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ANL ltr dtd 1 Mar 1967

U.S. Army Contract No. DA-19-129-AMC-69(X)O.I. 9044
QMC Project No. 7X93-15-004

Report:
Trenton RD 343-Q7
RMD 8576-Q7

Report Period:
1 September 1964 to 28 November 1964

NITROSO RUBBER

RESEARCH
DEVELOPMENT
And
PRODUCTION

CHEMICAL CORPORATION
CHEMICAL OPERATIONS TRENTON, NEW JERSEY

Thiokol

(6) NITROSO RUBBER
RESEARCH, DEVELOPMENT AND PRODUCTION,

(14) Rept. nos. [redacted] RD-343-Q7, [redacted] RMD-8576-Q7

(15) U. S. Army Contract [redacted] DA-19-129-AMC-69(X) [redacted]

(16) QMC Proj[redacted] [redacted] 7X93-15-004

Report Period: 1 September 1964 to (11) 28 Nov[redacted] [redacted]64,

(9) Rept. for 1 Sep-28 Nov 64. (12) 20p.

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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. This report covers work conducted from 1 September 1964 through 28 November 1964. The overall project leader is Mr. Joseph Green; the divisional project leader at Trenton is Mr. Warren Helmer. Other contributors to the program are Messrs. John Paustian, Joseph Castellano, Nathan Levine, Ernest Cottrill, David Kennedy and Richard Crooker at Denville and Messrs. Robert Hoffman, Malcolm Reynolds and Chan Wu at Trenton.

ABSTRACT

Additional CF_3NO and CF_3NO/C_2F_4 copolymer production lots were successfully completed. A total of 148 lb of CF_3NO and 208 lb of copolymer ~~has now been~~ prepared. A continuation of curing studies on these materials ~~has~~ not resulted in a significant increase in vulcanizate strength. Termonomer synthesis and terpolymerization studies were continued.

CONTENTS

TABLES

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 and 2). The nitroso rubber gum stock 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.

Vulcanizates of nitroso rubber have been prepared; however, even the best of the gum vulcanizates have very low tensile strength. Reinforcement of the vulcanizate with silica filler has resulted in improved, although still not satisfactory, physical properties. Extensive research and development studies have been conducted to investigate the effects of varying the nitroso and olefinic monomers (Ref 3 and 4). Terpolymers have been prepared and cured through pendant carboxy groups and the resulting vulcanizates have much greater tensile strength. The cured products continue to exhibit excellent solvent resistance, nonflammability, low temperature flexibility and excellent ozone resistance.

Field evaluation studies have been severely hampered by a shortage of nitroso rubber. Furthermore, the low temperature properties (utility at -40°F) still fall short of the desired serviceability (utility at -100°F) and the relatively low tensile strengths severely limit the usefulness of the rubber. Studies involving monomer variation have not resulted in decreased Tg values, although terpolymer preparation has resulted in products with improved mechanical properties.

The goals of the present program are threefold:

1. Produce a nitroso rubber with improved mechanical properties
2. Produce a nitroso rubber with improved low temperature properties
3. Prepare sufficient quantities of nitroso rubber for further evaluation.

Thiokol Chemical Corporation has conducted a four phase R and D program to meet these goals:

I. Monomer Synthesis and Scaleup
II. Polymer Synthesis and Scaleup
III. Polymer Production
IV. Compounding Studies.

The major effort during this report period was expended in four areas:

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

2. Polymerization studies to attain terpolymers

3. Production of monomer and polymer

4. Polymer curing studies.

II. TECHNICAL WORK

PHASE I - MONOMER SYNTHESIS

Task I. Process Development for Trifluoronitrosomethane (CF_3NO)

The objective of this task was the development of a process capable of operation at a production level of 10 to 50 pounds of CF_3NO per 24 hour period. This work has been successful and, with the successful operation of the production facility, no additional studies under this task have been done.

Task 2. Preparation of Tetrafluoroethylene (C_2F_4)

Tetrafluoroethylene is being received from the Thiokol production facility at Moss Point, Mississippi. No production runs were completed at either the Reaction Motors or Trenton facilities during this report period.

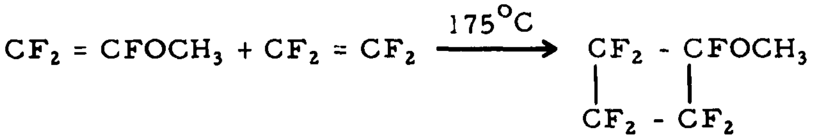
Task 3. New Nitroso Monomers

The object of this task 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 could become cross-linking sites for improved mechanical properties. Current work is concerned with the preparation of nitroso perfluoroaliphatic and perfluoroaromatic compounds containing carboxyl and halogen groups as cure sites.

A. Aliphatic Nitroso Compounds

The preparation of a primary perfluoronitrosocarboxylic acid by the pyrolysis of heptafluorocyclobutyl nitrite (I)(Ref 5) has been initiated. Compound I was reported to form in 96% yield by allowing a mixture of hexafluorocyclobutanone (II) and nitrosyl fluoride (FNO) to stand at room temperature (the applicability of ClNO to this reaction will be investigated). Compound II may be prepared (Ref 6) by the addition of C_2F_4 to methyltrifluorovinyl ether at 175°C and subsequent cleavage of the resulting methyl heptafluorocyclobutyl ether.

$$CF_2 = CF_2 + NaOCH_3 \xrightarrow{100^{\circ}C} CF_2 = CFOCH_3 + NaF \qquad (1)$$



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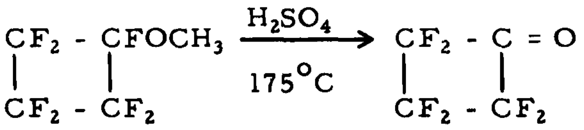

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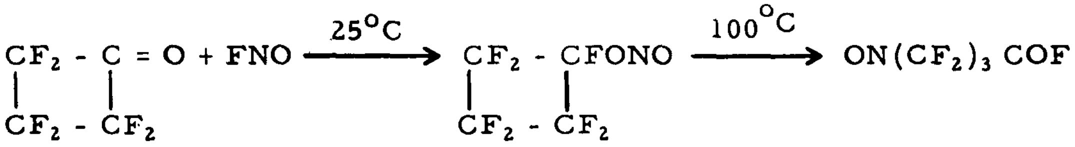


I

(4)

During this report period, attempts were made to effect reactions 1 and 2 in one step by passing C_2F_4 through a heated bed of $NaOCH_3$. Little evidence of reaction was observed at temperatures up to 250°C, but at that temperature an exothermic reaction began which yielded a material with a boiling point slightly below room temperature. Characterization of this material is in progress. Reactions 1 and 2 are also being run under standard conditions.

In another series of reactions, attempts to prepare trifluoroacrylic acid via the Grignard (equation 5) have not been successful.

$$CF_2 = CFI + Mg \longrightarrow CF_2 = CFMgI \xrightarrow[H_2O]{CO_2} CF_2 = CFCOOH \qquad (5)$$

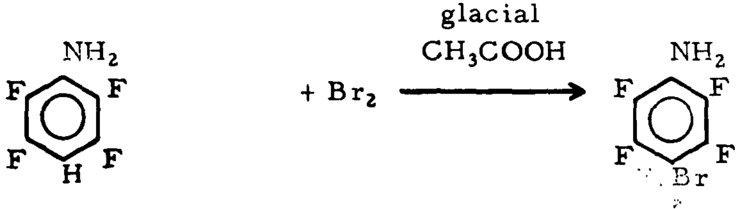
The preparation of this compound has also been reported (Ref 7) by the reaction of PhMgBr with $CF_2 = CFI$ and subsequent carbonation of the Grignard (equation 6). This route will be attempted if the series of reactions discussed above does not produce the desired nitroso acid.

$$CF_2 = CFI + PhMgBr \xrightarrow[-PhI]{} CF_2 = CFMgBr \xrightarrow{CO_2} CF_2 = CFCOOH \qquad (6)$$

An additional quantity of 2,2,3,3,4,4,5,5-octafluoropentanoic acid [$HCF_2(CF_2)_2CF_2COOH$] was prepared by the previously described procedure (Ref 8). An attempt to dehydrofluorinate this compound by refluxing with ethyl diisopropylamine for 8 hours resulted in complete destruction of the acid. Milder conditions will be required if the desired conversion is to be effected.

B. Aromatic Nitroso Compounds

p-Bromotetrafluoronitrosobenzene (III) was prepared in 64% yield by the performic acid oxidation of 4-bromo-2,3,5,6-tetrafluoroaniline (IV). IV, also a new compound, was prepared in 70% yield by the bromination of 2,3,4,6-tetrafluoroaniline (equations 7 and 8). Both compounds were characterized by infrared spectra and elemental analysis. The bromonitroso compound is of interest as a termonomer because of the potentially greater reactivity of the p-fluorine analog in curing studies.



IV

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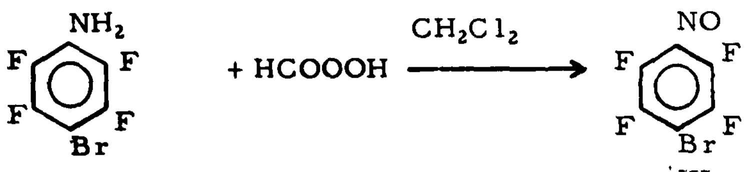
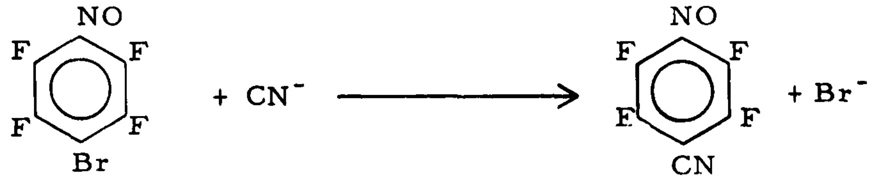


III

(8)

The reaction shown in equation 7 was carried out by simply adding a solution of bromine in glacial acetic acid to a solution of the aniline in glacial acetic acid at room temperature. The product, IV, was obtained as colorless crystals, mp 57-80°C (pentane). III was obtained by refluxing a mixture of 98% formic acid, 90% hydrogen peroxide and IV for five hours and chromatographing the resulting product on a column of acid-washed alumina. The pure product was obtained as colorless crystals which melted to a green liquid at 39-40°C. Thermochromism of this type is common to most aromatic nitroso compounds and is believed to be due to the formation of a dimer in the solid state. A 10 gm quantity of this product was prepared for polymerization studies.

It is known that the nitroso group has the strongest activating influence on an aromatic ring for nucleophilic substitution at the para position (Ref 9). The reaction of nucleophilic reagents with II was, therefore, thought to be a route to p-substituted perfluoronitroso compounds. The reaction of III with cyanide ion, for instance, would be one step in an alternate route to p-nitrosotetrafluorobenzoic acid (equations 9 and 10).



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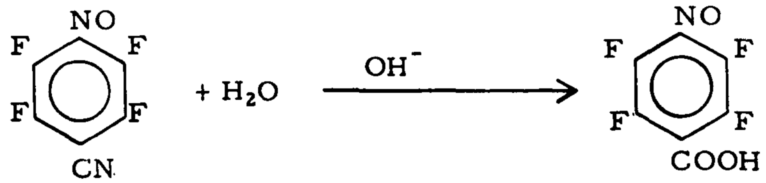

(10)

The reaction between III and sodium cyanide in ethanol solution, however, was found to proceed rapidly with the formation of a red-brown solid. The product was not fully characterized; however, it appeared that the solvent was involved in some way since H was found in the product. The same type of material was found when pentafluoronitrosobenzene was treated with either an ethanol or aqueous solution of sodium cyanide. A similar reaction appeared to take place between the nitroso compounds and an alcoholic or aqueous sodium hydroxide solution. The failure to detect any of the nitroso compounds in the products of these reactions indicates that initial attack of the nucleophilic reagent is probably on the nitroso group.

The attempts to prepare p-cyanotetrafluoroaniline by reaction of IV with sodium cyanide resulted in complete recovery of the starting material.

PHASE II. - POLYMERIZATION STUDIES

This phase has been composed of two tasks: (1) the development of the process for producing CF_3NO/C_2F_4 copolymer in 10 to 50 lb quantities per 24 hour period and (2) research toward the preparation of other nitroso polymers with improved properties.

The required production of copolymer in the production facilities was completed during this report period and, consequently, process development has been deemphasized. However, a very interesting method of bulk polymerization that yielded a very high molecular weight product was discovered during the last quarter (Ref 8) and some additional investigation of this process was done and is reported here in Task 1.

Task 1. Process Development and Improvement

The CF_3NO/C_2F_4 copolymer prepared in a modified bulk polymerization (Ref 8) was of higher molecular weight (up to 3,000,000) and yielded cured products of superior physical properties. The improvement in polymer properties was significant and further investigation of the method was warranted.

The polymerization was originally done in a sealed glass Y-tube under conditions such that a small quantity of low molecular weight polymer formed in one leg of the tube and a larger quantity of higher molecular weight polymer formed in the other leg. It was postulated that an initial partial polymerization consumed impurities and formed low polymer and that the purified monomers transferred to the other leg and polymerized to high polymer (Ref 8). Some experiments were done to test this hypothesis and to determine if still higher polymer could be formed under varied conditions.

The experiments were done using specially prepared reaction vessels consisting of two heavy-walled Pyrex tubes separated by a break seal. The monomers were introduced into one tube, allowed to react for a given time and then transferred to the other tube through the breakseal where they were allowed to react to completion. Using this procedure two variables — time and temperature of the initial polymerization — were studied and their effect on the molecular weight of the secondary polymerization product was determined. The data, which has been summarized in Table I, confirmed the observation that the two-step bulk polymerization yielded higher polymer than a similar one-step process. The data also indicated that the yield of polymer from the secondary polymerization was determined by both time and temperature of the initial reaction. This is to be expected since more monomer is consumed in the initial reaction at higher temperatures and greater reaction times.

The polymer molecular weight was not substantially affected by change in initial reaction time. This is shown in both series of experiments (098 and 16302 series, Table I) where, within each series, no consistent molecular weight deviation occurred. Initital reaction of as little as 5 percent of the monomers in 18 hours leads to high molecular weight product in the secondary reaction.

TABLE I

MODIFIED BULK COPOLYMERIZATION OF CF_3NO and C_2F_4

PREPOLYMERIZATION									
Exp. No.	098(1)	098-1	098-2	098-3	098-4	16302-1	16302-2	16302-3	16302-4
Time (days)	18	0.75	1	2	3	0.75	1	2	5
Temperature (°C)	-65	-85 to -80	-85 to -80	-85 to -75	-85 to -65	-65	-65	-65	-65
FINAL POLYMERIZATION									
Time (days)	-	14	14	14	14	21(2)	21(2)	21(2)	21(2)
Temperature (°C)	-	-65	-65	-65	-65	-65	-65	-65	-65
Yield (%) (3)	-	95	93	89	77	56	51	48	38
Inherent Viscosity $<\eta>$ (4)	0.7	1.59	1.67	1.56	1.48	0.97	1.09	0.92	0.90

---

(1) Control polymerization.
(2) Monomer remained after 21 days, polymerization was completed in one additional day at -25°C.
(3) Yield from final polymerization is based on total initial charge.
(4) 0.5 gm polymer in 100 ml FC-43.

The data relating initial reaction temperature to molecular weight of secondary product seem to indicate higher molecular weight from the lower temperature reactions; however, there is a variable in the reaction conditions that makes this uncertain. In series 098 where initial reactions were at -85°C, the secondary reactions at -65°C were complete within 14 days; however, in series 16302 where initial reactions were done at -65°C, the secondary reactions at -65°C were not complete after 21 days. In order to complete the latter reactions, they were allowed to warm up to -25°C. The polymerizations normally yield lower molecular weight products when done at higher temperatures; this could account for the lower molecular weights obtained in series 16302. The longer reaction time for series 16302 was due to a lower rate of initiation of polymerization (unreacted monomer was present after 21 days) and is possibly due to the absence of a catalytic impurity consumed in the initial reaction.

Another experiement was conducted to determine the effect of prepolymerization of monomers on a subsequent suspension polymerization. Here, CF_3NO and C_2F_4, in equimolar ratio, were allowed to react 12 and 24 hours at 65°C (two reactions) and the remaining monomers were transferred to suspension polymerization systems where they were allowed to polymerize at -25°C. The resultant products were of 0.5 and 0.6 inherent viscosity, respectively. These values are about the same as are obtained without pretreatment and indicate no improvement by the pretreatment.

Task 2. Experimental Nitroso Polymers

The efforts under this task included investigation of the reaction of nitrosyl fluoride (FNO) with tetrafluoroethylene (C_2F_4), preparation of copolymer and terpolymer containing p-bromotetrafluoronitrosobenzene (BrC_6F_4NO), and the preparation of terpolymer containing vinylidine fluoride ($C_2F_2H_2$).

A. Reaction of FNO and C_2F_4

The use of nitrosyl fluoride (FNO) as a comonomer with C_2F_4 should theoretically yield a polymer with low temperature properties superior to those of the CF_3NO/C_2F_4 copolymer. Previous efforts to study the FNO/C_2F_4 reaction have been hampered by the use of equipment capable of reacting with FNO. An apparatus of Monel and Teflon has now been constructed which allows the FNO/C_2F_4 reaction to be studied without the occurrence of contaminating side reactions previously obtained when glass equipment was used.

FNO and C_2F_4 (1:1 molar ratio) were allowed to react overnight at -80°C to yield a very small quantity of clear colorless liquid product. The liquid, on exposure to air, immediately decomposed to gaseous products.

It decomposed to gaseous and solid products when allowed to contact a sodium chloride plate (in nitrogen atmosphere). The solid decomposition product exhibited infrared absorptions for C-F. This reaction has been repeated several times apparently yielding the same product; however, no further characterization has been accomplished due to the handling difficulties encountered. The reaction of FNO, CF_3NO and C_2F_4 in 0.5:0.5:1.0 molar ratio was attempted at -65°C. The product was a clear slightly yellow liquid the infrared spectrum of which was similar to that of the CF_3NO/C_2F_4 copolymer.

B. BrC_6F_4NO/C_2F_4 Copolymer and $BrC_6F_4NO/CF_3NO/C_2F_4$ Terpolymer

Copolymer and terpolymers containing BrC_6F_4NO were prepared by allowing this material to react with C_2F_4 and C_2F_4/CF_3NO mixtures (Table II). The copolymer of BrC_6F_4NO and C_2F_4 was prepared from an equimolar mixture of the reactants in methylene chloride solvent at -25°C. The product, a hard resin, was rubbery in the temperature range of 55-130°C and soluble in the usual solvents for nitroso rubber. The polymer was analyzed for bromine and was shown to be essentially a 1:1 copolymer of the starting materials.

Terpolymers of $BrC_6F_4NO/CF_3NO/C_2F_4$ were prepared from monomer mixtures containing various proportions of BrC_6F_4NO. The proportion of BrC_6F_4NO in the polymer increased directly as the concentration of this component in the monomer feed increased. This observation was supported by the bromine analyses which indicated that the BrC_6F_4NO entered the polymer to approximately the same extent that it was present in the monomer feed. The physical properties of the polymers varied from resin to rubber being more resinous with increasing concentration of BrC_6F_4NO. Such behavior parallels that of the analogous C_6F_5NO terpolymer (Ref 10). The terpolymer prepared from a monomer feed containing 5% BrC_6F_4NO was obtained in 80% yield as a resilient rubber of relatively good physical properties. An additional quantity (21 gm) of this polymer was prepared for curing studies.

C. $C_2F_2H_2/CF_3NO/C_2F_4$ Terpolymers

The incorporation of vinylidine fluoride ($C_2F_2H_2$) into a nitroso rubber molecule can be expected to result in a polymer curable by the same techniques as the Vitons ($C_2F_2H_2/C_3F_6$ copolymers). The copolymerization of $C_2F_2H_2$ and CF_3NO was attempted as a preliminary step. Copolymerization at -15° to +20°C in bulk has been reported as being successful (Ref 3), but attempts at suspension copolymerization at -25°C in these laboratories did not yield polymer. Termpolymerizations in suspensions, however, were successfully effected (Table III). The presence of $C_2H_2F_2$ has not been proven

TABLE II

POLYMERS (1) CONTAINING BrC_6F_4NO

Exp. No.	Monomer Molar Feed Ratio			Conversion (2) (%)	Bromine Content		Product
	BrC_6F_4NO	CF_3NO	C_2F_4		(%Found)	(% Theoretical)	
E-16304-1	1.0	-	1.0	42	24.4	22.3	Brittle solid, rubber > 55°C
E-16304-2	1.0	trace	1.0	40	-	-	Brittle solid, rubber > 55°C
E-16305-4	0.7	0.3	1.0	43	-	-	Brittle solid, rubber > 50°C
E-16305-3	0.5	0.5	1.0	40	-	-	Slightly rubbery
E-16305-2	0.3	0.7	1.0	85	6.7	9.7	Rubber
E-16305-1	0.1	0.9	1.0	79	2.8	3.2	Rubber
E-16311	0.1	0.9	1.0	82	2.6	3.2	Rubber

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(1) Prepared in CH_2Cl_2 solution, 24 hours at -25°C.

(2) Based upon total charge.

directly due to the difficulty in detecting small amounts of $C_2H_2F_2$ by infrared or elemental analysis; however, its presence in the polymer has been shown indirectly. Pyrolysis of the polymer yielded, in addition to the gases COF_2 and CF_3-N=CF_2 which are obtained normally from the pyrolysis of CF_3NO/C_2F_4 copolymer, a solid ash which exhibited an absorption for CH at 3.4 μ in the infrared spectrum. Another indication that $C_2H_2F_2$ was included in the polymer was obtained by mass spectral analysis of the unreacted gases from one of the polymerizations. The analysis indicated that the polymer may contain 1 to 2 mole percent $C_2H_2F_2$.

The strongest evidence that the product is a terpolymer was obtained from its curing behavior. The CF_3NO/C_2F_4 copolymer may not be cured to any appreciable extent with hexamethylenediamine carbamate (DIAK), the curative used for Viton (Ref 8). Cure of terpolymer, on the other hand, was successfully effected when DIAK was used as the curative.

TABLE III

POLYMERS(1) CONTAINING $C_2H_2F_2$

Exp. No.	Monomer Molar Feed Ratio			Conversion(2) (%)	Inherent Viscosity(3) <n>	Product
	$C_2H_2F_2$	C_2F_4	CF_3NO			
212099	0.01	0.99	1.00	40	-	Rubber
E-16301	0.01	0.99	1.00	-	-	Rubber
E-16303	0.04	0.96	1.00	70	0.64	Rubber
E-16306-1	1.00	-	1.00	-	-	No reaction
E-16306-2	0.50	0.50	1.00	45	-	Gum
E-16306-3	0.75	0.25	1.00	63	0.54	Rubber
E-16306-4	0.875	0.125	1.00	71	0.63	Rubber
E-16312	0.04	0.96	1.00	79	-	Rubber

---

(1) Prepared in suspension, -25°C.
(2) Based upon total charge.
(3) 0.5% FC-43 solution.

PHASE III - PRODUCTION OF NITROSO RUBBER

The production of nitroso rubber and its precursors, CF_3CO_2NO and CF_3NO, was continued during this report period. Details of the facilities and equipment have been given in previous reports (Ref 10 and 11). Production of C_2F_4 has not been initiated on this program since this material is being received from the Thiokol production facility at Moss Point, Mississippi.

A. Production of Trifluoronitrosomethane

Two additional production runs were completed during this report period from which 52.6 lb of purified CF_3NO was obtained. Experimental details for these runs are summarized in Table IV. Operations were facile; no incidents were experienced. A total of 148.2 lb of purified CF_3NO has now been prepared in the production facility.

TABLE IV

CF_3NO PRODUCTION

Batch No.	5813	5860
CF_3CO_2NO Preparation		
$(CF_3CO)_2O$ Charge (lb)	70.6	70.6
$N_2O_3/(CF_3CO)_2O$ (mole ratio)	0.73	0.73
CF_3CO_2NO Pyrolysis		
Reactor Temp (°F)		
Reboiler	360-367	360-365
Condensate	280-285	255-260
Reaction time (hr)	26	30
CF_3NO Yield		
% based on $(CF_3CO)_2O$	34.5	26
Weight (lb)	25.8	26.8

Repurification of the CF_3NO before polymerization was deemed necessary to reduce the CF_3NO_2 content to the lowest possible level. The purification procedure involved passage of the CF_3NO at 5 psig through two low temperature molecular sieve columns; product condensation and collection was at liquid nitrogen temperatures. Details are given in Table V.

TABLE V

REPURIFICATION OF CF_3NO

Batch No.	5811	5816	5861	5862
Batch Charged	5809	5811	5860	5813
Sieve Temperature (^oF)	-	-80 to -110	-88 to -110	-90 to -118
Recovery (%)	-	98	92	85
Analysis (%)				
CF_3NO	-	99.3	99.2	99.3
CF_3NO_2	0.8	0.3	0.3	0.4
C_xF_y + Air	-	0.4	0.5	0.3

B. Production of CF_3NO/C_2F_4 Copolymer

Four additional copolymer batches were completed during this report period with a combined yield of 107.6 lb. Data for these polymerizations are given in Table VI. The total copolymer produced to date is now 208 lb, which fulfills the revised commitments for the program and no additional production batches have been scheduled. Of that material prepared, 68.3 lb has been shipped to the contracting agency.

In one batch (5814), both conversion and molecular weight was low. Since the CF_3NO charged to this batch was equivalent to that used in more successful batches, it is suspected that the C_2F_4 inhibitor was carried into the polymerization kettle during C_2F_4 transfer. The material could act as a chain terminator as well as an inhibitor, thus producing both effects.

TABLE VI

COPOLYMERIZATION OF CF_3NO/C_2F_4

Batch No.	5812	5814	5887	5891
CF_3NO Charged				
(Batch No.)	5810	5862	5861	5816
(lb)	23	22	19	13
C_2F_4 Charged (lb)	22.7	21.8	18.9	12.9
C_2F_4 Addn. Time (hr)	1	1	1.5	1
Reaction Time (hr)	24	29	26	28
Polymer Yield				
(%)	87	31	94.5	83.4
(lb)	39.5	11.3	35.6	21.3
Inherent Viscosity $\langle\eta\rangle$	0.84	0.29	(2)	0.87
Extrapolated Mol. Wt. ($\times 10^6$)	0.90	0.22	(2)	0.92

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(1) 0.5 gm polymer in 100 ml FC-43.
(2) Polymer incompletely soluble in either FC-43 or Freon 113. Appearance is that of high mol.wt. polymer.

Two other batches (5704 and 5807) had molecular weights equal to or less than 700,000; these two batches and batch 5814 were fractionated to effect products of improved physical properties (Table VII). The fractionation was effected by dissolving the rubber in Freon 113 in a closed reactor at elevated temperatures, then filtering while still hot. On cooling, the high molecular weight fraction precipitated and was separated, washed with additional Freon, and dried under vacuum. The low molecular fractions (from the

Freon solutions) were combined and vacuum dried. This material is a viscous liquid. Of a total of 64.3 lb charged to this process, a total of 34.1 lb of high molecular weight rubber and 20.6 lb of low molecular weight liquid was recovered.

TABLE VII

FRACTIONATION OF NITROSO RUBBER

Batch No. (Fract.)	Batch No. (Charge)	Wt. Charged (lb)	Inherent Viscosity(1) of Charge $\langle\eta\rangle$	Wt. Recovered High Mol. Wt. Fract. (lb)	Inherent Viscosity(1) High Mol. Wt. Fract. $\langle\eta\rangle$
5928	5807	29	0.73	14.1	0.75
5939	5814	11.3	0.29	5.5	0.40
5953	5704	24.0	0.73	14.5	1.10

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(1) 0.5 gr polymer in 100 ml FC-43.

PHASE IV. COMPOUNDING AND CURING STUDIES

A. CF_3NO/C_2F_4 Copolymer Cures

The nitroso copolymer vulcanizates prepared from the production batches using the standard formulation (Hi-Sil 303X, 15 phr; DIAK No. 1, 2.5 phr; and triethylenetetramine, 1.25 phr) was slightly porous and of low tensile strength. Elimination of DIAK No. 1 (hexamethylenediamine carbamate) from the formulation resulted in a nonporous vulcanizate but the tensile strength was not improved (Ref 8). During this report period a filler study was performed in an attempt to improve the physical properties of the vulcanizates. The fillers evaluated included a complete spectrum of carbon blacks (thermal, furnace, channel and acetylene) as well as nonblack fillers of various chemical compositions, particle size and surface activity. The latter fillers evaluated were Hi-Sil 233 (Silica, pH approx. 7, particle size 0.022 μ), Hi-Sil 404 (Silica, pH 9.4, particle size 0.08-0.13μ), Quso H-40 (Silica, pH 4, particle size 0.016 μ), Hydrite 10S (aluminum silicate-hydrated), Baynal (aluminum hydroxide), Barytes No. 91 (barium sulfate), Silene EF (calcium silicate), and Ultrasil 4580 (silicic acid). None of the fillers significantly improved the properties of the elastomer compared with that containing Hi-Sil 303 as the filler.

Early attempts to cure nitroso terpolymer ($C_6F_5NO/CF_3NO/C_2F_4$) did not result in a satisfactory vulcanizate. When the standard formulation and cure cycle (one hour at 250°F, 18 hours at 212°F) were used, the terpolymer seemed to degrade (Ref 10). During this report period, the terpolymer was further evaluated using 15 phr of Hi-Sil 303 and varying concentrations of TETA. Satisfactory vulcanizates were obtained when these compounds were cured at 150°F for one hour instead of 250°F. The tensile strength and elongation of a specimen containing 2.5 phr TETA was approximately 150 psi and 100%, respectively. This tensile may be a little low because of slight porosity in the test sample.

In the previous report (Ref 8), it was stated that use of a hot mill ($>$200°F) effected non-porous vulcanizates with the standard formulation, presumably because of the loss of volatiles. These volatiles were identified by their infrared spectra as COF_2, $CF_3N{=}CF_2$ and CF_3NCO, the same compounds reported by Schultz (Ref 12) from the thermal and ultraviolet degradation of CF_3NO/C_2F_4 copolymer. Since evolution of these materials ceased after a period of time at constant temperatures, it can be concluded that only the lower molecular weight polymers were being degraded. The data of Schultz show an intrinsic viscosity increase with temperature treatment.

B. $CF_3NO/C_2H_2F_2/C_2F_4$ Terpolymer Cures

Terpolymers containing vinylidene fluoride ($C_2H_2F_2$) as a termonomer were investigated. Two polymers prepared from monomer mixtures containing 0.5% and 2.0% $C_2H_2F_2$ were cured with DIAK, a typical Viton ($C_2H_2F_2$ copolymer) curing agent and with the standard nitroso copolymer curing agents (triethylenetetramine (TETA) plus DIAK). The properties of these vulcanizates are given in Table VIII.

The nitroso copolymer cannot be cured with DIAK alone (Ref 8), but such a cure was obtained with the terpolymer (099a and b, Table VIII). Tensile strengths were low, however, indicating that the $C_2H_2F_2$ content of the polymers is too low. The TETA/DIAK vulcanizates exhibited somewhat higher tensiles, but were slightly porous.

TABLE VIII

CURES OF $CF_3NO/C_2H_2F_2/C_2F_4$ TERPOLYMER

Batch No.	099a	099b	16301a	16301b	16303a	16303b
Ingredients (phr)						
Terpolymer I(1)	100	100	100	100	-	-
Terpolymer II(2)	-	-	-	-	100	100
Hi-Sil 303	-	-	15	15	-	15
Thermax MT	20	20	-	-	20	-
DIAK No. 1	1	1	2.5	2.5	1	2.5
TETA(3)	-	-	1.25	1.25	-	1.25
Magnesium Oxide	15	15	-	-	15	-
Post Cure(4) (hr/°F)	-	18/212	-	18/212	18/212	18/212
Tensile Strength (psi)	107	138	272	240	288	265
Elongation (%)	700	725	375	250	1125	525
Modulus (psi at 200% elongation)	35	47	196	207	72	139
Porosity	No	No	Yes	Yes	No	Yes

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(1) 0.5% $C_2H_2F_2$ in monomer charge.
(2) 2.0% $C_2H_2F_2$ in monomer charge.
(3) Triethylenetetramine.
(4) Initial one hour cure at 250°F for all formulations.

III. SUMMARY

1. Production of an additional 52.6 pounds of CF_3NO was successfully effected. The CF_3CO_2NO utilized in these reactions was also prepared in the production facility.

2. CF_3NO/C_2F_4 copolymer production to date is 208 pounds.

3. Modifications of bulk copolymerization techniques have again resulted in very high molecular weight polymer.

4. Attempts to prepare carboxy-substituted fluoroaromatic and fluoroaliphatic nitroso compounds have not yet been successful.

5. Additional laboratory terpolymers containing BrC_6F_4 or $C_2H_2F_2$, in addition to CF_3NO and C_2F_4, were prepared.

6. Attempts to improve vulcanizate properties by modifications of curing conditions or formulations have not been entirely successful.

IV. REFERENCES

1. Minnesota Mining and Manufacturing Co., U.S. Army Contracts DA-129-QM-1043 and 1684.

2. G. Crawford, 5th JANAF Elastomer Conference, October 1958.

3. Minnesota Mining and Manufacturing Co., U.S. Army Contract DA-19-129-QM-1043, Summary Report, 15 August 1960.

4. Ibid., DA-19-129-QM-1684, Summary Report, 23 December 1962.

5. S. Andreades, J. Org. Chem. 27, 4157 (1962).

6. D. England, J. Am. Chem. Soc., 83, 2205 (1961).

7. R. Sterlin, L. Pinkina, I. Knunyants and L. Nezgovanov, Khim. Nauka i Prom. 4, 809 (1959); C.A. 54, 10837i.

8. Thiokol Chemical Corporation, Nitroso Rubber Research, Development and Production, U.S. Army Contract DA-129-AMC-69(X) O.I. 9044, QMC Project 7X93-15-004, Report Trenton RD 343-Q6, RMD 8576-Q6.

9. F. Kalberer, Bull. soc. fribourg. sci. nat., 44, 225 (1954).

10. Thiokol Chemical Corporation, Nitroso Rubber Research, Development and Production, U.S. Army Contract DA-129-AMC-69(X) O.I. 9044, QMC Project 7X93-15-004, Report Trenton RD 343-Q4, RMD 8576-Q4.

11. Ibid., Report Trenton RD 343-Q3, RMD 8576-Q3.

12. A. Schultz, N. Knoll, and G. Morneau, J. Polymer Sci. 62, 211 (1962).

THIOKOL CHEMICAL CORPORATION, CHEMICAL OPERATIONS, TRENTON, N.J. AND REACTION MOTORS DIVISION, DENVILLE, N.J., NITROSO RUBBER RESEARCH, DEVELOPMENT AND PRODUCTION, by J. Green, J. Paustian, W. Helmer, R. Hoffman and M. Reynolds, 1 September 1964 to 28 November 1964, 20 pp. incl. tables and refs. (Trenton Project No. RD 343-Q7, RMD Project No. 8576-Q7, QMC Project No. 7X93-15-004), U. S. Army Contract No. DA-19-129-AMC-69(X)O.I. 9044.

Unclassified Report

Additional CF_3NO and CF_3NO/C_2F_4 copolymer production lots were successfully completed. A total of 148 lb of CF_3NO and 208 lb of copolymer has been prepared. A continuation of curing studies on these materials has not resulted in a significant increase in vulcanizate strength. Termonomer synthesis and terpolymerization studies were continued.

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