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U.S. Army Contract No. DA-19-129-AMC-69(X)O.I. 9044

QMC Project No. 7X93-15-004



Report:

Trenton RD 343-Q5

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Report Period:

1 March 1964 to 31 May 1964

**NITROSO**

**RUBBER**

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RESEARCH  
DEVELOPMENT  
And  
PRODUCTION

CHEMICAL CORPORATION  
CHEMICAL OPERATIONS TRENTON, NEW JERSEY

**Thiokol**

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**NITROSO RUBBER  
RESEARCH, DEVELOPMENT AND PRODUCTION.**

~~Report Form RD-343-05~~

U. S. Army Contract No. DA-19-129-AMC-69(X) O-I-9044

TO QMC Project ~~7X93/15/004~~ 7X93/15/004

Report Period: 1 March 1964 to 31 May 1964

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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 March 1964 through 31 May 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 Mr. John Paustian, Dr. Joel Kaufman, Mr. David Kennedy, Mr. Fred Hoffman, Mr. Richard Crooker, and Dr. Stanley Tannenbaum at Denville and Messrs. Robert Hoffman and Malcolm Reynolds at Trenton.

ABSTRACT

The preparative processes developed for  $\text{CF}_3\text{CO}_2\text{NO}$ ,  $\text{CF}_3\text{NO}$ , and the  $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$  copolymer have been operated successfully, ~~in the production facility~~. Single production runs yielded 15 lb of  $\text{CF}_3\text{NO}$  and 13.5 lb of copolymer (mol. wt.  $\approx 1,500,000$ ). Copolymer development and termonomer studies were continued. The heat of the  $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$  copolymerization has been determined experimentally. The value is  $74.8 \pm 0.5$  kcal/mole. 

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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 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 ( $T_g$ ) is  $-51^{\circ}\text{C}$ . This low  $T_g$  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  $-40^{\circ}\text{F}$ ) still fall short of the desired serviceability (utility at  $-100^{\circ}\text{F}$ ) and the relatively low tensile strengths severely limit the usefulness of the rubber. Studies involving monomer variation have not resulted in decreased  $T_g$  values to date, although terpolymer preparation has resulted in products with improved mechanical properties.

The goals of the present program are fourfold:

1. Produce a nitroso rubber with improved mechanical properties
2. Produce a nitroso rubber with improved low temperature properties
3. Prepare 700 pounds of nitroso rubber for further evaluation
4. Fabricate various end items.

# *Thiokol*

Thiokol Chemical Corporation has initiated a five-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
- V. Fabrication

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

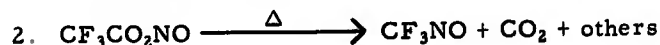
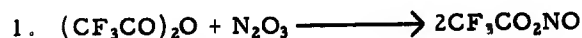
1. Preparation of nitroso monomer containing a carboxy functional group for terpolymerization studies
2. Polymerization studies to attain high molecular weight polymer
3. Construction of the production facility
4. Production of monomer and polymer

II. TECHNICAL WORK

PHASE I - MONOMER SYNTHESIS

Task 1. Process Development for Trifluoronitrosomethane (CF<sub>3</sub>NO)

The objective of this task is the development of a process capable of operation at a production level of 10 to 50 pounds of CF<sub>3</sub>NO per 24-hour period. The process which has been investigated for the attainment of this goal involves the preparation and the pyrolytic decarboxylation of trifluoroacetyl nitrite.



The development of processes for these two preparative reactions had been essentially completed during previous report periods (Ref 5). Operation of these processes at the production level has been successfully effected (cf. Phase III, below); thus, only a minor effort was given this Task during this report period.

The bench-scale reactor was utilized for three additional CF<sub>3</sub>NO preparations (total CF<sub>3</sub>NO yield, 74 gm) to supply material for continued laboratory polymer development.

In addition, the pyrolysis reaction was studied further to determine the caustic requirements for the purification train. In this work, both distilled water and 5% caustic scrubbers were used; aliquots of each were titrated before and after a standard pyrolysis. Based upon the equations:



and the quantity of CF<sub>3</sub>CO<sub>2</sub>NO charged to the pyrolysis, a total of 40.9 gm NaOH/liter of solution should have been neutralized. The number determined

experimentally was 34.86 gm/liter, indicating incomplete absorption or possibly that the first of the reactions as written above is not quantitative with respect to  $\text{CO}_2$ . The pH of the water scrubber was unchanged and therefore it was removed from the purification system.

Samples of  $\text{CF}_3\text{NO}$  obtained from the initial production runs were further purified for use in polymerization studies. Approximately 500 gm was purified by passage through molecular sieve columns to yield products of 99+% purity.

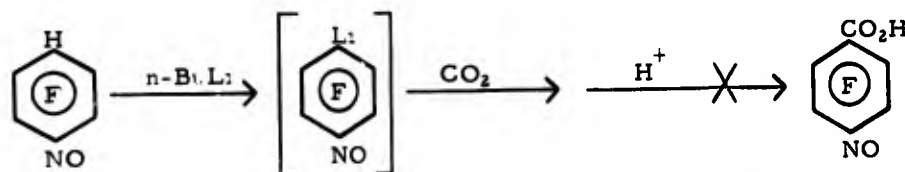
### Task 2 Preparation of Tetrafluoroethylene ( $\text{C}_2\text{F}_4$ )

One additional laboratory-scale  $\text{C}_2\text{F}_4$  preparation by the debromination of tetrafluorodibromoethane was completed (55 gm). No additional runs were scheduled because of the availability of  $\text{C}_2\text{F}_4$  from the Thiokol production facility at Moss Point, Mississippi. For safety reasons, this material is shipped gas phase at about 200 psig.

### Task 3. New Nitroso Monomers

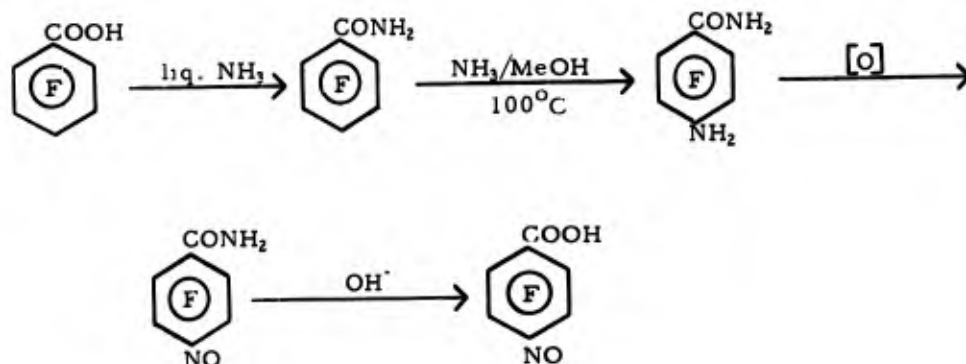
The objective of this task is the preparation of new monomers that improve the low-temperature properties of nitroso rubber or provide functionalities which could become crosslinking sites for improved mechanical properties. Preparation of fluoroaromatic nitroso compounds has been investigated because the lability of the para fluorine atom of pentafluoro-nitrosobenzene toward nucleophilic reagents suggests its use as a site for crosslinking (Ref 5).

Another monomer of great interest is p-nitrosotetrafluorobenzoic acid because of the general ease of crosslinking through a carboxy group. An approach to this compound (Ref 5) involved lithiation of 2,3,5,6-tetrafluoro-nitrosobenzene with butyllithium, followed by carbonation of the desired intermediate and acidification



Infrared analysis of the product obtained showed that it was in the desired compound

Another route to the nitroso acid was by oxidation of *p*-aminotetrafluorobenzoic acid (Ref 5). Early attempts were hampered by poor yields of the amino acid and the great difficulty in obtaining it pure; therefore, a related synthesis was begun. Pentafluorobenzoic acid was converted through the acid chloride to the known (Ref 6) pentafluorobenzamide. Ammonia and methanol at 100°C and 130 psig converted it to *p*-aminotetrafluorobenzamide, mp 176.5-179°C (Ref 7), in 20% yield.



Elemental analyses are in excellent agreement with this structure. When sufficient quantities are obtained, oxidation to the nitroso-amide and its hydrolysis to nitroso-acid will be carried out.

## PHASE II - POLYMERIZATION STUDIES

The tasks of this phase continue to be: (1) the development of the process for producing CF<sub>3</sub>NO/C<sub>2</sub>F<sub>4</sub> copolymer in 10 to 50 pound quantities per 24-hour period and (2) research toward preparation of other nitroso polymers with improved properties. The first of these tasks has been emphasized during this report period in order to expedite the transfer of the CF<sub>3</sub>NO/C<sub>2</sub>F<sub>4</sub> copolymer technology from the laboratory to the production plant. The process which has been proved out in laboratory studies and which will be used in production is a suspension polymerization in which the monomers are suspended in a water solution of lithium bromide, using magnesium carbonate as the suspending agent. The production process, however, will involve some variables not encountered in laboratory preparations and the effect of these variables had to be determined before the process could go to the production plant. The variables were evaluated as to their effect on

extent of conversion and molecular weight of product. Work on Task 1 has also included some efforts to improve the polymerization process through the use of catalysts and pressure.

Work on Task 2 this report period has been limited to efforts to prepare a copolymer of FNO/C<sub>2</sub>F<sub>4</sub>.

#### Task 1. Process Development and Improvement

In anticipation of problems that may arise in production, particularly those due to impurity of reactants and contamination of the system due to the equipment, the following factors were investigated and evaluated.

##### 1. Purity of CF<sub>3</sub>NO

Previous investigations on this program have shown that CF<sub>3</sub>NO may contain impurities, particularly nitrogen oxides, which inhibit the formation of high molecular weight polymer. The CF<sub>3</sub>NO prepared in the production facility had to be checked to determine whether it could be used as obtained or if further purification was necessary. In addition, the possible formation of impurities during CF<sub>3</sub>NO storage and the effect of these impurities on the copolymerization had to be determined. These determinations were done directly by polymerizing the CF<sub>3</sub>NO in question and observing the extent of conversion and the molecular weight of the product. Molecular weights were determined and compared as functions of inherent viscosity.

The experiments showed, as reported in Table I, that CF<sub>3</sub>NO may be kept at least 10 days in stainless steel cylinders at -20°C without detrimental effect on its subsequent polymerization. The polymerization is affected by impurities initially present in the CF<sub>3</sub>NO and data included in Table II show that CF<sub>3</sub>NO containing 1.8 wt percent CO<sub>2</sub> and 0.7 wt percent of a mixture of CF<sub>3</sub>NO<sub>2</sub> and COF<sub>2</sub> yields polymer of substantially lower molecular weight than a control, apparently due to the CF<sub>3</sub>NO<sub>2</sub> content. It is apparent that this monomer must be further purified before polymerization.

It is noteworthy that some of the experiments summarized in these tables resulted in markedly high conversions to polymers. These high conversions were also normally accompanied by higher molecular weights. The proximate cause for this effect is not as yet known; however, it is hoped that future experiments will result in a solution.

TABLE I  
EFFECT OF CF<sub>3</sub>NO STORAGE TIME ON POLYMERIZATION

| Expt. No. | Storage Time<br>(hr) | Reaction<br>Vessel | Conversion<br>(%) | Percent<br>High<br>Mol. Wt.<br>Fraction | Inherent Viscosity* |              |
|-----------|----------------------|--------------------|-------------------|---|---------------------|--------------|
|           |                      |                    |                   |   | Unfractionated      | Fractionated |
| 212082 A  | 0                    | Pyrex glass        | 68                | 78                                      | 0.72                | 1.22         |
| 212082 B  | 48                   | Pyrex glass        | 91                | 77                                      | 1.00                | 1.22         |
| 212082 C  | 240                  | Pyrex glass        | 86                | 91                                      | 1.08                | 1.32         |

\* 0.5 gm polymer/100 gm solvent



TABLE II  
EFFECT OF VARIABLES ON  $CF_3NO/C_2F_4$  POLYMERIZATION

| Expt. No.  | Variable                 | Conversion (%) | Percent High Mol. Wt. Fraction | Inherent Viscosity* |              |
|------------|--------------------------|----------------|--------------------------------|---------------------|--------------|
|            |                          |                |                                | Unfractionated      | Fractionated |
| 212082 B   | Control                  | 91             | 77                             | 1.00                | 1.22         |
| 212083 A   | $CF_3NO - 97.5\%$        | 73             | 71                             | 0.50                | 0.64         |
|            | $CO_2 - 1.8\%$           |                |                                |                     |              |
|            | $CF_3NO_2/COF_2 - 0.7\%$ |                |                                |                     |              |
| 4329-941-1 | Technical Grade LiBr     | 75             | 83                             | 1.01                | -----        |
| 212084-A1  | Technical Grade LiBr     | --             | 79                             | 0.80                | 1.15         |
|            | Technical Grade LiBr     |                |                                |                     |              |
| 212084-A2  | Technical Grade LiBr     | --             | --                             | 0.82                | -----        |
|            | Technical Grade LiBr     |                |                                |                     |              |
| 212084-C   | FC 43 Contamination      | --             | 75                             | 0.81                | -----        |
| 212084-B   | Deionized Water          | --             | 74                             | 1.02                | 1.23         |

-----  
\* 0.5 gm polymer/100 gm solvent

## 2. Corrosion Study

As a check of the possible corrosion of the steel reactor by the lithium bromide solution, samples of the same type stainless (316) were contacted with the solution for a period of three weeks at room temperature. Neither staining nor a weight change occurred during this period, even at the interface of a partially immersed metal sample.

## 3. Purity of Lithium Bromide

A reagent grade of lithium bromide has been used in laboratory polymerizations; however, use of a technical grade in production would result in significant savings. Experiments, shown in Table II, indicate that use of technical grade lithium bromide is not detrimental to conversion or molecular weight and that it may be used in the production process.

## 4. Purity of Water

Distilled water has been used in laboratory polymerizations; however, it is desired that deionized water be used at the production plant. A polymerization conducted using deionized water (Table II) yielded high quality polymer and showed conclusively that deionized water may be used in production.

## 5. Contamination by FC43

The stirrer of the production reactor requires a liquid seal and FC43 may be used for this purpose. An experiment was conducted to determine if the presence of a small amount of FC43 due to leakage at the stirrer seal would affect the polymerization. The product from the experiment was of lower molecular weight than the control, but the difference was of the same magnitude observed in parallel experiments and therefore cannot be considered significant (Table II). The presence of small amounts of FC43 has no apparent effect on the polymerization.

The above experiments were on a small scale in sealed glass tubes. To more closely approximate the reaction conditions to be employed in the production reactor, an existing steel autoclave was modified for intermediate-scale polymerizations. This autoclave was of 403 stainless steel and 300 ml volume. Tests had shown that this steel would not resist corrosion; therefore, glass liners were fabricated and inserted. The area of the head would not allow a

mechanical seal for an agitator shaft, thus agitation was effected magnetically with a stirring bar. It was expected that polymerization of up to 50 gm total monomer charges would be facile.

For operation, the volumes of the tubing connecting each monomer to the reactor were made equal and the magnitude determined. Allowing each monomer to expand into these volumes (previously evacuated) to equivalent pressures would then effect the transfer of equivalent monomer quantities (pressures were kept below criticality). At this point, the valves to the monomer storage cylinders were closed and the monomers in the calibrated volumes were allowed to expand into the reactor (evacuated) containing brine at  $-25^{\circ}\text{C}$ .

It was hoped that this apparatus could be used to determine the optimum charging conditions (incremental, bulk, or alternate addition) as well as the optimum working pressure and time of reaction. However, the agitation proved to be insufficient, at least after polymer formation began, and only low molecular weight polymers were obtained. The autoclave has now been modified to include a motor-driven agitator with a rotary seal in the bottom of the vessel.

Of significance, however, was an experiment in which 20 gm of each monomer was added simultaneously and in one charge. No temperature rise was noted which indicated that Carius tube fracture in some small scale experiments was due to poor seals and not to an uncontrollable exothermic polymerization. The rather high heat of polymerization value does indicate, however, the possibility that the polymerization can become uncontrollable and that adequate provisions for temperature control and heat transfer must be made.

## 6. Catalysts

Three organo-phosphorous compounds,  $\text{C}_6\text{H}_5\text{POCl}_2$ ,  $\text{C}_6\text{H}_5\text{PCl}_2$ , and  $(\text{C}_6\text{H}_5)_2\text{PCl}$ , were investigated as catalysts for the  $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$  polymerization. Polymerizations were done in bulk to minimize masking side effects and to permit use of lower temperatures. Experiments were conducted at  $-25^{\circ}$ ,  $-65^{\circ}$  and  $-80^{\circ}\text{C}$  and the results evaluated in terms of the conversions and visual observation of the products (Table III). The only effects noted were some increase in conversion at  $-25^{\circ}\text{C}$  in the presence of the phosphines,  $\text{C}_6\text{H}_5\text{PCl}_2$  and  $(\text{C}_6\text{H}_5)_2\text{PCl}$ ; however, the products were obviously of lower molecular weight and inferior in physical properties to the control.

TABLE III  
EFFECT OF ORGANO-PHOSPHOROUS COMPOUNDS  
ON  $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$  POLYMERIZATION

| <u>Exp. No.</u> | <u>Compound</u>                      | <u>Reaction<br/>Temp<br/>(°C)</u> | <u>Reaction<br/>Time<br/>(days)</u> | <u>Conversion<br/>(%)</u> | <u>Observation</u> |
|-----------------|--------------------------------------|-----------------------------------|-------------------------------------|---------------------------|--------------------|
| 081-4           | None                                 | -25                               | 3                                   | 67                        | Rubbery gum        |
| 081-1           | $\text{C}_6\text{H}_5\text{POCl}_2$  | -25                               | 3                                   | 67                        | Rubbery gum        |
| 081-2           | $\text{C}_6\text{H}_5\text{PCl}_2$   | -25                               | 3                                   | 89                        | Soft gum           |
| 081-3           | $(\text{C}_6\text{H}_5)_2\text{PCl}$ | -25                               | 3                                   | 79                        | Soft gum           |
| 081-8           | None                                 | -65                               | 21                                  | 67                        | Soft gum           |
| 081-5           | $\text{C}_6\text{H}_5\text{POCl}_2$  | -65                               | 21                                  | 66                        | Soft gum           |
| 081-6           | $\text{C}_6\text{H}_5\text{PCl}_2$   | -65                               | 21                                  | 68                        | Soft gum           |
| 081-7           | $(\text{C}_6\text{H}_5)_2\text{PCl}$ | -65                               | 21                                  | 68                        | Soft gum           |
| 081-12          | None                                 | -80                               | 21                                  | 17                        | Paste              |
| 081-9           | $\text{C}_6\text{H}_5\text{POCl}_2$  | -80                               | 21                                  | 17                        | Paste              |
| 081-10          | $\text{C}_6\text{H}_5\text{PCl}_2$   | -80                               | 21                                  | 14                        | Paste              |
| 081-11          | $(\text{C}_6\text{H}_5)_2\text{PCl}$ | -80                               | 21                                  | 19                        | Paste              |

## 7. Heat of Polymerization

The heat of the  $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$  polymerization has been experimentally determined. It was found (Ref 8) that this polymerization could be effected in 30 minutes or less in bulk at 80 atmospheres in the temperature range of  $-20^\circ\text{C}$  to  $20^\circ\text{C}$ . This technique was utilized for this determination.

The monomers were charged to a Parr calorimeter (at an initial temperature of  $25^\circ\text{C}$ ) to approximately 52 atmospheres. The rate of temperature rise in the first experiment indicated that the polymerization was essentially complete in 1.5 hours; therefore, subsequent reactions were run for two-hour periods. Corrections for unconverted monomers and external heat sources (such as solenoid valves) were made. Analysis of the unconverted monomers after reactions showed that  $\text{CF}_3\text{NO}$  and  $\text{C}_2\text{F}_4$  were still in a 1:1 molar ratio and were basically unchanged.

The heat of polymerization was found to be  $74.8 \pm 0.5$  kcal/mole (average of three determinations).

### Task 2. Experimental Nitroso Polymers

Another attempt was made to copolymerize FNO and  $\text{C}_2\text{F}_4$ . In a previous attempt (Ref 9), the reactants were placed in a Monel cylinder with no other material present and allowed to remain in contact for 10 days at  $-40^\circ\text{C}$ . Infrared and spectrographic analysis of the gaseous products identified many low molecular weight products but no polymer formation was indicated.

In the latest attempt the reactants were held in contact for 72 hours at  $-65^\circ$ , 48 hours at  $-25^\circ$ , and 75 hours at  $25^\circ\text{C}$ . The cylinder contents were collected in an apparatus constructed of Monel and Kel-F. Apparently no reaction had occurred in the cylinder but a decrease of vapor pressure in the collection apparatus and the collection of a low boiling liquid in the Kel-F cold trap indicated that a reaction occurred in the collection apparatus.

The gaseous products did not include FNO as determined by infrared analysis but did contain  $\text{C}_2\text{F}_4$  and  $\text{F}(\text{CF}_2)_x\text{NO}$ . The liquid decomposed when exposed to the atmosphere and was not identified.

### PHASE III - PRODUCTION OF NITROSO RUBBER

The receipt and installation of equipment for the preparation of both  $\text{CF}_3\text{NO}$  and the nitroso copolymer has been completed. Details of this equipment have been given in previous reports (Ref 5 and 9); each has been operated successfully. No provisions have been made for  $\text{C}_2\text{F}_4$  synthesis; this material is currently being received from the Thiokol production facility at Moss Point, Mississippi.

#### A. Production of Trifluoronitrosomethane

Two  $\text{CF}_3\text{CO}_2\text{NO}$  runs were completed during this report period, each followed by pyrolyses to  $\text{CF}_3\text{NO}$ . Experimental details for these runs are summarized in Table IV.

The first  $\text{CF}_3\text{NO}$  run was on a small scale and served to check out the equipment. This run produced 6 pounds of product containing 80.0 percent  $\text{CF}_3\text{NO}$ , 13 percent  $\text{CO}_2$  and 7 percent of an  $\text{NO}_2$  species (calculated as  $\text{CF}_3\text{NO}_2$ ). In addition, there was a trace of  $\text{COF}_2$ .

The next  $\text{CF}_3\text{NO}$  run utilized an increased caustic level for improved  $\text{CO}_2$  removal. This run produced 15 pounds of product containing 97.5 percent  $\text{CF}_3\text{NO}$ , 1.8 percent  $\text{CO}_2$  and 0.7 percent or less of a mixture of  $\text{CF}_3\text{NO}_2$  and  $\text{COF}_2$ . Each of these products could be purified to greater than 99 percent purity by an additional pass through a molecular sieve column; material so purified was used in the copolymerization described below.

Two additional  $\text{CF}_3\text{NO}$  preparations (each preceded by a  $\text{CF}_3\text{CO}_2\text{NO}$  preparation) were initiated with reactant charges similar to those of XP5599 and XP5600 (Table IV). Mechanical difficulties were experienced, however, and little or no  $\text{CF}_3\text{NO}$  was collected. In one such experiment, an over-pressure occurred in the molecular sieve column causing rupture of the column and loss of product. In the other, an FC43 line in the reboiler section of the pyrolysis unit was broken. This forced premature shutdown of the operation and only 2 pounds of  $\text{CF}_3\text{NO}$  was collected. Additional  $\text{CF}_3\text{CO}_2\text{NO}$  and  $\text{CF}_3\text{NO}$  runs are in progress.

#### B. Production of $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ Copolymer

One  $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$  copolymerization was successfully effected at the production facility. The polymerization was at  $-25^\circ\text{C}$  with the monomers in

TABLE IV  
INITIAL  $\text{CF}_3\text{CO}_2\text{NO}$  AND  $\text{CF}_3\text{NO}$  PRODUCTION

|  | <u><math>\text{CF}_3\text{CO}_2\text{NO}</math></u> |               |
|--|---|---------------|
|  | <u>XP5591</u>                                       | <u>XP5599</u> |
| $(\text{CF}_3\text{CO})_2\text{O}$ , wt (lb)                       | 18.1  | 41.6          |
| $\text{N}_2\text{O}_3$ , wt (lb)                                   | 4.3   | 10.0          |
| Mol. Ratio $\text{N}_2\text{O}_3/(\text{CF}_3\text{CO})_2\text{O}$ | 0.664   | 0.664         |
| Reaction Temp ( $^{\circ}\text{F}$ )                               | 10 to 32  | 15 to 40      |
| $\text{N}_2\text{O}_3$ Addition Time (hr)                          | 3-1/2   | 4-1/4         |
| NO Sparging Time (hr)  | 2-1/2   | 1             |

|   | <u><math>\text{CF}_3\text{NO}</math></u> |               |
|---|--|---------------|
|   | <u>XP5592</u>                            | <u>XP5600</u> |
| Reboiler Temp ( $^{\circ}\text{F}$ )    | 345 to 360                               | 350 to 360    |
| Heating Oil Temp ( $^{\circ}\text{F}$ ) | 410                                      | 410           |
| Reflux Temp ( $^{\circ}\text{F}$ )      | 300 to 340                               | 280 to 340    |
| Time to empty nitrite reactor (hr)      | 4  | 7             |
| Yield of liquid product (lb)            | 6-1/2                                    | 15            |
| Wt of KOH in scrubber (lb)              | 9-1/2                                    | 40            |
| Strength of KOH-Start                   | 4-1/2%                                   | 15%           |
| Strength of KOH-Finish                  | 0.23%                                    | 3.3%          |

aqueous suspension. A total of 20.4 pounds of monomers was charged; the resultant copolymer weighed 13.5 pounds. This polymer had an extrapolated intrinsic viscosity of 1.06, indicating a molecular weight of  $\sim 1,500,000$ . Fractionation resulted in the isolation of a high molecular weight fraction with an extrapolated intrinsic viscosity of  $> 1.3$  (molecular weight  $\sim 2,000,000$ ). This fraction represented 73 percent of the total.

#### PHASE IV - COMPOUNDING AND CURING STUDIES

The objective of this phase is to establish the best methods of realizing the unusual properties of nitroso rubber through formulation studies. Initial studies in this Phase have been reported (Ref 5). No additional work was completed during this report period because of insufficient polymer quantities. Sufficient  $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$  copolymer and  $\text{CF}_3\text{NO}/\text{C}_6\text{F}_5\text{NO}/\text{C}_2\text{F}_4$  terpolymer are now available and work on this Phase will be continued during the next report period.

#### PHASE V - FABRICATION

The objective of this phase of work is to conduct studies toward developing specific compounds of nitroso rubber that can be used in extrusions, moldings and proofed goods and to produce gaskets, reinforced hose, and coated fabric. This phase is scheduled to begin about August 1964.



III SUMMARY

1. Production of 19.8 pounds of  $\text{CF}_3\text{NO}$  was successfully effected.  $\text{CF}_3\text{CO}_2\text{NO}$  utilized in these runs was also prepared in the production facility.
2.  $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$  copolymer was successfully prepared in the production facility. One batch (13.5 pounds) was completed which had a molecular weight of  $\sim 1,500,000$  before fractionation.
3. Attempts to prepare carboxy-substituted fluoroaromatic nitroso compounds have not yet been successful.
4. Use of  $\text{CF}_3\text{NO}$  stored in stainless steel cylinders at  $-20^\circ\text{C}$  for up to 10 days results in a polymer equivalent to that from freshly prepared  $\text{CF}_3\text{NO}$ .
5. Selected phosphines and phosphine oxides were found to be ineffective in increasing the molecular weight of the copolymer.
6. Technical grade LiBr may be substituted for reagent grade LiBr in the polymerization process; deionized water may also be substituted for distilled water.
7. The presence of FC43 does not interfere with the copolymerization.
8. Copolymerization of FNO and  $\text{C}_2\text{F}_4$  has not yet been successful.
9. The heat of polymerization for  $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$  is  $74.8 \pm 0.5$  kcal/mole.

IV. REFERENCES

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