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QMC Project No. 7X93-15-004

Report:

Trenton RD-343-Q3

RMD 8576-Q3

Report Period:

1 September 1963 to 30 November 1963

NITROSO RUBBER

RESEARCH DEVELOPMENT And PRODUCTION

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CHEMICAL CORPORATION
CHEMICAL OPERATIONS TRENTON, NEW JERSEY

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Thiokol

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Report, ~~Trenton~~ RD-343-Q3 ~~and RMD 8576-Q3~~

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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 through 30 November 1963. The overall project leader is Dr. Marvin M. Fein; divisional project leaders are Mr. Joseph Green at Denville and Mr. Warren Helmer at Trenton. Other contributors to the program are Mr. John Paustian, Dr. Jerome Hollander, Mr. David Kennedy, Mr. Fred Hoffman, Mr. Richard Crooker, Mr. Francis McPeek and Dr. Stanley Tannenbaum at Denville and Messrs. Robert Hoffman and Malcolm Reynolds at Trenton.

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ABSTRACT

Additional safety testing of the trifluoroacetyl nitrite indicate that the process developed for CF_3NO production can be operated without undue hazard. Successful purification of CF_3NO has been achieved through the use of water and 5% caustic scrubbers followed by a cold (-80 to -100°C) molecular sieve column to remove the last trace of impurities. Approximately 30 g of pentafluoronitrosobenzene has been prepared. CF_3NO/C_2F_4 copolymers were prepared with intrinsic viscosities of 0.70. Construction of the production facility has been started at Bristol, Pa.

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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, 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, 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 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 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. Development of a practical procedure for the purification of CF_3NO
2. Preparation of nitroso monomers containing carboxy functional groups for terpolymerization studies
3. Polymerization studies to attain high molecular weight polymer
4. Construction of the production facility.

II. TECHNICAL WORK

PHASE I - MONOMER SYNTHESIS

Task 1. Process Development for Trifluoronitrosomethane (CF_3NO)

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_3NO per 24 hour period. The process being emphasized, and the one which will be used for initial production, is that involving the production and the pyrolytic decarboxylation of trifluoroacetyl nitrite.

1. $(CF_3CO)_2O + N_2O_3 \longrightarrow 2CF_3CO_2NO$

2. $CF_3CO_2NO \xrightarrow[\Delta]{} CF_3NO + CO_2 + \text{others}$

A. PREPARATION OF TRIFLUOROACETYL NITRITE

The nitrite is best prepared by the interaction of dinitrogen trioxide and trifluoracetic anhydride (Ref 5, 6). The preparation is facile, and no difficulty has been experienced in the preparation to date.

An additional four batches have been completed to date, the largest of which yielded 231 gm of product. The total yield of these four batches was 697 gm. This material was used for safety testing and decarboxylation studies.

The first of the above preparations utilized trifluoroacetic anhydride "as received" and without fractional distillation. The trifluoroacetyl nitrite produced from this anhydride was similar to the CF_3CO_2NO prepared from rectified anhydride; "as received" anhydride was, therefore, used in subsequent reactions. All nitrite prepared was stored in the dark at 0°C.

B. SAFETY EVALUATION OF TRIFLUOROACETYL NITRITE

Previous data indicated that CF_3CO_2NO will not ignite below 42°C under initiation at concentrations greater than 50% (with N_2); at lower concentrations the initiated ignition temperature is above 60°C (Ref 6). Since these conditions can be expected at some point in the reactor during the thermal decarboxylation, it was decided to test the ignitability (or detonability) of CF_3CO_2NO under simulated reactor conditions.

For this test, the reaction diluent (FC-43) was charged to a round-bottomed flask topped with a column which served as an air cooled condenser. Electrodes were positioned immediately above the surface of the FC-43. The FC-43 was then brought to a vigorous reflux, and CF_3CO_2NO was injected below the FC-43 level. The CF_3CO_2NO vaporized immediately, and a spark was induced by a Tesla coil between the electrode. No effect of the spark was observed. The FC-43 reflux was maintained and gradual CF_3NO formation was observed (yellow ⟶ green ⟶ blue). During this time, the vapor phase was sparked at frequent intervals; at no time was an ignition or a detonation experienced. It is, therefore, assumed that dilution of the CF_3CO_2NO vapors by FC-43 has resulted in a process which can be operated without undue hazard.

Additional detonation testing of CF_3CO_2NO has been completed in a manner similar to that previously reported (Ref 6). The nitrite was confined in stainless steel tubing 11/16 in. ID and subjected to the detonation of 50 gm of tetryl. The CF_3CO_2NO did not propagate the detonation; therefore, if piping between the reactor and the CF_3CO_2NO storage vessel is stainless steel and less than 11/16 in., no propagation back to the storage vessel should occur.

C. PREPARATION OF TRIFLUORONITROSOMETHANE

Process development work on the preparation of CF_3NO has been continued at a high level of effort with emphasis given the pyrolytic decarboxylation of CF_3CO_2NO. Methods of continuous CF_3NO purification were also emphasized.

1. Reaction

A process for the continuous preparation of CF_3NO has been described (Ref 6). In this process, CF_3CO_2NO is charged at a measured rate to a reactor consisting of a boiler for an inert diluent (FC-43), and a large vapor volume is heated by the ascending FC-43 vapors in which the decarboxylation takes place. A water-cooled condenser returns the FC-43 and the unreacted CF_3CO_2NO to the boiler. This apparatus has been used successfully during this report period to prepare CF_3NO in purities >99.5%. A schematic diagram of this apparatus is shown as Figure 1. The largest reactor of this type used to date has an FC-43 volume of 80 ml and a vapor-phase reactor volume of 600 ml.

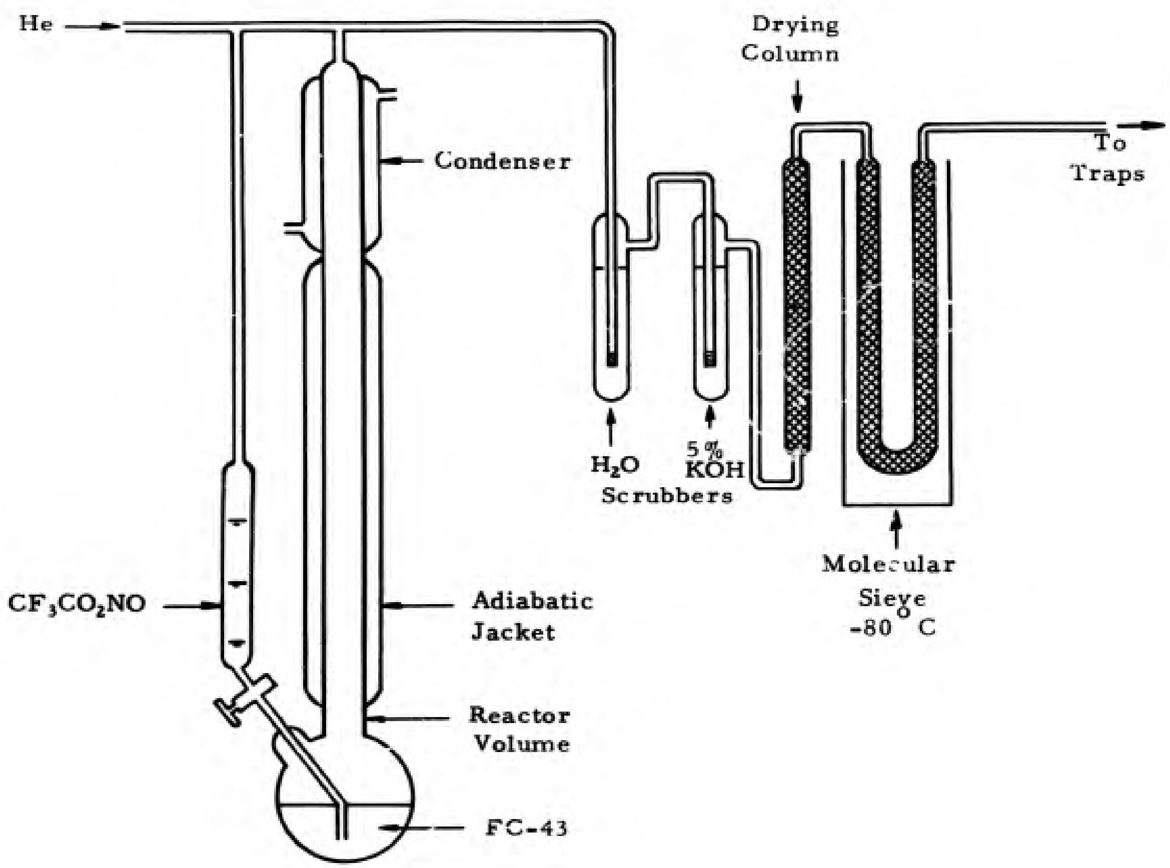


Figure 1. Laboratory Apparatus for CF_3NO Production

The average rate of CF_3CO_2NO charged to this reactor has been 26 gm per hour, although rates up to twice that have been successfully used. The average rate corresponds to a CF_3NO production of about 8-9 gm per hour. Thus, a reactor of only 10 gallons volume should easily be capable of producing CF_3NO at a rate of two pounds per hour.

A total of 17 reactions were completed during this report period with a total CF_3NO yield of 114 gm; of this quantity, 69 gm were of 98.5% or greater purity.

One sample of CF_3CO_2NO was stored in the dark at 40^oC for a period of two weeks as an accelerated aging study to determine the effect of nitrite storage on CF_3NO yield. A pyrolysis was effected with fresh nitrite followed by pyrolyses under equivalent conditions at weekly intervals. Yields of CF_3NO were 51% with fresh nitrite and 41% and 28% after one and two week storage. No apparent yield reduction has been experienced with nitrite stored for an equivalent length of time at 0^oC. Therefore, refrigerated storage is mandatory, and it is suggested that the nitrite be used as soon after preparation as possible.

2. Purification

The formation of CF_3NO in the CF_3CO_2NO decarboxylation is accompanied by a large number of other compounds. In addition to the formation of CF_3NO, CO_2, N_2O, NO, NO_2, CF_4, C_2F_6, C_3F_8, C_4F_{10}, COF_2, CF_3NO_2 and $(CF_3NO)_2$ are among the other products identified. The products considered to be most deleterious to the copolymerization with C_2F_4 are the oxides of nitrogen (with the possible exception of N_2O), CF_3NO_2 and $(CF_3NO)_2$. Methods for removing these materials were studied intensively during this report period.

Data received from 3M (Ref 3) indicated that the use of a water scrubber was sufficient to remove all but the CO_2, and that the CO_2 could be removed by a 4X molecular sieve. The recommendation of fractional distillation (60 plate) for the purest possible CF_3NO was also made by 3M.

The use of low temperature fractional distillation was not considered for this program because of the cost of the equipment, the difficulty of obtaining 60 plates on a production scale, and the need for a continuous unit. Therefore, other methods of purification of the process stream were investigated.

The original attempts at purification have been reported (Ref 6). The water scrubber was found to be ineffective, but the substitution of 5% caustic

(KOH or NaOH) did effect a significant reduction in the level of the nitrogen oxides. The investigation of caustic and other scrubbers in combination with cold traps and molecular sieve columns was continued, and the data are summarized in Table I.

Since NO forms complexes with many transition metals of low valence state (e.g., ferrous, chromous), the use of these materials in scrubbers was investigated. It was thought that NO_2 would be reduced to NO, followed by NO removal as the complex. Ferrous sulfate (in both neutral and acid solution) was found to be somewhat effective, but not enough of the oxides were removed to recommend its use in the purification train. The use of chromous chloride (prepared in solution from chromium chloride in a Jones reductor) was found to remove CF_3NO as well, thereby reducing the yield of product. It may be possible to complex CF_3NO in this manner, and then regenerate it at will. This possibility will be investigated as time permits.

The use of more concentrated caustic was also investigated. In one experiment, 50% NaOH was used to determine the effect of much stronger solutions. Although absorption of neat NO_2 was found to be complete, analysis of CF_3NO process streams passed through this solution indicated significant NO_2 concentrations. In addition, recoveries were very low. Thus, significant breakdown of the CF_3NO apparently occurred and subsequent work was performed with 5% caustic.

Success was obtained through the use of water and 5% caustic scrubbers to remove the bulk of the nitrogen oxides and CO_2 followed by a cold (-78 to -100°C) molecular sieve column to remove the last trace of impurities. Material purified in this manner was contaminated only with traces of fluorocarbons. It was found essential to cool the molecular sieve, because at higher temperatures the nitrogen oxides would eventually elute from the column. The use of cold traps (-100°C) was also found to be effective at the laboratory scale, but on a plant scale some impurities conceivably might be swept through.

The analyses of CF_3NO obtained from Peninsular Chem Research (PCR) were reported in the previous quarterly report. It was noted that there were discrepancies in the analyses obtained at the two facilities. These samples were reanalyzed at Thiokol-RMD using improved techniques and, as a result, CF_3NO purities of 84.6 to 93.5% were found (majority $>$ 88% instead of the 85 to 89% range previously reported.

TABLE I

PYROLYSES OF CF_3CO_2NO IN FC-43

Experiment No.	CF_3CO_2NO (g)	Addition Time (min)	Purification System	Product Wt (g)	Crude Yield (%)	Assay (%)[1] CF_3NO	COF_2	NO_2	N_2O
866	13.0	150	Dry Ice trap + 5% $FeSO_4$ + 5% KOH	---	---	94.5	---	0.5	5.0
872	13.9	52	5% KOH	4.96	51.6	91.5	0.3	5.4	2.8
876	18.4	75	5% KOH + 15% $FeSO_4$ + 50% KOH	5.7	44.8	80.0	---	3.8	2.3
879	22.0	97	50% KOH + 15% $FeSO_4$ + Dry Ice	---	---	84.5	0.6	11.3	3.6
882	35.0[2]	---	5% NaOH + 15% $FeSO_4$ (acidified + -100°C Trap)	7.0	---	99+	---	---	---
884	42.8	275	5% NaOH + 15% $FeSO_4$ (acidified + -100°C Trap)	13.0	44.0	98	---	1.0	1.0
887	22.3	70	5% NaOH + 15% $FeSO_4$ (acidified)	---	---	96.8	0.1	2.0	0.8
888	43.5	126	5% NaOH + Mol. Sieve at -78°C	17.7	58.8	75.2	6.1	1.0	23.7
890	32.1	---	Counter-Current H_2O Scrubber +5% NaOH + Mol. Sieve at -78°C	---	---	75.0	contains air		
891	28.4	50	5% NaOH + H_2O + Mol. Sieve at -78°C	3.8	19.3	98	---	---	---
892	36.7	88	5% NaOH + H_2O + Mol. Sieve at -78°C	11.8	46.5	99	trace	trace	---
894	45.0	112	5% NaOH + H_2O + Mol. Sieve at -78°C	13.5	43.3	99.5	trace	---	---
895	55.0	150	5% NaOH + H_2O + Mol. Sieve at -78°C	17.0	44.7	99	trace	trace	---
896	57.4	163	5% NaOH + H_2O + Mol. Sieve at -78°C	19.8	50.0	98.6	0.4	0.7	---

(1) CF Materials make up the remainder.
(2) Reaction not completed.

Task 2. Preparation of Tetrafluoroethylene (C_2F_4)

The objective of this task is the preparation of sufficient quantities of C_2F_4 for both the polymer research studies and for production of the required amount of nitroso rubber.

The quantities required for the polymer development tasks are being prepared at Thiokol-RMD by the debromination of tetrafluorodibromoethane, Freon 114-B2.

$$CF_2Br\ CF_2Br + Zn \longrightarrow CF_2 = CF_2 + ZnBr_2$$

Initial preparations have been reported (Ref 6); four additional runs were completed during this report period. The total weight of the C_2F_4 obtained was 124 gm. In the last of the reactions, the zinc was used "as received" instead of activated by washes with carbon tetrachloride and dilute hydrochloric acids as previously. The "as received" zinc appeared to be equivalent in all respects; there was no induction period. All products were shown to be of > 98% purity, the impurities being C_2F_6 and C_3F_8.

Task 3. New Nitroso Monomers

The objective of this task is to prepare new fluorinated nitroso monomers. Some monomers will contain functional groups capable of acting as cross-linking sites for the vulcanization of nitroso rubbers. Other monomers will impart improved low temperature properties to nitroso rubbers.

Carboxy-substituted fluorinated nitroso compounds have been chosen as termonomers because of the general ease of crosslinking through carboxy groups. As described in the second quarterly report, the first method chosen for the preparation of carboxy-substituted nitroso compounds was the preparation and pyrolysis of carboxy-substituted hydroxamic acids.

$$[(CF_2)_xCO]_2O + NH_2OH \longrightarrow HO_2C(CF_2)_xCONHOH$$

$$HO_2C(CF_2)_xCONHOH \xrightarrow{\Delta} HO_2C(CF_2)_xNO$$

This was an extension of the reported preparation of trifluoronitrosomethane by pyrolysis of trifluoroacethydroxamic acid (Ref 7).

$$CF_3COOCH_3 + NH_2OH \longrightarrow CF_3CONHOH + CH_3OH$$

$$CF_3CONHOH \xrightarrow{\Delta} CF_3NO + (CH_2O)_n$$

All attempts to repeat the preparation of trifluoronitrosomethane by this method have failed. As reported in the second quarterly report, neither the low-melting hygroscopic solid obtained from the reaction of trifluoroacetic anhydride with hydroxylamine hydrochloride nor the white crystalline solid which melted at 72° to 75° C obtained from the reaction of methyl trifluoroacetate with hydroxylamine yielded trifluoronitrosomethane on pyrolysis at reduced pressure. During this report period, the reaction of trifluoroacetic anhydride with hydroxylamine hydrochloride was repeated under strictly anhydrous conditions. The white crystalline solid obtained, which melted at room temperature, failed to yield trifluoronitrosomethane on pyrolysis.

Trifluoroacetic anhydride was also allowed to react with a methanol solution of anhydrous hydroxylamine, freshly prepared from hydroxylamine hydrochloride and sodium methoxide. No trifluoronitrosomethane was obtained on pyrolysis of the low-melting solid obtained from this reaction.

The second method chosen for the preparation of carboxy-substituted nitroso compounds was the reaction of dicarboxylic acids or their derivatives with nitrosyl chloride in the presence of ultraviolet light. The preparation of trifluoronitrosomethane by reaction of trifluoroacetic acid with nitrosyl chloride in the presence of ultraviolet light has been reported (Ref 4).

$$CF_3COOH + NOCl \xrightarrow[h\nu]{} CF_3NO + CO_2 + HCl$$

Extension of this reaction to fluorinated dicarboxylic acids or their monosubstituted derivatives should give carboxy-substituted nitroso compounds or dinitroso compounds.

$$HO_2C(CF_2)_xCO_2H + NOCl \xrightarrow[h\nu]{} HO_2C(CF_2)_xNO + ON(CF_2)_xNO$$

$$RO_2C(CF_2)_xCO_2H + NOCl \xrightarrow[h\nu]{} RO_2C(CF_2)_xNO$$

R = alkyl

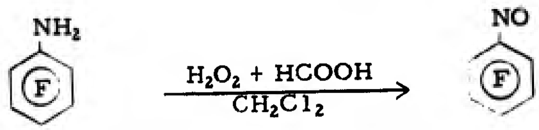
Nitrosyl chloride was bubbled through molten perfluoroglutaric acid in a quartz reaction flask for four hours while being irradiated with a 140 watt external ultraviolet lamp. The system was swept continuously with dry nitrogen. Small amounts of a blue liquid and a green liquid were collected in a Dry Ice-acetone cooled trap. The presence of carbon dioxide in the gases collected in a liquid nitrogen cooled trap indicated that the desired reaction did proceed to some extent. The identities of the blue liquid, which is probably 4-nitrosoperfluorobutyric acid or 1,3-dinitrosoperfluoropropane, and the green liquid, which may be 1-nitroso-3-nitroperfluoropropane, have not been definitely established.

Methyl perfluorosuccinate was chosen as the most readily available fluorinated dicarboxylic acid derivative that would undergo reaction with nitrosyl chloride in the desired manner. The presence of the methyl ester would make the formation of the mono nitroso compound more likely, and the relatively low boiling point of the product would make its isolation more feasible.

In an attempt to prepare methyl perfluorosuccinate, methanol was added to an equimolar amount of perfluorosuccinic anhydride. The isolation of the product included distillation at reduced pressure. The major product obtained was the desired methyl perfluorosuccinate.

The methyl perfluorosuccinate was allowed to react with nitrosyl chloride under irradiation with a 140 watt ultraviolet source. Carbon dioxide was identified among the gaseous products of the reaction. A small amount of blue liquid, whose identity has not yet been established, was obtained. Seventy-eight percent of unreacted starting methyl perfluorosuccinate was also recovered.

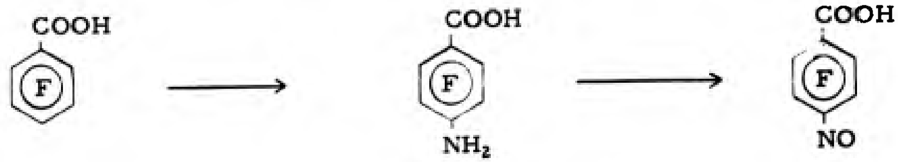
The investigation of carboxy-substituted fluorinated aliphatic nitroso compounds has been extended to the preparation of carboxy-substituted fluoro-aromatic nitroso compounds. Brooke, Burdon, and Tatlow have reported the preparation of pentafluoronitrosobenzene (Ref 8).



Using their procedure of direct oxidation of pentafluoroaniline with 90% hydrogen perioxide and 90% formic acid in methylene chloride solution, 29 gm of pentafluoronitrosobenzene, mp 42^{o}-$44^{o}C$ have been prepared. The bright blue solid has been further purified by recrystallization from ethanol, mp 44^{o}-$44.5^{o}C$. This will be used in copolymerization studies with tetrafluoroethylene and terpolymerization studies with trifluoronitrosomethane and tetrafluoroethylene. Three grams of pentafluoronitrosobenzene, mp 42^{o}-$44^{o}C$, was received from Peninsular Chem Research Company for evaluation.

During the investigation of the oxidation of pentafluoroaniline, it was found that use of 30% hydrogen peroxide in glacial acetic acid, a method used successfully by Holmes and Bayer (Ref 9) for the oxidation of 2, 6-dichloro- and 2, 4, 6-trichloroanilines to the corresponding nitroso compounds, yielded only pentafluoronitrobenzene.

The route chosen for the preparation of p-nitrosotetrafluorobenzoic acid involved the amination of pentafluorobenzoic acid and oxidation of the resulting aminotetrafluorobenzoic acid.



Ammonium pentafluorobenzoate, prepared by passing ammonia into an ether solution of pentafluorobenzoic acid, was treated with sodium amide in liquid ammonia. The pale orange solid isolated from the reaction mixture by acidification and extraction with ether, was identified as p-aminotetrafluorobenzoic acid by its infrared spectrum. This was refluxed with 90% hydrogen peroxide and 90% formic acid in methylene chloride. Although a green color appeared in the methylene chloride solution during reflux and in ether solution during workup, only an orange solid, possibly p-nitrotetrafluorobenzoic acid, was obtained.

Pentafluorobenzoic acid was allowed to react with sodium amide in liquid ammonia; the product is currently being worked up.

One of the fluorinated nitroso monomers that has been chosen for copolymerization with tetrafluoroethylene and terpolymerization with trifluoronitrosomethane and tetrafluoroethylene is nitrosyl fluoride (FNO). The advantages in low temperature properties that may be obtained by incorporation of nitrosyl fluoride into nitroso rubbers is discussed fully in the first quarterly report (Ref 5). During the first report period, nitrosyl fluoride (contaminated with NO_2) had been prepared by pyrolysis of a $NOBF_4$-NaF mixture.

$$NOBF_4 + NaF \xrightarrow{250^{\circ}C} FNO + NaBF_4$$

An improved method of preparation which yields pure nitrosyl fluoride was worked out during this report period. The nitrosyl fluoride was prepared by the decomposition of an $FNO \cdot xHF$ complex (composition unspecified) purchased from Ozark-Mahoning Company. The hydrogen fluoride was removed by passing the complex compound through a 6 ft column containing sodium fluoride at room temperature. Nitrosyl fluoride was obtained in high yield and with only a trace of NO_2. Identity and purity were determined from the infrared spectrum of the product (Figure 2).

PHASE II - POLYMERIZATION STUDIES

Polymerization studies were continued to develop capabilities of producing CF_3NO/C_2F_4 copolymer in 10 to 50 pound quantities per 24 hour period. The trifluoronitosomethane used in these experiments was either prepared in these laboratories (under process development studies) or purchased from Peninsular Chem Research (1 lb). All the tetrafluoroethylene used in this work was prepared in these laboratories. Suspension, bulk and solution polymerizations were investigated during this report period. The suspension polymerization method used was described previously (Ref 6).

Initial supplies of CF_3NO, both from Peninsular and that prepared at Thiokol-RMD, were of low purity with much of the impurity being nitrogen oxides. The first 20 polymerizations resulted in low molecular weight products, presumably due to the presence of impurities, and are not reported in the tables. During this report period it was demonstrated that monomer contaminated with NO_2 inhibits the production of high molecular weight copolymer (Table II). This may be due to either chain transfer or deviation from 1:1 stoichiometry. Most of the NO_2 can be removed by trap to trap distillation during the process of introducing the monomers to the reaction container. As a result of this procedure, higher molecular weight polymer is obtained. The use of purer CF_3NO to begin with also yields higher molecular weight polymer (Table III).

To determine the effect of COF_2 on the polymerization, several different batches of CF_3NO were studied. The results indicate that COF_2 (in the amount present in the CF_3NO) does not inhibit the production of high molecular weight CF_3NO/C_2F_4 copolymer (Table IV).

Several bulk polymerizations were carried out during this report period. The monomers were condensed from a calibrated vacuum rack into a Carius tube which was then sealed and placed in a freezer maintained at -65°C. The bulk mixtures were allowed to react for 30 days. The tubes were then opened, and the product was purified by placing in a vacuum oven for several hours to

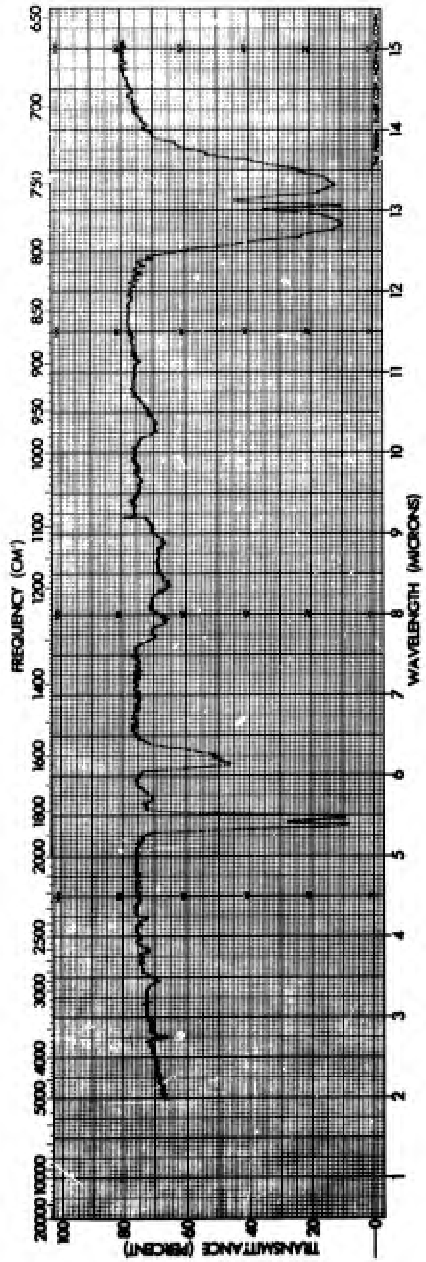


Figure 2. Infrared Spectrum of FNO Prepared at Thiokol

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TABLE II

EFFECT OF NO_2 ON COPOLYMERIZATION OF CF_3NO/C_2F_4

Exp. No.	CF_3NO No.	Type of Reaction	NO_2 (%)	Properties
091-17	855-8	bulk	15.0	viscous liquid
091-16	855-7	bulk	9.3	viscous liquid
091-13	855-6	bulk	4.3	soft gum
091-15	855-7	bulk	purified (1)	gum
091-14	855-6	bulk	purified	gum
092-4	855-7	suspension	9.3	viscous liquid
092-2	855-4	suspension	2.8	gum
092-1	855-4	suspension	purified	gum
092-3	855-6	suspension	purified	gum
092-5	855-7	suspension	purified	gum
092-6	855-8	suspension	purified	gum

(1) Purified by trap to trap distillation

TABLE III

ADDITIONAL COPOLYMERS OF CF_3NO AND C_2F_4

Exp. No.	CF_3NC No.	Polymerization Method	CF_3NO (%)	NO_2 (%)	N_2O (%)	Polymer Properties
088-11	866	bulk	94.5	0.5	5.0	viscous liquid
096	882	bulk	100	---	---	soft gum
095	093-1	suspension	100	trace	---	gum
097-1	882	suspension	100	---	---	gum
097-2[1]	882	suspension	100	---	---	gum
099-1	884	suspension	98[2]	1.0	1.0	soft gum
098	882	solution (CS_2)	100	---	---	viscous liquid

(1) 100 percent pure C_2F_4

(2) Further purified by trap to trap distillation

remove unreacted monomers. The bulk polymerization did not result in higher molecular weights than those obtained in suspension polymerizations using the same monomers (Tables II, III, and VI).

One solution polymerization was run using CS_2 as a solvent. The reaction was carried out in a sealed Carius tube at -25°C for 24 hours with agitation. The resulting product was a viscous liquid (Table III).

The effect of polymerization time on polymer properties was investigated. Initial studies indicate that increased polymerization time may result in higher molecular weight polymer. Stainless steel appears to have no effect on the molecular weight (Table V).

Intrinsic viscosity values (Table VI) have been obtained for several polymers prepared during this report period. Values corresponding to molecular weights between 4×10^5 and 5×10^5 have been obtained for two batches (one bulk and one suspension). Fractionation of the polymer has produced 60% yields of polymer with intrinsic viscosities of 0.70 corresponding to a molecular weight of 8×10^5. These molecular weights are still significantly lower than have been reported in the literature (Ref 4). Infrared spectra of a sample (batch 088-8) of Thiokol-RMD prepared nitroso rubber and a sample of 3M polymer were similar with no obvious differences.

Three small batches of CF_3NO/C_2F_4 copolymer have been prepared for formulation studies to determine the effect of molecular weight of the gum stock on physical properties of the cured polymer.

During this period an attempt was made to prepare copolymer from FNO and C_2F_4.

$$F\text{-}N = O + CF_2 = CF_2 \longrightarrow \text{copolymer.}$$

The reaction was run in a Monel cylinder in bulk at -40°C for ten days. Infrared and mass spectrographic analysis of the resulting mixture identified an array of products including COF_2, NO_2, CF_3NO, C_2F_4, -C=O, and other CF containing materials. No polymer was obtained in this reaction. Varying reaction conditions will be investigated in an attempt to prepare FNO/C_2F_4 copolymer.

PHASE III - PRODUCTION OF NITROSO RUBBER

Construction work has been started at Bristol, Pennsylvania, to provide services in two existing reinforced concrete bays where the nitroso rubber

TABLE IV

EFFECT OF COF_2 ON SUSPENSION COPOLYMERIZATION OF CF_3NO/C_2F_4

Exp. No.	CF_3NO No.	CF_3NO (%)	COF_2 (%)	NO_2 (%)	N_2O (%)	Polymer Properties
092-8	874-4	90.3	0.3	1.1	2.7	gum, fractionated $[\eta] = 0.57$
092-11	876	80.0	0	3.8	2.3	soft gum
092-12	855-6	93.5	0	4.3	2.2	soft gum

TABLE V

SUSPENSION POLYMERIZATION OF CF_3NO AND C_2F_4
(Variables-Time and Container Material)

Exp. No.	CF_3NO No.	NO_2(%)	Reaction Time (hr)	Polymer Properties
100-3	889	0	43	soft gum (stainless steel cylinder)
100-4	855-7	purified [1]	43	soft gum (glass)
100-5	855-6	purified	48	soft gum (glass)
100-1	855-6	purified	72	gum (glass)

---

(1) Purified by trap to trap distillation

TABLE VI

INTRINSIC VISCOSITIES OF CF_3NO/C_2F_4 COPOLYMERS

Exp. No.	CF_3NO No.	Polymerization Method	NO_2(%)	Intrinsic Viscosity
088-7	855-3	bulk	2.0	0.4
088-8	855-3	bulk	2.0	0.23 0.50 fractionated
090-7	855-3	suspension	purified[1]	0.2
092-5	855-7	suspension	purified	0.46
092-8	874-4	suspension	1.1	0.57 fractionated
100-1	855-6	suspension	purified	0.36
051	894	suspension 72 hr	0	0.70 fractionated

(1) Purified by trap to trap distillation.

production will be conducted. Each bay measures about 6-1/2 x 7 x 11 feet high in which the glass monomer production equipment and the 25 gallon polymerization reactor will be housed.

A circulating brine system cooled by direct injection of CO_2 will furnish refrigeration for the polymerization and necessary cold traps. The Liquid Carbonic Division has furnished a six ton unit which has been installed and piped up to a 100 gallon brine tank equipped with a stainless steel 7-1/2 hp brine pump. A 12 kw oil heating system has been delivered and will be piped up to the pyrolysis unit (Figure 5).

The reaction vessels and condenser shown in Figures 3,5, and 7 have been purchased and should be delivered between mid-January and the first of February. A 25 gallon stainless steel polymerization reactor is on order and should be delivered by mid-February.

Production of CF_3NO should start about 1 March 1964. Tetrafluoroethylene monomer will be produced as required by treating tetrafluorodibromoethane (Freon 114B2) with zinc dust. The material and equipment flow sheets (Figures 3-10) summarize the proposed reaction schemes.

PHASE IV - COMPOUNDING AND CURING STUDIES

The objective of this phase of work is to establish by formulation studies the best methods of realizing the unusual properties of nitroso rubber. Compounding and curing studies are scheduled to begin as soon as a sufficient quantity of polymer is available.

PHASE V - FABRICATION

The objectives of this phase of work are: (1) to conduct studies toward developing specific compounds of nitroso rubber that can be used in extrusions, moldings and proofed goods and (2) to produce gaskets, reinforced hose and coated fabric. This phase is scheduled to begin around August 1964.

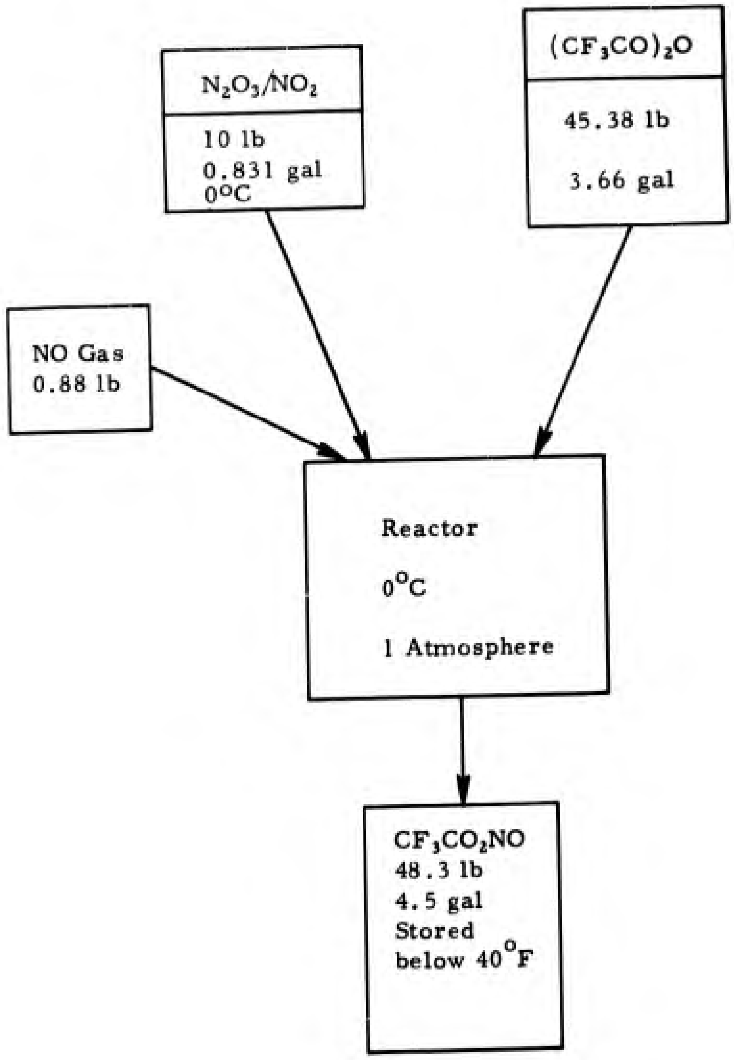

Figure 3. Material Flow Chart of CF_3COONO Production

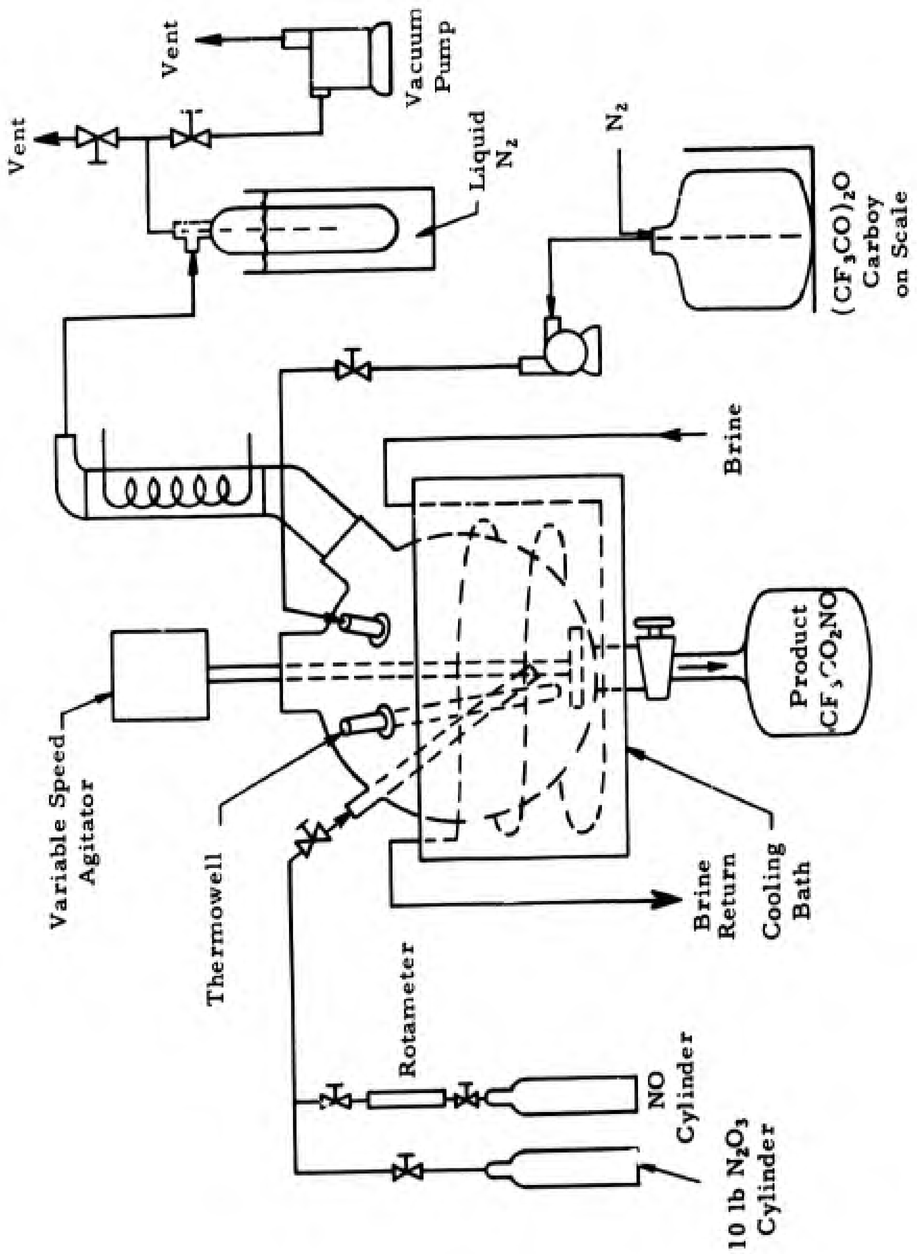

Figure 4. Equipment Flow Chart for CF_3COONO Production

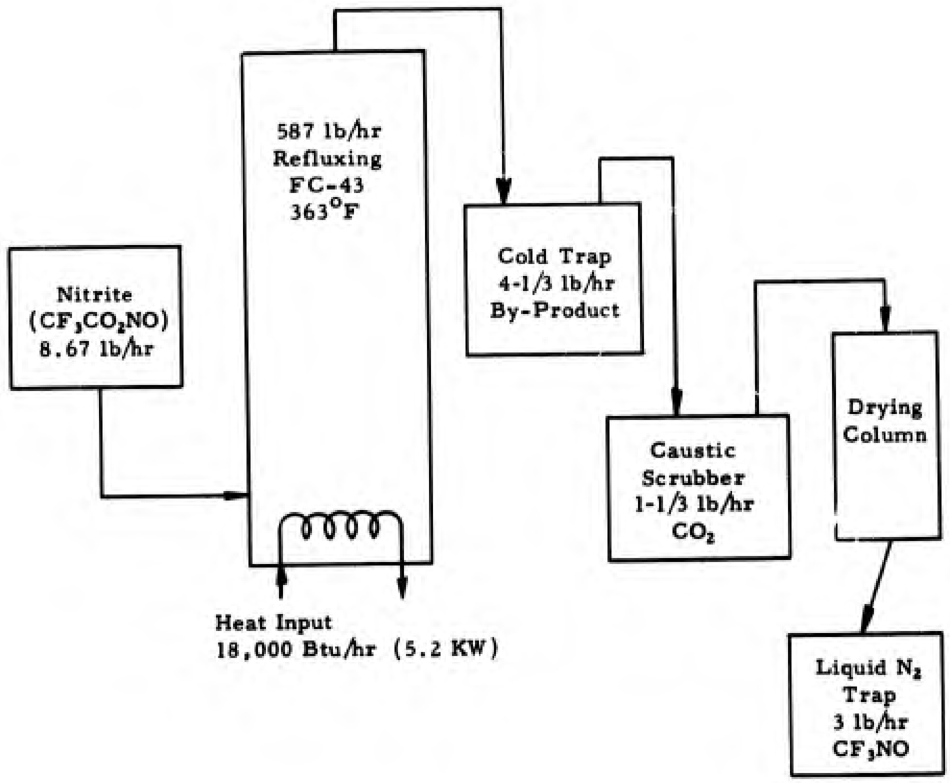

Figure 5. Material Flow Chart for CF_3NO Production

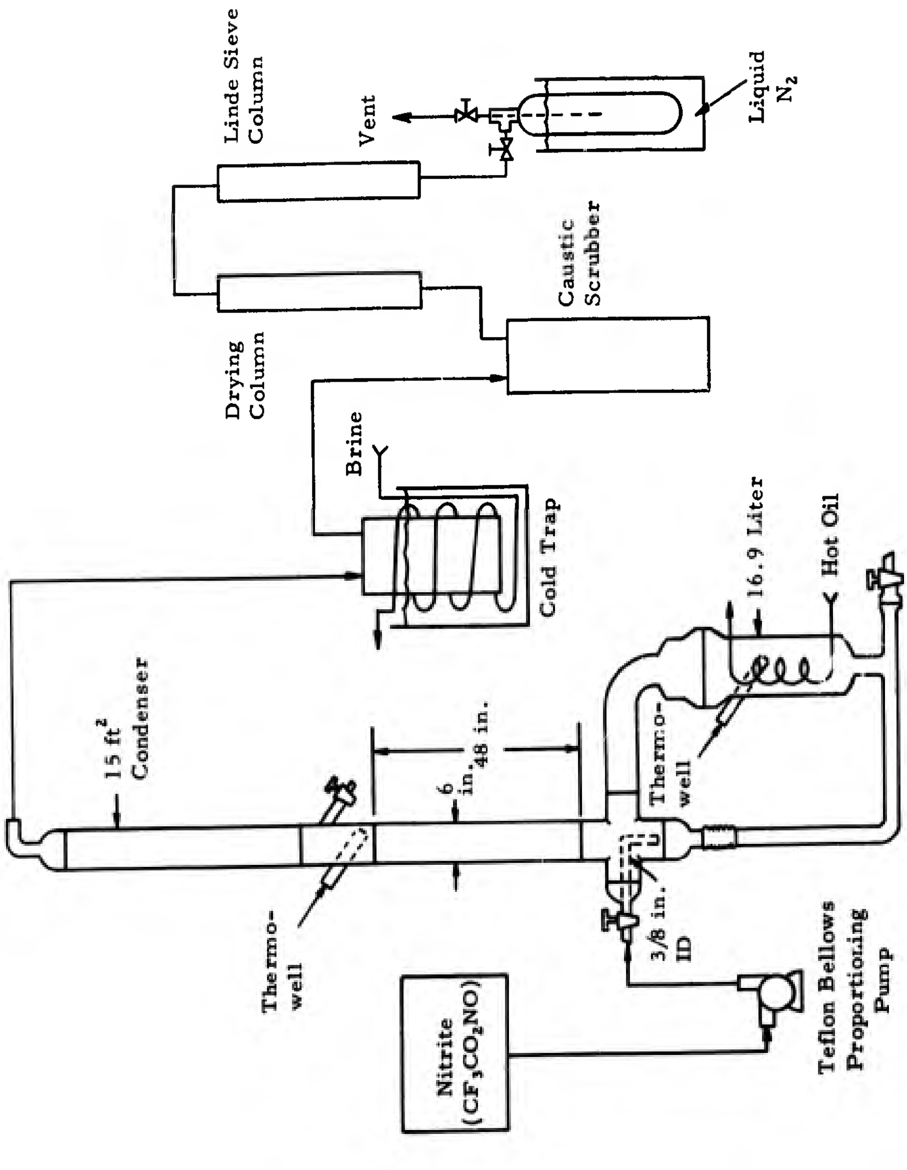

Figure 6. Equipment Flow Chart for CF_3NO Production

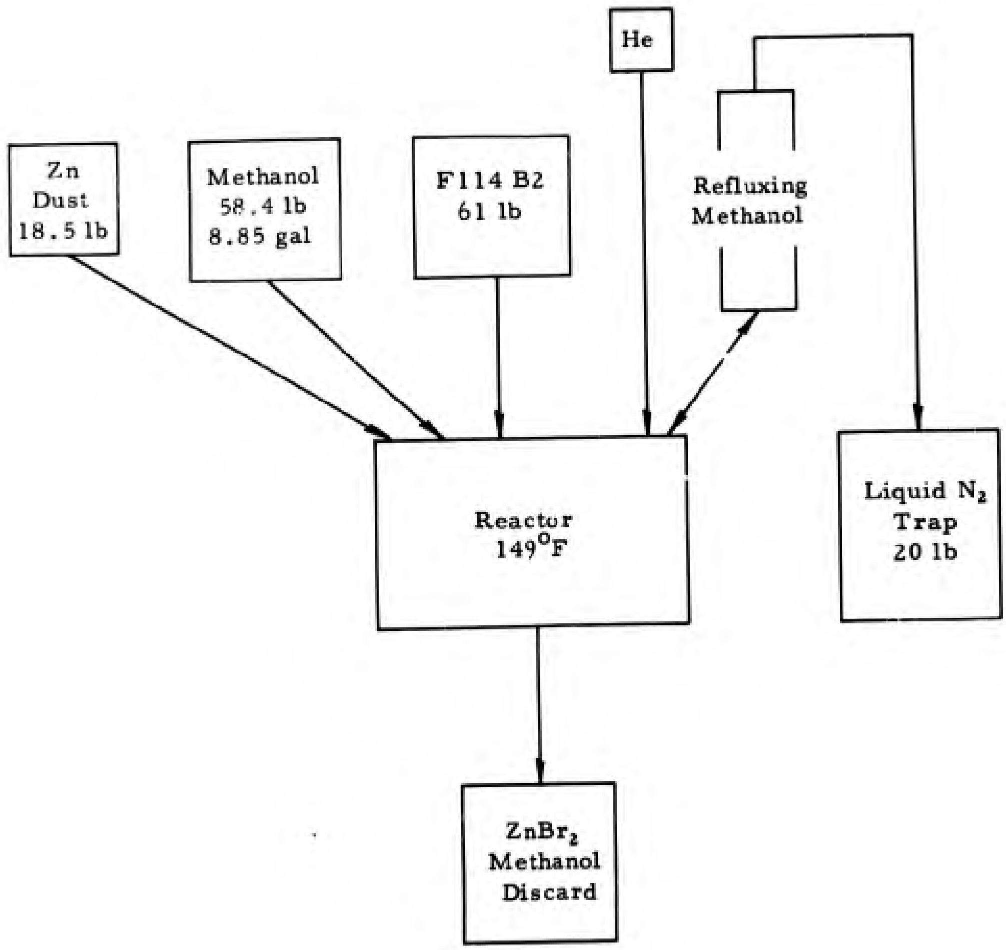

Figure 7. Material Flow Chart for C_2F_4 Production

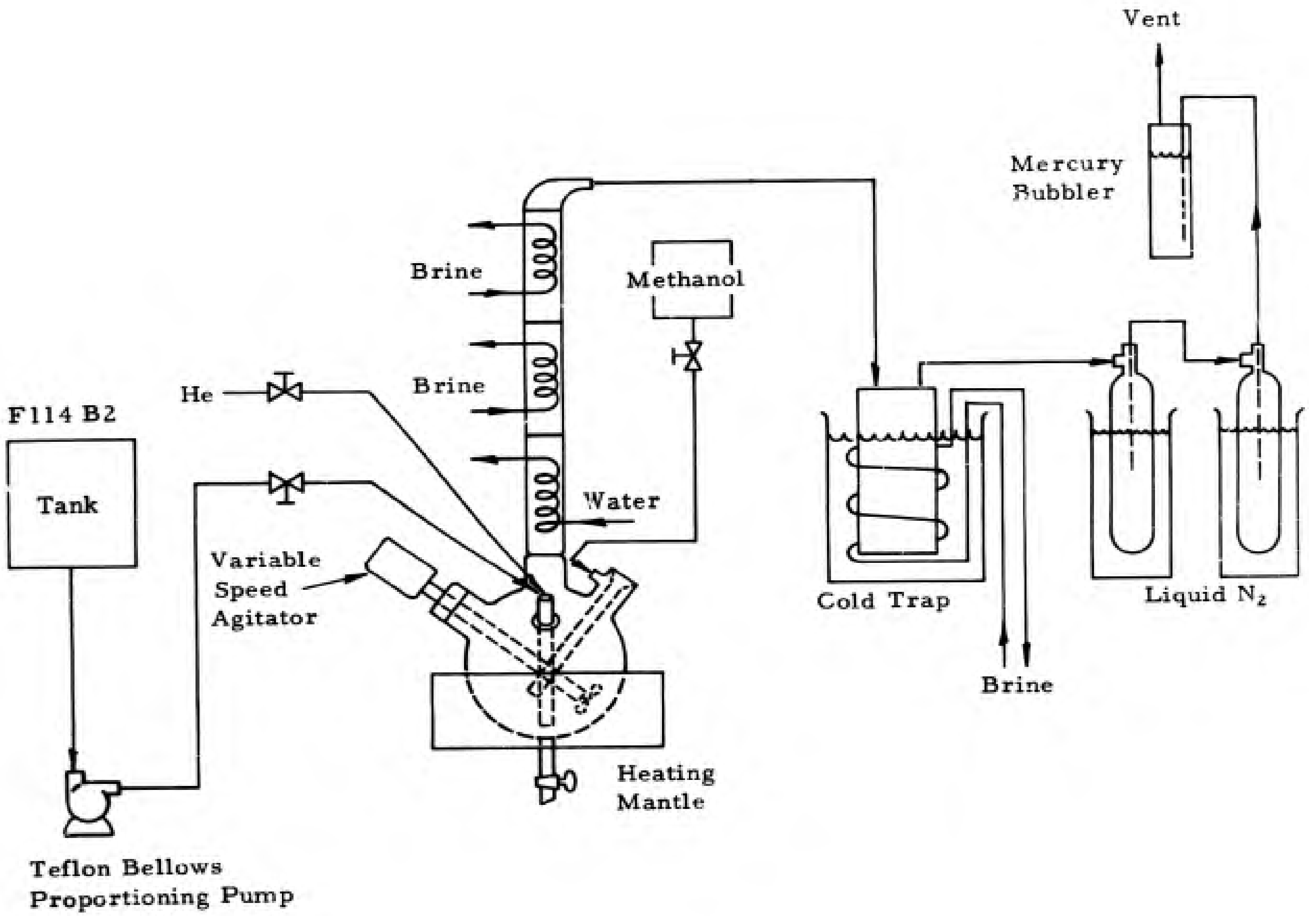

Figure 8. Equipment Flow Chart for C_2F_4 Production

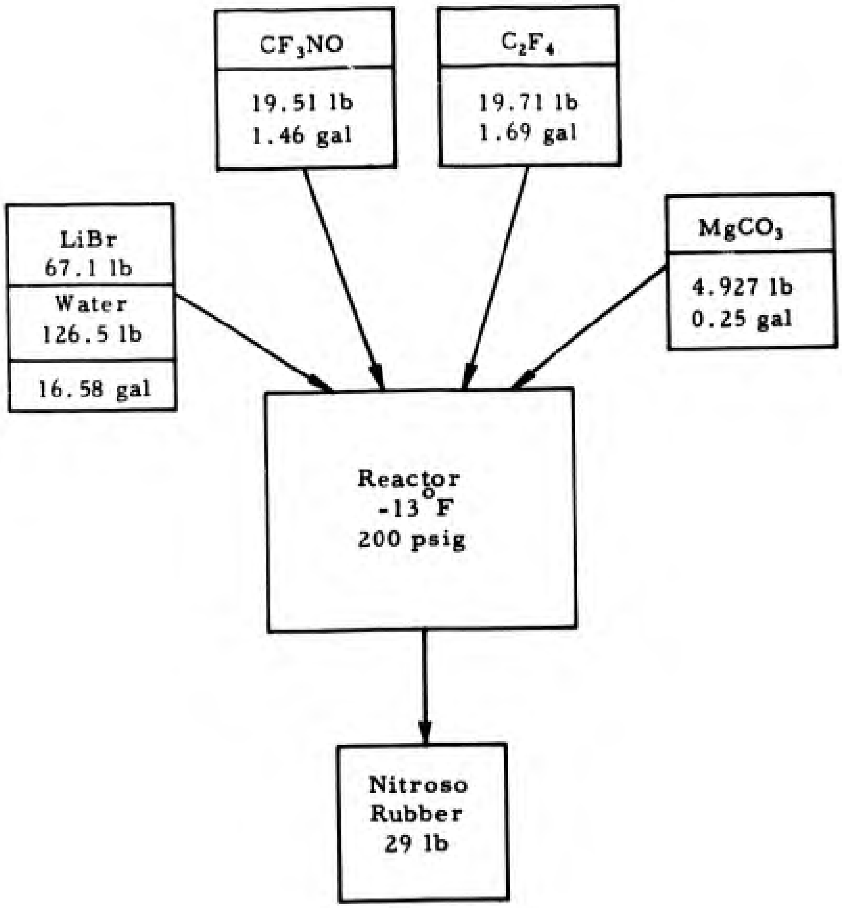

Figure 9. Material Flow Chart for Nitroso Rubber Production

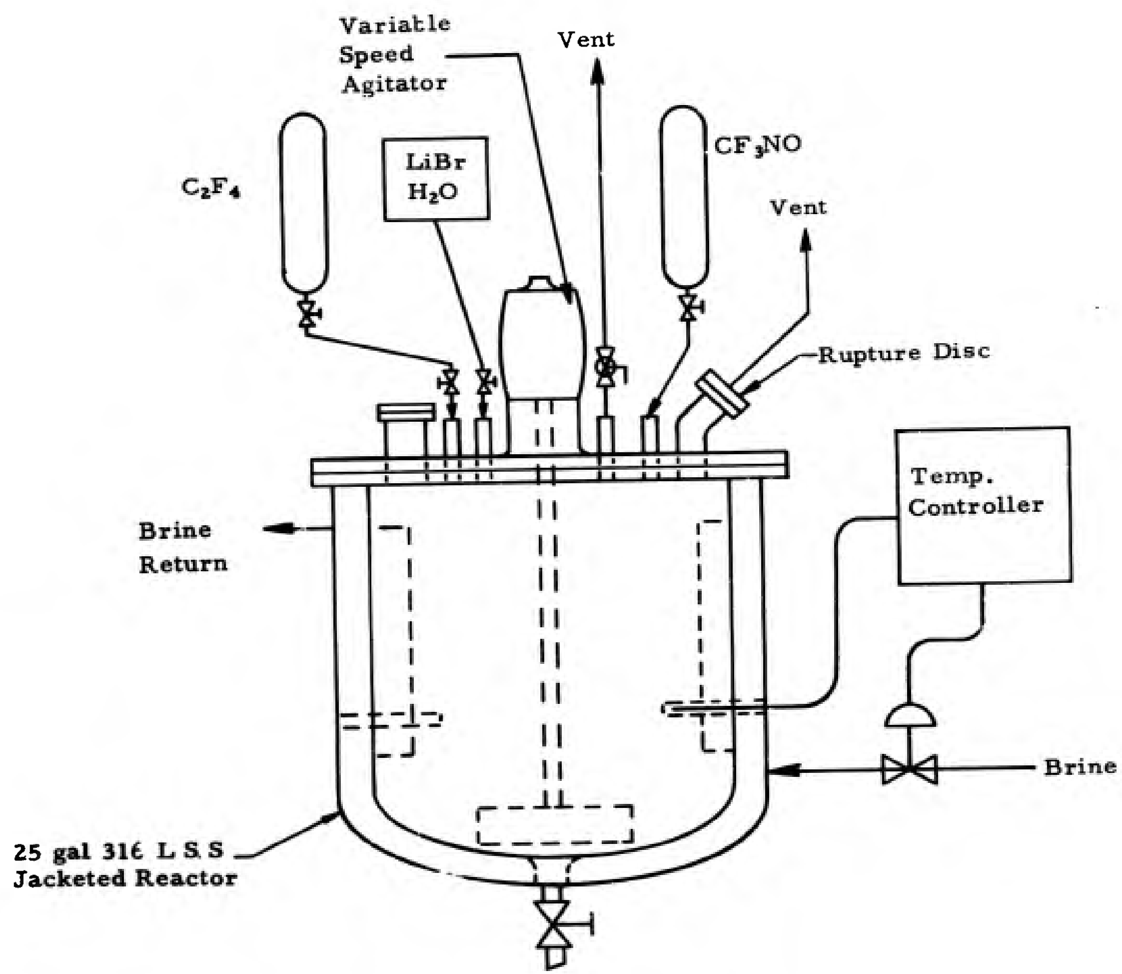

Figure 10. Equipment Flow Chart for Nitroso Rubber Production

III. SUMMARY

1. A total of 700 gm of trifluoroacetyl nitrite was prepared during this report period with the largest batch yielding 231 gm of product. "As received" trifluoroacetic anhydride was used.

2. Sparking tests indicate that dilution of the CF_3CO_2NO vapors by FC-43 has resulted in a process which can be operated without undue hazard.

3. Additional detonation testing of CF_3CO_2NO showed that the detonation did not propagate when the nitrite was confined in stainless steel tubing 11/16 in. ID.

4. A total of 114 gm of CF_3NO was prepared in 17 batches during this report period. Of this quantity, 69 gm were of 98.5% or greater purity.

5. Successful purification of CF_3NO was achieved through the use of water and 5% caustic scrubbers to remove the bulk of the nitrogen oxides and CO_2 followed by a cold (-80 to -100°C) molecular sieve column to remove the last trace of impurities.

6. Approximately 125 gm of tetrafluoroethylene of greater than 98% purity was prepared to date; the impurities are C_2F_6 and C_3F_8.

7. Attempts to prepare carboxy-substituted fluorinated aliphatic nitroso compounds were unsuccessful.

8. Approximately 30 gm of pentafluoronitrosobenzene have been prepared.

9. Polymerization studies indicated that nitrogen oxide impurities in CF_3NO inhibit the formation of high molecular weight polymers.

10. CF_3NO/C_2F_4 copolymers were prepared with intrinsic viscosities of 0.70.

11. Construction of the production facility has been started at Bristol, Pennsylvania.

12. Monomer and polymer production equipment has been placed on order.

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