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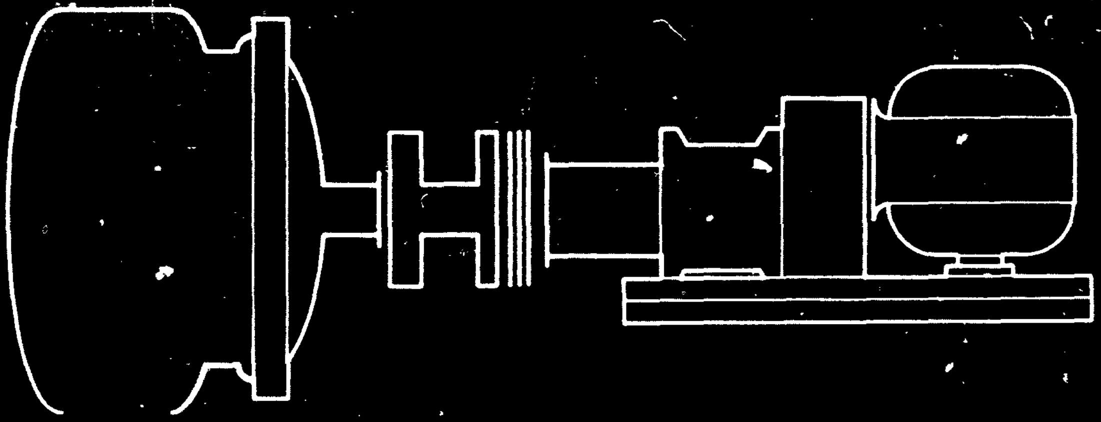

Thiokol
REACTION MOTORS DIVISION

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~~Submitted by:~~ Joseph Green
(10) by JOSEPH GREEN, [redacted]
~~Applied Chemical Research Section~~

Approved by:
MURRAY S. COHEN, Manager
Chemistry Department

DAVID J. MANN
Director of Research

FOREWORD

This report was prepared by Thiokol Chemical Corporation under U. S. Army Contract No. DA-19-129-AMC-69(X)O.I. 9044, QMC Project No. 7X93-15-004 with Mr. Frank Babers as project engineer. Previous reports under this contract have been issued as joint reports of the Reaction Motors Division and Chemical Operations Division under Thiokol Project No. 343 and 8576. The present report is issued as a Reaction Motors Division report under Project No. 8652. It covers the work conducted from 29 November 1964 through 28 February 1965. The project leader is Mr. Joseph Green. Other contributors to the program are Joseph Castellano, Ernest Cottrill, David Kennedy, Nathan Levine and Nathan Mayes.

ABSTRACT

The production phase of the program was completed during the previous quarterly period. The present emphasis is toward the preparation of fluorinated aliphatic and aromatic nitroso compounds with functional groups and their terpolymerization with CF_3NO and C_2F_4 to polymers which may be cured through the functional groups. New methods were explored to prepare nitrosoperfluoroaliphatic and nitrosoperfluoroaromatic acids and, as a result, the new compound — 4-nitroso-2,3,5,6-tetrafluorobenzoic acid — was synthesized.

Terpolymers were prepared containing the functional monomers: vinylidene fluoride, trifluoroethylene, acrylic acid, and 4-nitroso-2,3,5,6-tetrafluorobenzoic acid. Curing studies were carried out on vinylidene fluoride and trifluoroethylene terpolymers.

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I. INTRODUCTION

Army-sponsored research oriented toward the development of a chemical and fuel resistant arctic rubber has resulted in the preparation of a 1:1 copolymer of trifluoronitrosomethane and tetrafluoroethylene, generally referred to as nitroso rubber (Ref 1 through 4). The nitroso rubber exhibits excellent solvent resistance, is nonflammable and is resistant to most solvents except those which are halogenated. The glass transition temperature (Tg) is -51°C. This low Tg value is attributed to rotation of the chain about the N-O bond.

Field evaluation studies of nitroso rubber have been severely hampered by the availability of only laboratory quantities of the rubber. As a result, Thiokol Chemical Corporation has conducted an Army-sponsored nitroso rubber research, development and production program. To date this program has been successful in the development of a process for pilot plant production of nitroso rubber; 200 pounds of the rubber have actually been produced in the pilot plant (Ref 5).

Vulcanizates of nitroso copolymer have been prepared; however, even the best of the gum and silica-reinforced vulcanizates have very low tensile strength. As a result, all efforts during this quarterly period have been directed to the synthesis and characterization of various nitroso terpolymers. The objective of this work is to produce polymers with functional sites for controlled crosslinking and improved mechanical properties without significantly affecting the chemical resistance and low temperature properties. This work includes three tasks:

1. Preparation of nitroso monomers containing functional groups for terpolymerization studies.

2. Polymerization studies to attain high molecular weight curable terpolymers.

3. Polymer characterization.

II. TECHNICAL WORK

PHASE I - MONOMER SYNTHESIS

The object of this phase is the preparation of new fluorinated nitroso monomers that would be expected to improve the low temperature properties of nitroso rubber and/or to provide functionalities which may be used to cross-link the rubber and yield a product with improved mechanical properties. Current work has concerned the preparation of nitrosoperfluoroaliphatic acids, a nitrosoperfluoroolefin and nitrosoperfluoroaromatic acid. These compounds are designed for terpolymerization with trifluoronitrosomethane and tetrafluoroethylene to provide curing sites in these polymers.

A. Aliphatic Nitroso Compounds

Two aliphatic nitroso perfluoro acids, 3-nitrosoperfluoropropanoic acid and 4-nitrosoperfluorobutanoic acid, have previously been synthesized and incorporated into terpolymers (Ref 4). The terpolymers have been compounded and cured and have been shown to possess physical properties superior to copolymers not containing the nitroso acid compounds. The nitroso acid monomers have previously been prepared in low yields by difficult methods and work has been done here to investigate new procedures for obtaining these or analogous compounds more facilely and in higher yields.

1. 3-Nitrosoperfluoropropanoic Acid and 4-Nitrosoperfluorobutanoic Acid

An effort was made to prepare 3-nitrosoperfluoropropanoic acid (I) and 4-nitrosoperfluorobutanoic acid (II) by previously described procedures (Ref 4) in order to substantiate these procedures and to obtain the products for reference purposes.

$ONCF_2CF_2COOH$ I

$ONCF_2CF_2CF_2COOH$ II

The procedures that were investigated involved the reaction of perfluorosuccinic or perfluoroglutaric anhydride with N_2O_3 to obtain the respective dinitrosyl compounds, III and IV, and, subsequently, photolysis and hydrolysis of the compounds to obtain the respective nitroso acids, I and II.

$$\underset{\text{III}}{ONOOC(CF_2)_2COONO} \qquad\qquad \underset{\text{IV}}{ONOOC(CF_2)_3COONO}$$

This reaction sequence is illustrated in Equations 1 and 2.

$$\underbrace{OC(CF_2)_nCOO} + N_2O_3 \longrightarrow ONOOC(CF_2)_nCOONO \qquad (1)$$

$$ONOOC(CF_2)_nCOONO \xrightarrow[-CO_2]{h\nu} ON(CF_2)_nCOONO \xrightarrow{H_2O}$$

$$ON(CF_2)_nCOOH \qquad (2)$$

The dinitrosyl derivatives of both perfluorosuccinic acid and perfluoroglutaric acid (III and IV) were prepared in good yields (> 90%) consistent with the literature procedure (Equation 1); however, the subsequent photolysis of the derivatives yielded the desired product in only one case. Photolysis was conducted in a Pyrex flask using an Hanovia ultraviolet lamp (2537 A). When dinitrosylperfluorosuccinate (III) was photolyzed for 2 hours, brown decomposition products and N_2O_3 were obtained, but there was no evidence that any of the desired nitroso product formed. Similar treatment of dinitrosylperflouroglutarate (IV) over periods of 12 to 16 hours yielded, after hydrolysis, the desired product, 4-nitrosoperfluorobutanoic acid (II), in 12 to 38% yields. The product (II) was characterized by its infrared spectrum, elemental analysis and equivalent weight.

2. 5-Nitrosoperfluoropentanoic Acid

The preparation of nitrosoperfluoroaliphatic acids is being investigated through the reaction of terminally unsaturated perfluoroaliphatic acids with nitrosyl halides. The system chosen to study this type of reaction is addition of FNO to perfluoro-4-pentenoic acid (V) to yield 5-nitrosoperfluoropentanoic acid (VI) or possibly 4-nitrosoperfluoropentanoic acid (VII).

$CF_2 = CFCF_2CF_2COOH$

V

$ON(CF_2)_4COOH$

VI

$$CF_3\overset{NO}{\overset{|}{C}}FCF_2CF_2COOH$$

VII

To date, the investigation has been concerned with the preparation of the intermediate, perfluoro-4-pentenoic acid (V). This preparation was attempted previously, without success, by the dehydrofluorination of 2,2,3,3,4,4,5,5-octafluoropentanoic acid (VIII) using ethyldiisopropyl amine (Ref 5).

$HF_2C(CF_2)_3COOH$

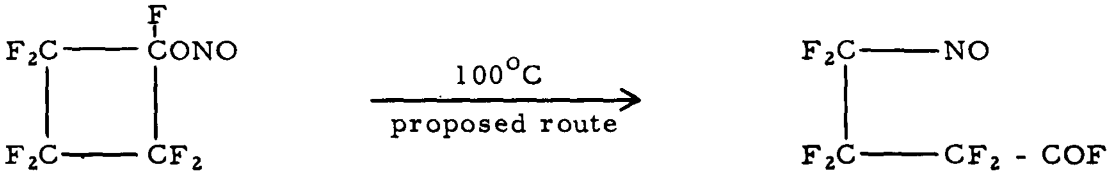
VIII

During this report period attempts to dehydrofluorinate using a weaker base that would not degrade the material were investigated. Amberlite IR-45, a weak base ion-exchange resin, has been used successfully to dehydrofluorinate sensitive compounds (Ref 6) and its use for this purpose was attempted here. Stirring an ether solution of the acid (VIII) with the resin for 72 hours at room temperature gave no reaction and the starting material was recovered. Other dehydrohalogenating agents will be investigated for this reaction in future experiments.

3. 4-Nitrosoperfluorobutanoyl Fluoride

Two routes have been investigated for preparation of 4-nitrosoperfluorobutanoyl fluoride (X). They are:

- Pyrolysis of heptafluorocyclobutyl nitrite (Equation 3)
- Addition of NOF to perfluoroglutaric anhydride (Equation 4).



X

(3)

$$\underline{OC(CF_2)_3COO} + FNO \longrightarrow \underset{IX}{FOC(CF_2)_3COONO} \xrightarrow[-CO_2]{h\nu \text{ or } \Delta} \underset{X}{FOC(CF_2)_3NO} \quad (4)$$

The first route requires the preparation of heptafluorocyclobutyl nitrite which was proposed using a series of reactions (Ref 5) that start with the synthesis of methyl trifluorovinyl ether. Repeated attempts to synthesize this ether by reaction of tetrafluoroethylene with sodium metholate have yielded either trace amounts of product or no product at all. As a result of the synthetic difficulties, the first route has been abandoned in favor of the second, the more direct one.

Synthesis of 4-nitrosoperfluorobutanoyl fluoride by the second route, as illustrated in Equation 4, has been attempted with apparent success. The intermediate, nitrosyl perfluoroglutaryl fluoride (IX), was obtained in 72.5% yield on allowing an equimolar mixture of FNO and perfluoroglutaric anhydride to react 12 hours in a Monel cylinder at room temperature. A higher yield, 86.6%, was obtained by bubbling FNO through the anhydride in a Kel-F tube at 0°C for 35 minutes. The intermediate (IX), a yellow liquid, was characterized by it infrared spectrum (nitrite C = O, 2000 cm^{-1}; acid fluoride C = O, 1885 cm^{-1}; N = O, 1695^{-1}), elemental analysis and mass spectrum (Table I). The material hydrolyzed to form perfluoroglutaric acid upon exposure to the atmosphere or upon contact with water.

Conversion of the intermediate (IX) to 4-nitrosoperfluorobutanoyl fluoride (X) was attempted by pyrolysis and photolysis. Pyrolysis of the material added dropwise to a flask held at 150°C, yielded a blue-green liquid distillate which, after hydrolysis and extraction with ether, gave a green liquid. This liquid was, by virtue of its color, apparently a nitroso compound. The liquid decolorized on standing at room temperature before it could be analyzed. In other pyrolysis experiments in which decomposition in the vapor state or in FC43 solution was attempted, none of the desired product formed.

TABLE I

PARTIAL MASS SPECTRUM OF NITROSYL PERFLUOROGLUTARYL FLUORIDE

m/1	Relative Intensity	Probable Ion Fragment
46	0.5	NO_2^+
47	<u>100.0</u>	COF^+
74	3.0	$O = C\text{-}ONO^+$
78	11.5	$CFCOF^+$
97	15.5	CF_2COF^+
109	5.0	$CFCFCOF^+$
128	1.5	CF_2CFCOF^+
144	0.5	$CF_2CF_2COO^+$
197	19.5	$CF_2CF_2CF_2COF^+$
252	0.5	$ONOOCCF_2CF_2CFCOF^+$
271	Molecular ion is not observed	

The photolysis of IX was studied in one experiment in which a 40 gm sample was irradiated with a Hanovia ultraviolet lamp for 2 hours to yield 0.4 gm of blue liquid. After hydrolysis, the ultraviolet and visible spectra of this material were identical to those of 4-nitrosoperfluorobutanoic acid (II). This route will be further investigated to establish the identity of the product and optimize the yield.

4. Nitrosotrifluoroethylene

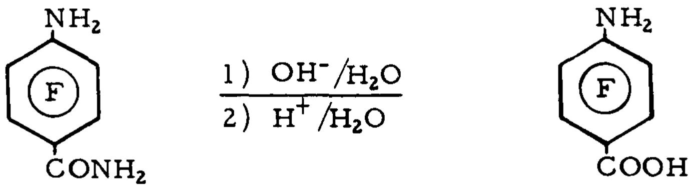
Haszeldine has reported the synthesis of nitrosotrifluoroethylene (XI) by the photolysis of trifluoroiodoethylene and nitric oxide in the presence of mercury as illustrated in Equation 5 (Ref 7).

$$2CF_2 = CFI + 2NO \xrightarrow[Hg]{h\nu} \underset{XI}{2CF_2 = CFNO} + I_2 \qquad (5)$$

It was reported that the compound polymerized with tetrafluoroethylene to a linear polymer containing pendant trifluoroethylene groups. This compound would be desirable for preparing $CF_3NO/CF_2 = CFNO/C_2F_4$ terpolymers containing sites of unsaturation for curing, and several attempts were made to prepare it using the published procedure. None of the attempts was successful and none of the nitrosotrifluoroethylene compound was obtained.

B. Aromatic Nitroso Compounds

The nitrosoperfluoroaromatic acid, 4-nitroso - 2,3,5,6-tetrafluorobenzoic acid (XIV) was prepared from 4-amino - 2,3,5,6-tetrafluorobenzamide (XII) in a two-step procedure involving as an intermediate, 4-amino-2,3,5,6-tetrafluorobenzoic acid (XIII). The procedure is illustrated in Equations 6 and 7.



XII XIII

(6)

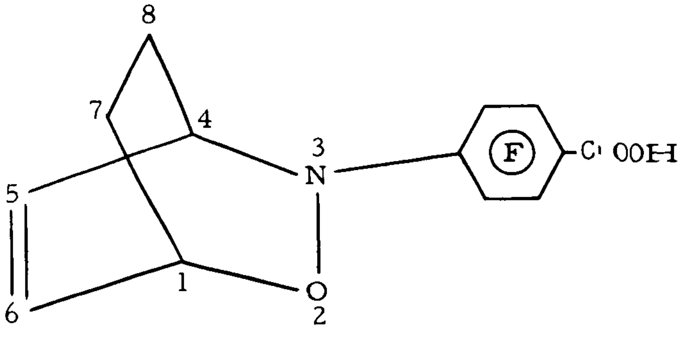
XIV

(7)

The intermediate, 4-amino-2,3,5,6-tetrafluorobenzoic acid (XIII), was prepared using a modification of Belf's method (Ref 8). It was obtained in 64 to 70% yields by refluxing 4-amino-2,3,5,6-tetrafluorobenzamide (XII) with 20% aqueous sodium hydroxide for 10 hours. The pure acid was obtained as colorless crystals, mp 176-7°C (Lit. mp 181-181.5°C, Ref 8) and was characterized by its elemental analysis, infrared spectrum and equivalent weight (calcd. 209, found 208). The observed pKa was 3.65.

The desired product, 4-nitroso-2,3,5,6-tetrafluorobenzoic acid (XIV), was obtained on allowing the intermediate amino acid (XIII) to react with performic acid in a large volume of methylene chloride for 4 to 6 hours at reflux temperature. After treatment with water to destroy unreacted performic acid, the product was separated from unreacted starting material utilizing the difference in their distribution coefficients in the methylene chloride-water system. Yields obtained using this separation were 28 and 34%. Higher yields (38 to 47%) were obtained by extracting the aqueous solution with ether and separating the product from the starting material by column (silica gel) chromatography. The starting material was recovered from attempts to oxidize the amino acid with peracetic acid. The performic acid experiments are summarized in Table II.

The product, 4-nitroso-2,3,5,6-tetrafluorobenzoic acid, was blue in solution, but it could be isolated only as the pale yellow dimer, mp 224-6°C (dec.). It decomposed on attempted recrystallization from chloroform or carbon tetrachloride. The compound decomposes on prolonged exposure to air at room temperature. Decomposition may be catalyzed by light, but this has not been definitely established. Characterization was done by elemental analysis, equivalent weight (calcd. 233, found 225) and formation of the bicyclooxazine derivative (XV). Bicyclooxazine derivatives have been used to characterize other fluoroaromatic nitroso compounds and the reaction is apparently general for these compounds. The other derivatives that have been prepared are those of pentafluoronitrosobenzene, mp 68-9°C and 4-bromo-2,3,5,6-tetrafluoronitrosobenzene, mp 101-3°C. The derivative of 4-nitroso-2,3,5,6-tetrafluorobenzoic acid (XIV), 3-(4'-carboxy-2',3',5',6'-tetrafluorophenyl)-2-oxa-3-azabicyclo[2,2,2]octene-5, mp 174-6°C (dec.), was characterized by elemental analysis and NMR spectrum.



XV

TABLE II

PERFORMIC ACID OXIDATION OF 4-AMINO-2,3,5,6-TETRAFLUOROBENZOIC ACID (XIII) TO 4-NITROSO-2,3,5,6-TETRAFLUOROBENZOIC ACID (XIV)

Starting Materials				Product				
XIII (gm)	CH_2Cl_2 (ml)	98% HCOOH (ml)	90% H_2O_2 (ml)	XIV (gm)	Yield (%)	mp (°C)	Method of Purification	Notes
2.0	100	20	5	1.0	47	222-5	Chromatograph	
2.0	100	20	5	0.8	38	223-5	Chromatograph	(1)
2.0	100	20	5	1.0	47	210-3	Chromatograph	(2)
5.0	250	40	10	1.8	34	224-6	Solvent Separation	
5.0	250	40	10	1.5	28	223-5	Solvent Separation	

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(1) The material decomposed on attempt to chromatograph on acid-washed alumina.

(2) The material decomposed on attempts to recrystallize from $CHCl_3$ and CCl_4.

PHASE II - POLYMERIZATION STUDIES

Approximately 200 pounds of high molecular weight, high purity CF_3NO/C_2F_4 copolymer have been prepared on this program. Gum and silica-reinforced vulcanizates of this copolymer have exhibited very low tensile strengths. As a result, the efforts during this quarterly period have been directed toward the synthesis of various nitroso terpolymers containing functional sites for subsequent crosslinking.

The termonomers investigated during this report period were vinylidene fluoride ($CH_2 = CF_2$), trifluoroethylene ($CHF = CF_2$), and the carboxy compounds, acrylic acid and 4-nitroso-2,3,5,6-tetrafluorobenzoic acid. Polymers that contain vinylidene fluoride of trifluoroethylene are expected to be curable through reaction of the labile hydrogen atoms somewhat similar to that of curing Viton ($CF_2 = CFCF_3/CH_2 = CF_2$ copolymer). Polymers of this type may also be amenable to dehydrofluorination to yield sites of unsaturation for curing with peroxides, sulfur, radiation, etc. Polymers that contain carboxy groups should be curable through reaction of the carboxy groups with basic materials including metal hydroxides, metal oxides, and salts of weak acids.

A. $CF_3NO/C_2F_4/CH_2 = CF_2$ Terpolymer

The first products, deemed to be $CF_3NO/C_2F_4/CH_2 = CF_2$ terpolymer, were synthesized utilizing suspension polymerization (Ref 5). All evidence for the presence of $C_2H_2F_2$ in the polymer was indirect because no direct analysis for small quantities of $CH_2 = CF_2$ in the terpolymer was available. Since that time a titration procedure has been developed which does enable direct analysis for small amounts of $CH_2 = CF_2$ or $CHF = CF_2$. The titration is based on the reaction of acidic hydrogens in the polymer with base. In this case, a Freon 113 solution of the polymer is treated with excess of a standard solution of dibutylamine in Freon 113. An immediate reaction occurs, probably dehydrofluorination, and the amount of hydrogen originally present in the polymer may be determined by back titration with a standard solution of trifluoroacetic acid in Freon 113. Using this titration, it has been determined that the previously obtained suspension polymers contained up to 0.6 mole percent $CH_2 = CF_2$.

The more recent investigation of $CH_2 = CF_2$ terpolymer preparation utilized a bulk polymerization conducted at two temperatures. Bulk nitroso polymerizations are usually conducted at low temperatures (-65°C) to prevent violent reaction; however, under such conditions reaction is slow and 2 to 3 weeks are necessary to obtain high molecular weight polymer in high yield. In the bulk preparation of $CH_2 = CF_2$ terpolymer, reaction was allowed to occur for 24 hours at -65°C and, subsequently, for 24 hours at -25°C. In this manner a violent reaction was prevented by having the initial reaction take place at -65°C and the overall polymerization time was greatly decreased by the subsequent fast reaction at -25°C. The products obtained from polymerizations of this type were rubbery gums containing up to 0.6 mole percent $CH_2 = CF_2$. Examples of these polymerizations are presented in Table III.

B. $CF_3NO/C_2F_4/CHF = CF_2$ Terpolymers

Preparatory to synthesizing terpolymer containing $CHF = CF_2$, the ability of $CHF = CF_2$ to copolymerize with CF_3NO, previously reported (Ref 4), was investigated. A $CF_3NO/CHF = CF_2$ copolymer was obtained on reaction of these monomers, in bulk, 20 hours at -65°C and 120 hours at -25°C. The polymer obtained was a stiff rubber which was soluble in acetone, but not soluble in fluorocarbon solvents.

The two-temperature bulk polymerization procedure was similarly used to prepare $CHF = CF_2$ terpolymers. A series of such polymerizations was made in which the proportion of $CHF = CF_2$ in the monomer charge was varied between 2 and 25 mole percent (Table IV). The $CHF = CF_2$ content of the resulting polymers was directly proportional to the concentration of $CHF = CF_2$ in the monomer charge. Thus, polymers of $CHF = CF_2$ content varying between 0.8 and 27 mole percent were obtained. In a number of instances, the ratio of monomers found in the polymer closely approximated the ratio of monomers in the charge. This was true in every case in which the total polymerization time was four days. It was also true for some two-day polymerization products, but other two-day polymerization products contained smaller proportions of $CHF=CF_2$ than were in the monomer charges. Because of the irregularity in the two-day reaction products, no definite correlation could be made between reaction time and $CHF = CF_2$ content; however, there is some indication that the amount of $CHF = CF_2$ in the polymer is dependent on reaction time as well as concentration of $CHF = CF_2$ in the monomer charge.

The $CHF = CF_2$ terpolymerization was also investigated using suspension polymerization at -25°C (suspension medium was an aqueous solution of $MgCO_3$ and LiBr). Two polymerizations in which the monomer charges contained 25 and 2 mole percent $CHF = CF_2$ yielded, respectively, a soft gum and a relatively tough elastomer. Under the conditions of these experiments (Table IV) the high proportion of $CHF = CF_2$ in the monomer charge led to low conversion and low molecular weight product. The $CHF = CF_2$ content of this product is not

TABLE III

BULK POLYMERIZATION OF $CF_3NO/C_2F_4/CH_2 = CF_2$ TERPOLYMERS (1)

Reaction Number	$CH_2 = CF_2$ Charged (Mole %)	Total Charge (Grams)	Conversion (%)	$CH_2 = CF_2$ In Polymer (2) (Mole %)	Polymer
E16321-3	5.0	11.0	80	0.6	Elastomeric gum
E16321-4	2.0	11.0	84	0.5	Elastomeric gum

---

(1) Reacted 24 hours at -65°C and 24 hours at -25°C.

(2) Values obtained by titration.

TABLE IV

$CF_3NO/C_2F_4/CHF = CF_2$ TERPOLYMER (1)

Reaction Number	Reaction Conditions: Type	Time and Temperature (hr/°C): Initial	Time and Temperature (hr/°C): Subsequent	$CHF = CF_2$ Charged (Mole%)	$CHF = CF_2$ in Polymer (2) (Mole %)	Total Charge (3) (Grams)	Conversion (%)	Remarks
E16315-A	Suspension	24/-25	--	25	--	11.4	47	Soft gum, IR shows no C-H
E16315-B	Suspension	24/-25	--	2	1.4	11.9	68	Stiff elastomer
E16316-A	Bulk	20/-65	120/-25	50	--	1.79	78	Tough elastomer
E16316-B	Bulk	20/-65	120/-25	20	--	1.91	94	Tough elastomer
E16320-1	Bulk	24/-65	24/-25	5	4.7	11.2	73	Elastomeric gum
E16321-1	Bulk	24/-65	24/-25	5	2.6	11.6	75	Elastomeric gum
E16330-A	Bulk	24/-65	24/-25	5	2.1	93.6	80	Elastomeric gum
E16320-2	Bulk	24/-65	24/-25	2	2.1	11.3	78	Elastomeric gum
E16321-2	Bulk	24/-65	24/-25	2	1.6	11.3	82	Elastomeric gum
E16326	Bulk	24/-65	24/-25	2	0.8	192.0	87	Elastomeric gum
E16330-B	Bulk	24/-65	72/-25	5	4.9	117.0	81	Elastomeric gum
E16331	Bulk	24/-65	72/-25	25	27	22.9	82	Tough elastomer

---

(1) $CF_3NO/CHF = CF_2$ copolymer is included for reference.

(2) Values obtained by titration.

(3) Largest single reaction approximately 12 grams. Larger total charges are several combined reactions.

known, but it was apparently low since no CH absorptions could be seen in the infrared spectrum. The low porportion of $CHF = CF_2$ in the monomer charge led to higher conversion and high molecular weight product (a tough elastomer) containing 1.4 mole percent $CHF = CF_2$.

C. $CF_3NO/C_2F_4/CH_2{=}CHCOOH$ Terpolymer

Liquid terpolymer containing acrylic acid ($CH_2 = CHCOOH$) has been prepared and cured to rubbery products using tris-imine (MAPO) curative (Ref 9). It was of interest here to prepare a high molecular weight polymer of this composition and determine its curability and properties. Preparation of the liquid terpolymer had been accomplished in solution polymerization using a chain transfer solvent such as Freon 113. In efforts to obtain high molecular weight products, the polymerization was investigated using a non-chain transfer solvent, methylene chloride, and bulk polymerization.

The solution polymerizations (Table V) yielded only low molecular weight products as indicated by their soft gum-like or liquid consistency. Several of the polymerizations attempted at room temperature exploded in the sealed tubes due to overpressures. The bulk polymerizations (Table VI), when conducted at low temperature (-65°C), yielded only CF_3NO/C_2F_4 copolymer. When the bulk polymerizations were done at higher temperatures (0°C or above) liquid terpolymers were obtained.

Terpolymerization of acrylyl chloride ($CH_2 = CHCOCl$) rather than the acid was investigated to obtain high molecular weight $CH_2 = CHCOOH$ terpolymer (the acid would result from hydrolysis of the acid chloride). Several bulk polymerizations attempted at -25°C for 72 hours yielded only liquid products. An attempt to copolymerize CF_3NO and $CH_2 = CHCOCl$ under the same conditions resulted in no reaction.

D. $CF_3NO/C_2F_4/ONC_6F_4COOH$ Terpolymer

The preparation of 4-nitroso-tetrafluorobenzoic acid (ONC_6F_4COOH) terpolymer was preceded by an investigation of the copolymerization of CF_3NO and ONC_6F_4 COOH. The copolymerization was accomplished using a mixed solvent system of methylene chloride and ether. The mixed solvent was necessary to effect solution of both monomers. The polymerization, conducted at -25°C, yielded a copolymer resin (Table VII).

TABLE V

SOLUTION POLYMERIZATION OF $CF_3NO/C_2F_4/CH_2 = CHCOOH$ TERPOLYMER (1)

Reaction Number	Mole Ratio			Reaction Time and Temperature (hr/°C)		Solvent	Results
	CH_2=CHCOOH	C_2F_4	CF_3NO	Initial	Subsequent		
16314	0.1	0.9	1.0	23/-25	--	CH_2Cl_2	Soft gum, no COOH
16317-4	1.0	--	1.0	-/25	--	CH_2Cl_2	Exploded, overpressure
16317-5	0.5	0.5	1.0	-/25	--	CH_2Cl_2	Exploded, overpressure
16317-6	0.1	0.9	1.0	-/25	--	CH_2Cl_2	Exploded, overpressure
16318	0.5	0.5	1.0	20/25	--	CH_2Cl_2	Liquid polymer
16317-7	1.0	--	1.0	24/-65	120/-25	Freon 113	No reaction
16317-8	0.5	0.5	1.0	24/-65	120/-25	Freon 113	Liquid polymer
16317-9	0.1	0.9	1.0	24/-65	120/-25	Freon 113	Liquid polymer

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(1) $CF_3NO/CH_2 = CHCOOH$ copolymerization attempts are included for reference.

TABLE VI

BULK POLYMERIZATION OF $CF_3NO/C_2F_4/CH_2 = CHCOOH$ TERPOLYMER (1)

Reaction Number	Mole Ratio			Reaction Time and Temperature (hr/°C)		Results
	$CH_2 = CHCOOH$	C_2F_4	CF_3NO	Initial	Subsequent	
16317-1	1.0	--	1.0	24/-65	120/-25	No reaction
16317-2	0.5	0.5	1.0	24/-65	120/-25	Gum, no COOH
16317-3	0.1	0.9	1.0	24/-65	120/-25	Gum, no COOH
16319	Excess	0.9	1.0	20/10-20	--	Liquid and gum products, liquid terpolymer
16322-1	0.1	0.9	1.0	20/0	--	Liquid terpolymer
16322-2	0.1	0.9	1.0	20/0	3/50	Liquid terpolymer

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(1) A $CF_3 NO/CH_2 = CHCOOH$ copolymerization attempt is included for reference.

TABLE VII

$CF_3NO/C_2F_4/ONC_6F_4COOH$ TERPOLYMERS [1]

Reaction Number	Solvent System	Mole Ratio			Reaction Time and Temperature (hr/°C)		Product
		CF_3NO	C_2F_4	ONC_6F_4COOH	Initial	Subsequent	
16328-3	CH_2Cl_2-Et_2O	--	1.0	1.0	24/-25	--	Resin
16327	None	0.9	1.0	0.1	24/-25	3/50	Gum
16329-1	None	0.9	1.0	0.1	24/-25	4/50	60% of product was CF_3NO/C_2F_4 copolymer, 40% was a pasty terpolymer
16328-1	CH_2Cl_2-Et_2O	0.9	1.0	0.1	24/-25	--	Liquid
16328-2	CH_2Cl_2-Et_2O	0.5	1.0	0.5	24/-25	--	Gum
16329-2	CH_2Cl_2-$(CH_3)_2C{=}O$	0.9	1.0	0.1	24/-25	72/25	Soft rubber terpolymer; Soluble in FC43-Freon 113 mixture

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(1)A C_2 F_4/ONC_6F_4COOH copolymerization is included for reference.

Terpolymerizations were done in both bulk polymerization and mixed solvent solution polymerization (Table VII). Mixed solvent systems employed were methylene chloride-ether and methylene chloride-acetone. A bulk terpolymerization yielded a mixture containing 60 percent CF_3NO/C_2F_4 copolymer and 40 percent terpolymer. The terpolymer was a brown pasty solid. A solution terpolymerization in methylene chloride-acetone conducted at -25°C for 24 hours and 25°C for 72 hours yielded a soft rubber terpolymer that was soluble in a FC43-Freon 113 mixture. Because only very small quantities of ONC_6F_4COOH were available, the polymerizations were done on small scale (ca. 1 gram) and insufficient product was obtained for thorough analysis. The assignment of terpolymer structure to some products was done on the basis of infrared analysis.

PHASE III - COMPOUNDING AND CURING STUDIES

A. CF_3NO/C_2F_4 Copolymer

Previous studies showed that the best physical properties could be obtained with a compound containing 2.5 phr of triethylenetetramine (TETA) and 15 phr silica (Hi-Sil 303 or Quso H-40) as a filler. Additional nitroso cure studies, performed on an Air Force program to develop rocket propellant resistant elastomers, show that TETA containing copolymer can be cured to a tensile strength of 450 psi at temperatures as low as 120°F (Ref 10). Further efforts on the Air Force Program were conducted using diallylamine as an intermediate curative and subsequent reaction with peroxides, phenolic resin and sulfur; none yielded satisfactory cures. Diphenylguanadine, 2,4,6-triaminotriazine (melamine) and aminoacetic acid (glycine), the last alone and in combination with either resorcinol or chromium trifluoroacetate, were also investigated but cured products were not obtained (Ref 10).

B. Nitroso Rubber Terpolymers

In earlier studies no suitable formulations were found for curing the terpolymers $CF_3NO/C_2F_4/C_6F_5NO$ and $CF_3NO/C_2F_4/CH_2=CF_2$. The best tensile strength obtained with the $CH_2=CF_2$ terpolymer was under 300 psi. During this report period a formulation containing hexamethylenediamine carbamate, 2.5 phr, magnesium oxide, 10 phr, and Hi-Sil 303, 15 phr, was evaluated in two new batches of terpolymer containing 2 and 5 mole percent $CH_2=CF_2$, respectively. The tensile strengths were 400 and 280 psi, respectively, and some porosity was noted in each. The same formulation was evaluated in two batches of $CHF=CF_2$ terpolymer containing 2 and 5 mole percent $CHF=CF_2$, respectively. Both were cured for 1 hour at 250°F and post-cured for 20 hours at 212°F. The 2 mole percent sample exhibited a 420 psi tensile strength and 200 percent elongation while the 5 mole percent sample appeared degraded. Similar efforts performed on the Air Force program corroborated the poor cure results obtained with the 5 mole percent terpolymer (Ref 10).

Samples of a terpolymer containing 1 mole percent trifluoroethylene have been exposed to ionizing radiation from a Co^{60} source with no evidence of crosslinking (Ref 10).

III. SUMMARY

1. The synthesis of nitrosoperfluoroaliphatic acids, including 3-nitrosoperfluoropropanoic acid, 4-nitrosoperfluorobutanoic acid, 5-nitrosoperfluoropentanoic acid, and 4-nitrosoperfluorobutanoyl fluoride was investigated employing several different synthetic approaches. The most promising of these approaches at this time is the addition of NOF to perfluoroglutaric anhydride to yield nitrosyl perfluoroglutaryl fluoride as an intermediate which may be photolyzed to obtain 4-nitrosoperfluorobutanoyl fluoride.

2. The synthesis of 4-nitroso-2,3,5,6-tetrafluorobenzoic acid was accomplished.

3. A titration procedure was developed to determine vinylidene fluoride and trifluoroethylene content of nitroso terpolymers.

4. Nitroso terpolymer containing 0.6 mole percent vinylidene fluoride was prepared.

5. Nitroso terpolymers containing 0.8, 2.1, 4.9 and 27 mole percent trifluoroethylene were prepared. A total of 350 gm of these polymers was prepared for use in curing studies. Samples totaling 80 gm were submitted to the contracting agency.

6. Nitroso terpolymer containing 4-nitroso-2,3,5,6-tetrafluorobenzoic acid was synthesized in small scale experiments. A copolymer of this compound with tetrafluoroethylene was also synthesized.

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Unclassified Report

The production phase of the program was completed during the previous quarterly period. The present emphasis is toward the preparation of fluorinated aliphatic and aromatic nitroso compounds with functional groups and their terpolymerization with CF_3NO and C_2F_4 to polymers which may be cured through the functional groups. New methods were explored to prepare nitrosoperfluoroaliphatic and nitrosoperfluoroaromatic acids and, as a result, the new compound — 4-nitroso-2,3,5,6-tetrafluorobenzoic acid — was synthesized.

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Terpolymers were prepared containing the functional monomers: vinylidene fluoride, trifluoroethylene acrylic acid, and 4-nitroso-2,3,5,6-tetrafluorobenzoic acid. Curing studies were carried out on vinylidene fluoride and triterpolymers.

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