperfluorobutylamine still residue	1	-18	--	No
None	--	-22	810	--

Triperfluorohexylamine was incorporated on the mill. The quantities are somewhat in doubt because of the relatively high volatility of this material. While ethylene glycol diperfluorobutyrate gave the greatest decrease in brittle point, it was rapidly extracted by the 70:30 isooctane:toluene mixture, as shown by an increase in brittle temperature of one sample from -35 to -23 after 72 hours contact with the solvent. Triperfluorohexylamine reached a constant weight in contact with the isooctane:toluene only after 420 hours during which time the brittle temperature increased from -34 to -26. While higher molecular weight fluorocarbons would be satisfactory from the standpoint of solubility in isooctane:toluene, it is probable that compatibility will be low. More satisfactory results may be expected from some of the liquid fluorinated polymers which have been prepared.

Two linear polyesters, one from ethylene glycol and perfluorosuccinic acid, the other from ethylene glycol and perfluoroadipic acid, were tested with both the polyamine and sodium silicate cures. In each case severe bubble formation occurred in the polymers during cure, presumably because of further condensation of the polyesters. Moreover, it was found the silicate cure was almost entirely inhibited, the polyester reacting more rapidly with the alkaline curing agent than did the polymer. The polyesters may be satisfactory in a different curing system.

One peculiar property of the poly-FBA should be mentioned. A sample which had been cured in a silicate recipe with the inclusion

of 5% by weight of Philblack A was tested on the Bashore resiliometer. A resilience value of 10% on this instrument was found. Such a low value would indicate the usefulness of this polymer in applications for the deadening of mechanical or acoustical vibration.

SUMMARY and CONCLUSIONS

Exploratory preparations of fluorine-containing polyamides and polyesters may be of interest as fibres, films or plasticizers for fluorinated elastomers. They are not very rubbery, however, and lack low temperature flexibility so would be of little or no value as rubber compounds of themselves. A few unexplored types are yet to be studied; the effect of higher molecular weight on polymer properties also merits investigation.

No homopolymers could be prepared from the perfluoro-olefins but an extensive survey has been made of their copolymers with vinyl ethers; these were found to be quite stable and resistant to solvents, but also soft rather than rubberlike. Except for the preparation of a copolymer of very high fluorine content, there appears to be little justification for further work on this particular system. However, attempts to develop other perfluoro-olefin copolymers and to prepare homopolymers will continue.

Fluorinated acrylonitriles have been examined only in a preliminary fashion but further study is encouraged by preparation of a copolymer of butadiene and 2-perfluoropropyl acrylonitrile which combines rubber properties with moderate solvent resistance and a brittle temperature below -40°C.

Three fluorinated butadienes, namely perfluorobutadiene, 2-chloroperfluorobutadiene and 1-perfluoropropylbutadiene have been both homopolymerized and copolymerized. Although their homopolymers are of doubtful value because of high brittle points, these dienes may be useful as copolymer components since they should permit cross-linking by conventional vulcanizing agents.

Vinyl perfluoroacyl esters have been found to polymerize readily to form resinous or plastic rather than elastomeric products. Further investigation of this class of monomers does not appear to be justified.

Preliminary studies of the 1,1-dihydroperfluoroalkyl fumarates, sorbates and crotonates confirmed difficulties anticipated in connection with the homopolymerization and copolymerization of these relatively unreactive monomers. Further work will be considered as new methods or monomers become available but no intensive investigation is presently indicated.

The esters of acrylic acid with 1,1-dihydroperfluoroalkyl alcohols represent the most promising class of monomers examined and studies in this area constitute the major part of the past year's effort. 1,1-Dihydroperfluorobutyl acrylate has received particular attention; this monomer readily forms a rubbery homopolymer which is almost completely resistant to swelling by aqueous and non-fluorinated organic solvents at ordinary temperatures. The brittle point of the homopolymer is about -20°C; this appears to be close to the minimum for the homologous series. It has been lowered by the use of various hydrocarbon comonomers, although at the expense of solvent resistance. Butadiene has proven inadequate when used as a sole comonomer but promising results have been obtained with butadiene-containing terpolymer systems. Intensive efforts are being made to obtain a satisfactory balance between the low temperature brittle point and solvent resistance by such internal plasticization, but the use of a plasticizer as a compounding ingredient may ultimately be necessary to attain a sufficiently low brittle point. Choice of a plasticizer will depend to a large extent on the compounding recipe and curing conditions, but a modicum of exploratory work has been undertaken to

examine the compatibility and efficiency of some of the simple fluorocarbon derivatives; the 1,1-dihydroperfluoroalkyl phosphates, for example, were found to be compatible but did not markedly lower the brittle temperature - the low molecular weight polyesters, on the other hand, seem to be more effective but require new curing recipes. Soft, fluorine-containing polymers such as poly-(allyl perfluorobutyrate) may also be of interest as plasticizers. A rubber compound which is flexible at low temperatures because of the nature of its base polymer is, of course, much to be preferred over one which must be plasticized to develop the proper degree of flexibility.

Little emphasis has been placed on compounding and curing during the past contract year; it is believed such studies should not be pursued extensively until the optimum polymer of any given homologous series has been selected for development. The properties of poly-1,1-dihydroperfluorobutyl acrylate, however, have been sufficiently promising to justify a preliminary study of its curing characteristics and the development of a suitable curing recipe; this study has been limited to recipes known to be suitable for its unfluorinated analogue. Silicate and amine-oxide cures have been found operative but none has proven entirely satisfactory; other curing systems will be investigated as more of this polymer becomes available.

These exploratory polymerization studies have extended an early generalization about fluorinated polymers. Specifically, it has been verified that fluorine, either on the side chain or on the backbone, definitely promotes resistance to swelling or solution by non-fluorinated solvents. Furthermore, it has been concluded that side-chain fluorination does not increase the brittle point as markedly as skeletal fluorine yet is capable of providing very high solvent resistance.

Although the fluorine-containing polyacrylates appear the most promising fuel and oil resistant elastomers discovered under this research project, it would be premature to conclude that still better polymers cannot be found; the field of fluorinated polymers is relatively new and the number of known compounds is small.

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APPENDIX I

TABLE OF ABBREVIATIONS

AFB	Allyl perfluorobutyrate	$CH_2=CH-CH_2O_2CC_3F_7$
BD	Butadiene	$CH_2=CH-CH=CH_2$
BTF	Benzotrifluoride	$CF_3C_6H_5$
CFB	2-Chloroperfluorobutadiene	$CF_2=CCl-CF=CF_2$
FB	Perfluorobutadiene	$CF_2=CFCF=CF_2$
FBA	1,1-Dihydroperfluorobutyl acrylate	$CH_2=CHCO_2CH_2C_3F_7$
FBC	1,1-Dihydroperfluorobutyl crotonate	$CH_3CH=CHCO_2CH_2C_3F_7$
FBF	Bis-1,1-dihydroperfluorobutyl fumarate	$C_3F_7CH_2O_2CCH=CHCO_2CH_2C_3F_7$
FBMA	1,1-Dihydroperfluorobutyl methacrylate	$CH_2=C(CH_3)CO_2CH_2C_3F_7$
FBS	1,1-Dihydroperfluorobutyl sorbate	$CH_3CH=CHCH=CHCO_2CH_2C_3F_7$
FHA	1,1-Dihydroperfluorohexyl acrylate	$CH_2CHCO_2CH_2C_5F_{11}$
α-FPAN	α-Perfluoropropyl acrylonitrile	$C_3F_7C(CN)=CH_2$
1-FPB	1-Perfluoropropylbutadiene	$C_3F_7CH=CHCH=CH_2$
MFB	Methyl perfluorobutyrate	$C_3F_7CO_2CH_3$
n-OA	n-Octyl acrylate	$CH_2=CHCO_2C_8H_{17}$
VFB	Vinyl perfluorobutyrate	$CH_2=CHO_2CC_3F_7$
VFC_6	Vinyl perfluorocaproate	$CH_2=CHO_2CC_5F_{11}$
VFC_{10}	Vinyl perfluorocaprate	$CH_2=CHO_2CC_9F_{19}$
VFP	Vinyl perfluoropropionate	$CH_2=CHO_2CC_2F_5$
VFV	Vinyl perfluorovalerate	$CH_2=CHO_2CC_8F_{17}$
VIBE	Vinyl i-butyl ether	$CH_2=CHOC(CH_3)_3$
VIPE	Vinyl i-propyl ether	$CH_2=CHOCH(CH_3)_2$
VME	Vinyl methyl ether	$CH_2=CHOCH_3$
VNBE	Vinyl n-butyl ether	$CH_2=CHOC_4H_9$

APPENDIX II

Informal Report - April 24, 1951

The Curing of Fluorinated Acrylates

by: J. F. Abere

A. General:

The raw poly-FBA prepared by using an emulsion recipe is white, opaque, and quite tacky. It is easily banded on a cold mill, but despite its tackiness, it can be removed by peeling it back with a knife after the rolls have been stopped. After compounding ingredients have been added the handling properties of the batch improve and the usual "cutting back" procedure may be used in order to insure good mixing.

Until only very recently, the temperature of the rolls at the commencement of milling has been about 35° for the silicate recipes and at room temperature for the amine recipe. This has been the procedure because of the lack of a heating system for the micro mill. Now a suitable heating system is installed and there will be greater flexibility in the compounding process. At this time no evaluation has been made of the effect of mill temperature upon the results obtained with a given recipe. Since poly-FBA is easily worked on a cool mill, it is probable that a high roll temperature is unnecessary and may actually be undesirable.

These procedures, incorporating the use of a cool mill, deviate from the methods described in the literature for the curing of acrylates (see, for example, Service Bulletin H-6, Hycar Polyacrylic rubbers, August, 1950; B. F. Goodrich Chemical Company). Usually,

temperatures from 100 to 150°F. are advised but thus far no difficulties have been observed in getting good cures with poly-FBA when little or no heating is used.

The molding pressure has been 900 psi (gauge) in almost all the work performed with poly-FBA. On our press, and using the small mold, this results in a molding plate pressure of 1800 psi. This value is probably higher than necessary and it is likely that wide variations in plate pressure would produce little or no change in the character of the vulcanizate.

B. Amine Cure:

The most effective recipe of this type which we have used is as follows:

Poly-FBA	100.0
Red Lead	5.0
GMF (paraquinone dioxime)	1.0
TETA (triethylene tetramine)	1.0
Magnesium Oxide (calcined)	7.5
Iron Oxide (Fe_2O_3)	0.5
Temperature 298°F.	
Mold Pressure 1800 psi	
Time - Variable	

This recipe will give a soft and flexible cure if the time is about 1.5 hours. If a less extensible but stronger product is desired then a longer period may be used.

Our usual procedure is to get a good band of polymer working on the mill and then slowly add a mixed masterbatch of all the solid ingredients noted before. Finally, after the batch is well-mixed, the TETA is added either dropwise or in small portions on the end of a spatula. Milling is halted when the mixing is complete and the stock is completely homogeneous.

No attempt has been made to vary the components of this recipe in a systematic fashion. Doubling the vulcanizing ingredients in the formula shown above will produce a somewhat overcured vulcanizate. No work has been performed on the subject of proving or disproving the supposed mechanism of curing by the formation of amide linkages at each end of the TETA in this formula. Thus far, no difficulties with pitting or sticking have been observed in the molding operations.

C. Silicate Cure:

The most successful formula of this type is as follows:

Poly-FBA	100.0
Sodium Metasilicate nona-hydrate	6.72
Calcium hydroxide	2.72

Temperature - 310°F.

Time - 3 hours

Mold pressure 1800 psi

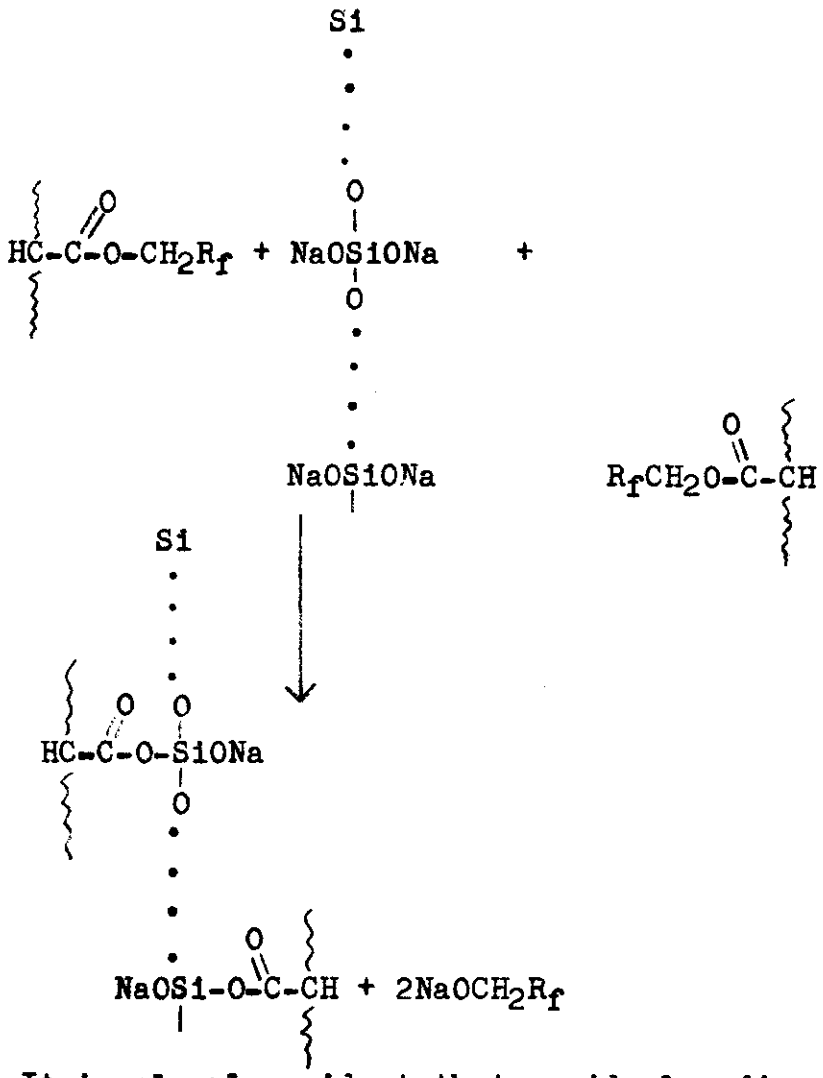
Once again, the first step is to get a good band running on the mill and once this is achieved, the lime is added slowly with enough time allowed for each addition to become fairly well mixed

with the polymer. After the final addition of lime, the milling is continued until a homogeneous batch is obtained. At this stage the metasilicate is carefully heated in a small glass container until it becomes completely liquified. Care must be taken not to induce boiling and thus drive off the water of hydration. With small batches, the molten metasilicate may be added all at once, but if the batch is large (above 10.0 g.), it is probably best to divide the metasilicate into several small portions and then melt and add each one separately.

The polymer may become excessively stiff in regions where the metasilicate concentrates after addition, but upon continuous milling the batch will become homogeneous and may be stripped off. Some signs of bin curing have occurred with batches which have been stored for several weeks.

In this method of vulcanization it is believed that the cross-links are formed by the following type of reaction:

(see reaction on following page)



It is clearly evident that residual sodium silicate groups may be expected to contribute greatly to a decrease in the water resistance of the vulcanizate. Once again, no work has been performed on the theroetical aspect of the supposed mechanism.

If a given batch of polymer, compounded with metasilicate, is subjected to varied times of cure, it is found that the tensile will rise to a maximum and then level off and give substantially the same value even though the time is extended considerably. However, the elongation does not appear to be adversely affected by the extended

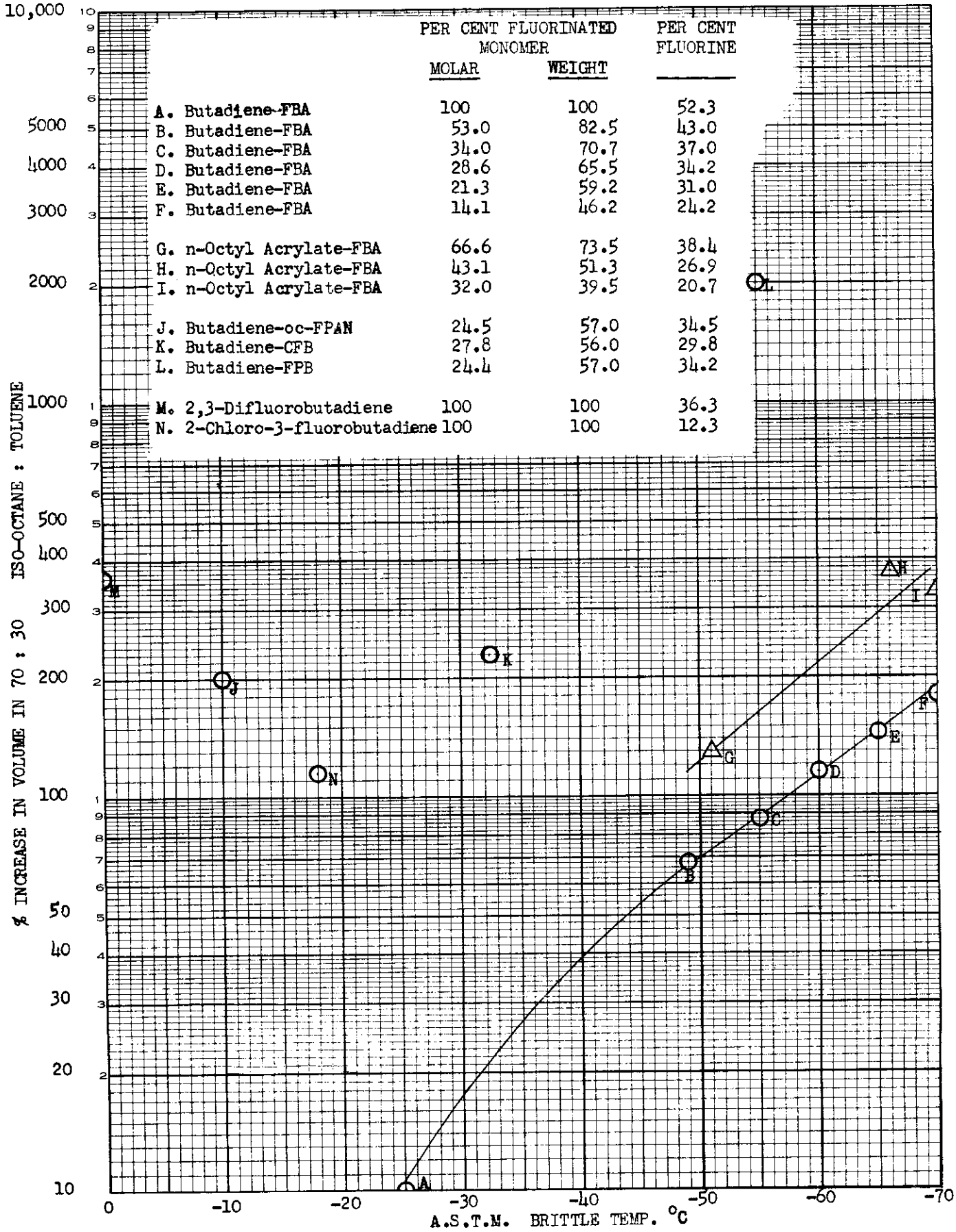
cure and, therefore, the curing time does not have to be fixed with exactness once the general shape of the curing curve is known.

In comparing the amine and the metasilicate cures, the latter is favored somewhat. It has a simple recipe, gives a more lively product with good elongation, and the curing curve levels out to suggest good long-range retention of original properties. Although it might be expected that the amine cure would give better resistance to water penetration, it was observed to yield a swelling volume of 100% in distilled water at room temperature compared with only 70% for the metasilicate cure.

D. Miscellaneous

Several other recipes have been checked but none have shown promise. Sulfur cures, 2,6-dichloroquinone chlorimine and paraquinone dioxime (GMF) were all ineffective when used as the essential ingredients of a recipe (see Quarterly Report for May - July, 1950). None of these formulae have been tested exhaustively and it is to be expected that new and successful formulae will be discovered in the future. A short bibliography of the most pertinent publications is enclosed.

Organic compounds containing isolated fluorine atoms tend to be unstable, in contrast to the stability of perfluoroalkyl-substituted materials. We do not expect, nor have our tests indicated, any significant decomposition during the molding operation such as has been reported for polyvinyl fluoride. However, until more experience has been obtained, precautions to protect personnel would be advisable.



	PER CENT FLUORINATED MONOMER		PER CENT FLUORINE
	MOLAR	WEIGHT	
A. Butadiene-FBA	100	100	52.3
B. Butadiene-FBA	53.0	82.5	43.0
C. Butadiene-FBA	34.0	70.7	37.0
D. Butadiene-FBA	28.6	65.5	34.2
E. Butadiene-FBA	21.3	59.2	31.0
F. Butadiene-FBA	14.1	46.2	24.2
G. n-Octyl Acrylate-FBA	66.6	73.5	38.4
H. n-Octyl Acrylate-FBA	43.1	51.3	26.9
I. n-Octyl Acrylate-FBA	32.0	39.5	20.7
J. Butadiene-oc-FPAN	24.5	57.0	34.5
K. Butadiene-CFB	27.8	56.0	29.8
L. Butadiene-FPB	24.4	57.0	34.2
M. 2,3-Difluorobutadiene	100	100	36.3
N. 2-Chloro-3-fluorobutadiene	100	100	12.3