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QMC Project No. 7X93-15-004

Report:

Trenton RD-343-Q1

RMD 8576-Q1

Report Period:

27 Feb to 31 May 1963

NITROSO RUBBER

RESEARCH
DEVELOPMENT
And
PRODUCTION

CHEMICAL CORPORATION
CHEMICAL OPERATIONS TRENTON, NEW JERSEY

Thiokol® CHEMICAL CORPORATION

NITROSO RUBBER
RESEARCH, DEVELOPMENT AND PRODUCTION

Report: Trenton RD-343-Q1 and RMD 8576-Q1

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Report Period: 27 February 1963 - 31 May 1963

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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 27 February through 31 May 1963. The overall project leader is Dr. Marvin 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, Mr. Francis McPeek and Dr. Stanley Tannenbaum at Denville and Messrs. Robert Hoffman and Malcolm Reynolds at Trenton.

ABSTRACT

The preparation of trifluoroacetyl nitrite by the interaction of trifluoroacetic anhydride and dinitrogen trioxide has been effected by replicate, small scale batches. Exploratory solution pyrolyses of the nitrite indicate that decarboxylation occurs at temperatures of 145°C or greater. Trifluoronitrosomethane was the major product. Small quantities of nitrosyl fluoride (FNO), for the synthesis of improved low temperature nitroso rubbers, were prepared by pyrolysis of nitrosyl tetrafluoroborate ($NOBF_4$) and sodium fluoride at 250°C.

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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 $-51^{\circ}C$; 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 carboxyl groups; 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 $-40^{\circ}F$) still fall short of the desired serviceability (utility at $-100^{\circ}F$) 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 & D program to meet these goals:

(I) Monomer Synthesis and Scaleup

(II) Polymer Synthesis and Scaleup

(III) Polymer Production

(IV) Compounding Studies

(V) Fabrication

Conferences were held with Minnesota Mining and Manufacturing Co. and Professor J. D. Park, University of Colorado, to gather detailed technical and safety information not normally found in technical reports. The conferences were highly informative with a free exchange of information. Personnel at 3M made the following recommendations to Thiokol, based on their extensive experience with nitroso rubber:

(1) Preparation of trifluoronitrosomethane (CF_3NO) by the vapor phase pyrolysis, liquid phase pyrolysis or by photolysis of trifluoroacetyl nitrite was not recommended for large scale production.

(2) The preparation of acid modified terpolymer was recommended because of its superior properties. Only gram quantities of acid nitroso monomer have been prepared by a cumbersome, low yield reaction which is not amenable to scaleup. The only method currently available for preparing the terpolymer is by low temperature bulk polymerization.

(3) Prepare the 700 pounds of polymer required by Natick-QM by bulk polymerization (30 days at -65°C) in small batches.

The most immediate problems on the program are to develop practical procedures for production of CF_3NO and for copolymerization of CF_3NO with C_2F_4. Three paths are possible for attaining nitroso monomer scaleup:

(1) Develop a new route to CF_3NO which bypasses the trifluoroacetyl nitrite route.

(2) Develop an improved procedure for decomposition of CF_3CO_2NO.

(3) Develop another nitroso comonomer which eliminates the requirement for CF_3NO.

It is obvious that pursuit of (1) and/or (3) will be longer range than (2). Hence, the major laboratory effort during this report period was expended in process development studies for the preparation of trifluoroacetyl nitrite and exploratory solution pyrolyses to trifluoronitrosomethane. Concurrent with this work, analytical procedures and techniques have been established. To initiate polymerization studies as soon as possible, one pound of trifluoronitrosomethane has been ordered from Peninsular ChemResearch, Inc. for delivery June 1. The preparation of new nitroso monomers has been initiated by investigating the synthesis of nitrosyl fluoride, FNO.

II. TECHNICAL WORK

PHASE I - MONOMER SYNTHESIS

Task 1 - Process Development for Trifluoronitrosomethane (CF_3NO)

The objective of this task is to develop the capability of producing nitroso monomers such as CF_3NO in quantities of 10 to 50 pounds per 24 hour period. The preparation of CF_3NO has been effected by several reactions, most of which can be excluded as production methods because of low yields, expensive starting materials, and difficult processing. The currently preferred route for CF_3NO preparation is through the formation and decarboxylation of trifluoroacetyl nitrite (CF_3CO_2NO) (Ref 5).

The trifluoroacetyl nitrite can be prepared by the interaction of trifluoroacetic anhydride $[(CF_3CO)_2O]$ with either dinitrogen trioxide (N_2O_3) or with nitrosyl chloride (NOCl) (Ref 5, 6).

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

$$(CF_3CO)_2O + NOCl \longrightarrow CF_3CO_2NO + \text{byproducts}$$

The first of these reactions is preferred because of superior yields and is effected by mixing the two starting materials at temperatures between -10^o and 25^oC using autogenous pressure or a reflux condenser to maintain the N_2O_3 in the liquid state (Ref 6).

The CF_3CO_2NO can be decarboxylated by either pyrolysis or photolysis. For processing reasons, pyrolysis is the preferred route for all but small-scale reactions. Concomitant with process development studies, an analytical development program must be conducted so that analytical methods for starting materials and products can be found and material specifications established.

A. PREPARATION OF TRIFLUOROACETYL NITRITE

Based upon a survey of the literature and discussions with personnel at Minnesota Mining and Manufacturing Co., a decision was made to concentrate on the interaction of $(CF_3CO)_2O$ and N_2O_3 as the best known method for CF_3CO_2NO preparation. Although other potential routes may be investigated, the bulk of the process development will be concerned with this reaction as a matter of expediency.

Although this reaction has been successfully replicated, production at the scale required for this program has not been attempted. Therefore, a developmental program is required to define the process variables, to determine the degree of hazard and to develop a process (including equipment design) which can be successfully operated at the required level.

Both starting materials are volatile (bp of N_2O_3 = 3.5°C, of $(CF_3CO)_2O$ = 39°C) so that the use of conventional flasks and condensers could result in significant material losses during charge and reaction. In addition, N_2O_3 will dissociate into NO and NO_2 except at very low temperatures and NO boils at -151°C. For these reasons, a vacuum rack was designed and constructed for these operations. Through use of this rack, it is possible to quantitatively transfer weighed charges of the starting materials, follow the course of the reaction by monitoring pressure changes, and then fractionate and transfer the product, CF_3CO_2NO. These techniques also eliminate exposure of the starting materials or product to oxygen or moisture, both deleterious.

A series of reactions have now been completed which served to define the conditions required for efficient processing and to prepare CF_3CO_2NO for analytical and processing studies.

The $(CF_3CO)_2O$ used in these experiments was obtained from Peninsular ChemResearch, Inc. As a routine procedure the anhydride was rectified before use. The column used had an estimated 15 theoretical plates; the fraction boiling between 39° and 39.5°C was taken and stored under dry nitrogen. After precision analytical techniques have been developed for the assay of this anhydride, it will be possible to accurately determine its rate of hydrolysis and the conditions required for its storage and handling as well as the determination of the effect of CF_3CO_2H on subsequent reactions. The vapor pressure of $(CF_3CO)_2O$ was determined and was found to conform to the equation $\log P = \frac{-2096.8}{T} + 9.753$. The $(CF_3CO)_2O$ vapor pressure curve is reproduced as Figure 1.

The dinitrogen trioxide was obtained from the Matheson Company, Inc., and used as received. The liquid phase in the cylinder was sampled at 0°C

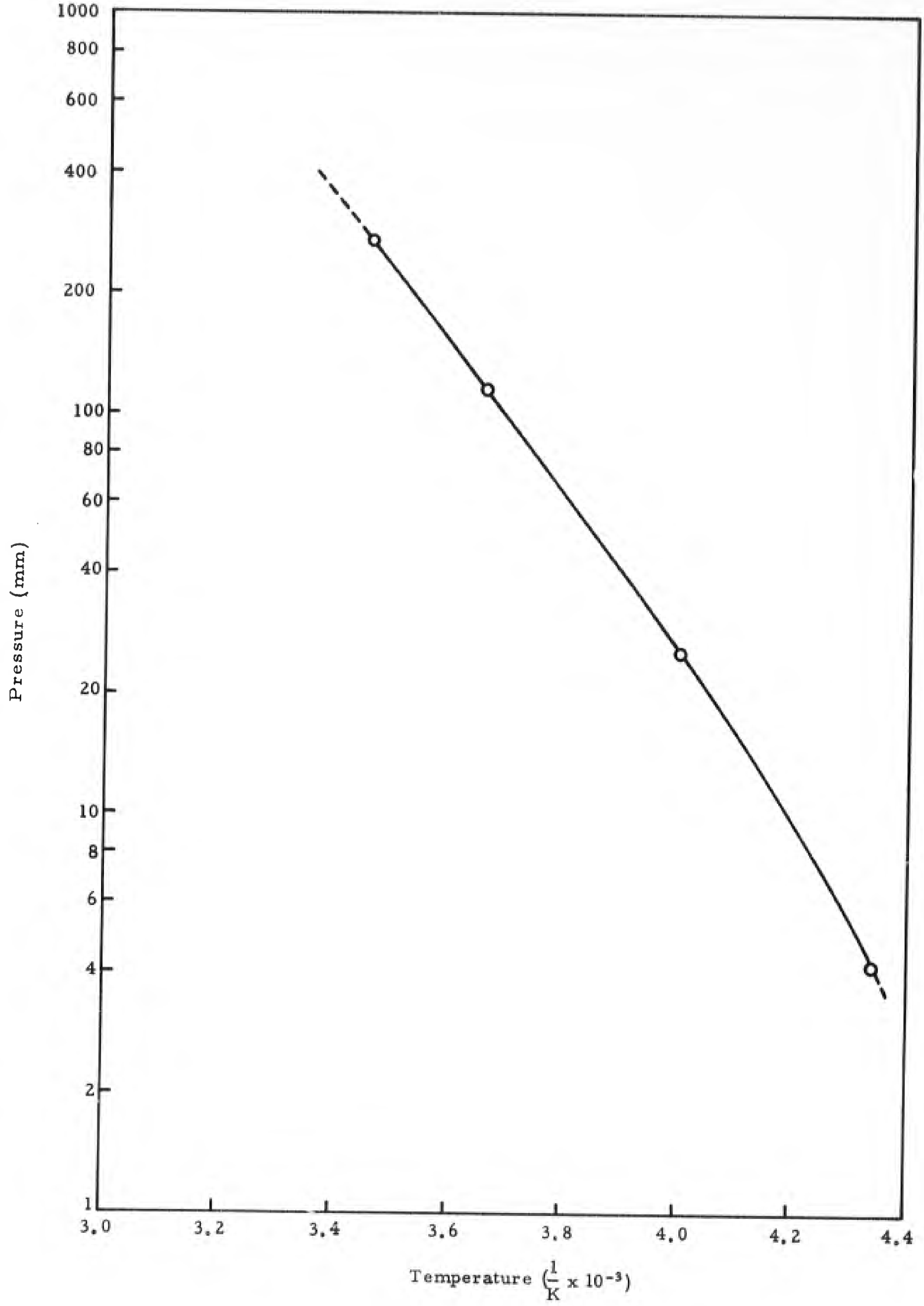


Figure 1. Vapor Pressure of Trifluoroacetic Anhydride

and allowed to dissociate into NO and NO_2 at room temperature. This mixture was found by mass spectral analysis to contain 43.2 percent NO and 56.8 percent NO_2, equivalent to 86.4 percent N_2O_3. The vapor phase in the cylinder is correspondingly rich in NO.

In the initial reactions equimolar quantities of the starting materials were transferred to a flask by condensation at liquid nitrogen temperature, then allowed to interact at 0°C with agitation. It was observed that NO left the reaction zone and that the product was contaminated with NO_2. This effect was confirmed by personnel at 3M who also indicated that NO_2 is quite soluble in the product and is difficult to remove. NO_2 is undesirable in the reaction mixture because of the conversion of the nitrite to the nitrate ($CF_3CO_2NO + NO_2 \longrightarrow CF_3CO_2NO_2$ + N In subsequent experiments NO was bubbled through the reaction mixture to convert the excess NO_2 to N_2O_3 and $(CF_3CO)_2O$ was charged in excess.

In a typical experiment, 3.55 g of N_2O_3/NO_2 (3.07 g, 0.04 mole of N_2O_3) and 14.6 g (0.07 mole) of $(CF_3CO)_2O$ were transferred *in vacuo* to a round bottomed flask, warmed to 0°C, and stirred until the color of the flask contents changed from blue to amber (20 minutes); NO was then slowly bubbled through the reaction mixture (amber to green) for 1.5 hours. An additional 1.5 g of anhydride was added and, in 20 minutes, the color returned to amber. The mixture was cooled to -21°C, and pumped on at less than 1 Torr for 30 minutes to remove the unreacted $(CF_3CO)_2O$ and nitrogen oxides. The residue was a light amber color which was identified by infrared analysis as the desired CF_3CO_2NO. The infrared spectrum of this material was equivalent to that of the reference obtained from 3M and Professor Park at the University of Colorado. The product yield 19.0 g (0.143 mole), was 90.8% of theory based on total anhydride charged. Total production to date has been 75 g. The process can now be scaled up to the laboratory production of 100 g/day. These preparations will be continued to supply product for conversion to CF_3NO, for development of analytical procedures, and for process development and safety evaluation.

B. SAFETY EVALUATION OF TRIFLUOROACETYL NITRITE

The literature indicates that under certain ill-defined conditions CF_3CO_2NO tends to detonate. Before scaleup to the multi-pound level can be considered it is necessary to quantitatively define the hazards related to preparing, handling and pyrolyzing the nitrite.

The explosive and rocket industries have developed many procedures for evaluation of potentially hazardous materials. Both the art and science of those skilled in these safety tests have been made available to this program. Trauzl block and modified card gap tests on trifluoroacetyl nitrite were initiated during this report period.

1. Trauzl Block Testing

The RMD Trauzl block test is a small-scale version of an explosives test (Ref 7) involving the initiation by detonation of a test sample in a lead cylinder. The RMD version employs a 2 1/2 in. x 2 in. lead cylinder with a cavity 1 in. in diameter and 2 in. deep. Between 1 and 3 grams of explosive are placed in the cavity along with a No. 8 blasting cap used as the initiation source. An indication of initiation and a qualitative estimate of the explosive power is obtained from the amount of deformation experienced by the lead cylinder. This deformation is reported in terms of the increased volume of the cylinder in units of cc per gram of explosive. An example of the type of results obtained with conventional explosives and reference standards is shown in Table I. The technique has proved most convenient in cases where the availability of material is limited and in cases where the test material is very volatile. In the latter case the samples are sealed into glass vials before transfer to the lead cylinder.

TABLE I

TRAUZL BLOCK RESULTS OF REFERENCE MATERIALS

Explosive	Expansion* (cc/g)
RDX	30
TNT	5
Nitroglycerine	30
Nitromethane	5
Nitromethane-Tetranitromethane mixture	22

---

*Expansion beyond that produced by No. 8 blasting cap.

Trifluoroacetyl nitrite was initiated by a No. 8 blasting cap in the Trauzl block test and the results are shown in Table II. These data indicate that the liquid does detonate, although the detonation is not very brisant.

TABLE II

TRAUZL BLOCK RESULTS OF CF_3CO_2NO

Sample Size (g)	No. of Tests	Expansion (cc/g)
1	2	3
3	2	5.7

2. Modified Card Gap Testing

Detonation testing of CF_3CO_2NO in 10 in. x 1/4 in. stainless steel tubes has been initiated, but the results are as yet too preliminary to be meaningful. The tests are designed to establish the following:

(1) whether the shock wave of a 50 g tetryl charge can be propagated by the trifluoroacetyl nitrite

(2) the sensitivity of the nitrite to such propagation

(3) the velocity of the propagation

(4) the critical diameter of the tube, i.e., the diameter below which the nitrite will not propagate the shock wave.

Further safety testing is planned to establish explosive limits of CF_3CO_2NO solvent mixtures as well as CF_3CO_2NO (g)/N_2 and CF_3CO_2NO (g)/CO_2 mixtures.

C. PREPARATION OF TRIFLUORONITROSOMETHANE

Concomitant with the CF_3CO_2NO studies, the preparation of CF_3NO and the development of improved processing methods have been initiated. The preparation of CF_3NO from CF_3CO_2NO has been effected by both photolysis and pyrolysis reaction, but both methods (at least in the current state of the art) have serious shortcomings. Photolysis, in general, will present greater processing difficulties and the decision has been made to concentrate on a pyrolysis method for the sake of expediency.

A vapor phase pyrolysis method has been developed at 3M (Ref 6) but 3M found the pyrolysis tube length/diameter ratio to be optimum at 840/1. This ratio is very large, and the design of equipment for efficient and safe operation at a reasonable scale is very difficult. Over and above the problem of the 840/1 L/D ratio, the detonability of the nitrite is a matter of concern. It seemed probable that the tendency for CF_3CO_2NO to detonate could be modified by dilution and that a solution pyrolysis could be operated with a minimum of equipment and control. Accordingly, a search was made for a high boiling ($>150^{\circ}C$), inert solvent for CF_3CO_2NO. Such a solvent may be FC-43, a 3M product consisting of isomers of $(C_4F_9)_3N$. FC-43 has a boiling point of 180°C at atmospheric pressure; thus, superheating of the CF_3CO_2NO cannot occur.

Several preliminary pyrolyses have been completed using FC-43 solutions of CF_3CO_2NO. These experiments were designed to determine the applicability of this approach and to determine the temperature range required. The first technique used involved heating the solution at a constantly increasing temperature and observing the change in pressure as a function of temperature. This was accomplished by maintaining the reactor at atmospheric pressure and allowing any generated gases to bleed into a calibrated, previously evacuated volume. The pressure in this volume was measured and plotted as a function of the reactor temperature. A blank run with FC-43 alone served to establish the contribution of the solvent to the change in pressure. A heating rate of 2.8°C/minute was used and a reactor temperature of 80°C was chosen as the point at which the pressure change was zero. Volume limitation of the system dictated the use of small quantities of CF_3CO_2NO.

The data (Figure 2) indicate that a significant increase in the rate of reaction occurs at about 140°C; CF_3NO was first observed visually at about 145°C. The products of this reaction were collected and sampled for mass spectroscopic analysis. Major constituents were identified as CF_3NO, CO_2, and NO_2. Small amounts of NO, CF_4 and COF_2 were also present as well as traces of as yet unidentified materials. As soon as the mass spectrometer is calibrated for these materials, it will be possible to obtain quantitative data for each experiment.

In other experiments, the pressure change resulting from the decomposition of CF_3CO_2NO was measured under isothermal conditions. The data obtained from two such experiments (at 130-132°C and 114-116°C) are shown in Figure 3.

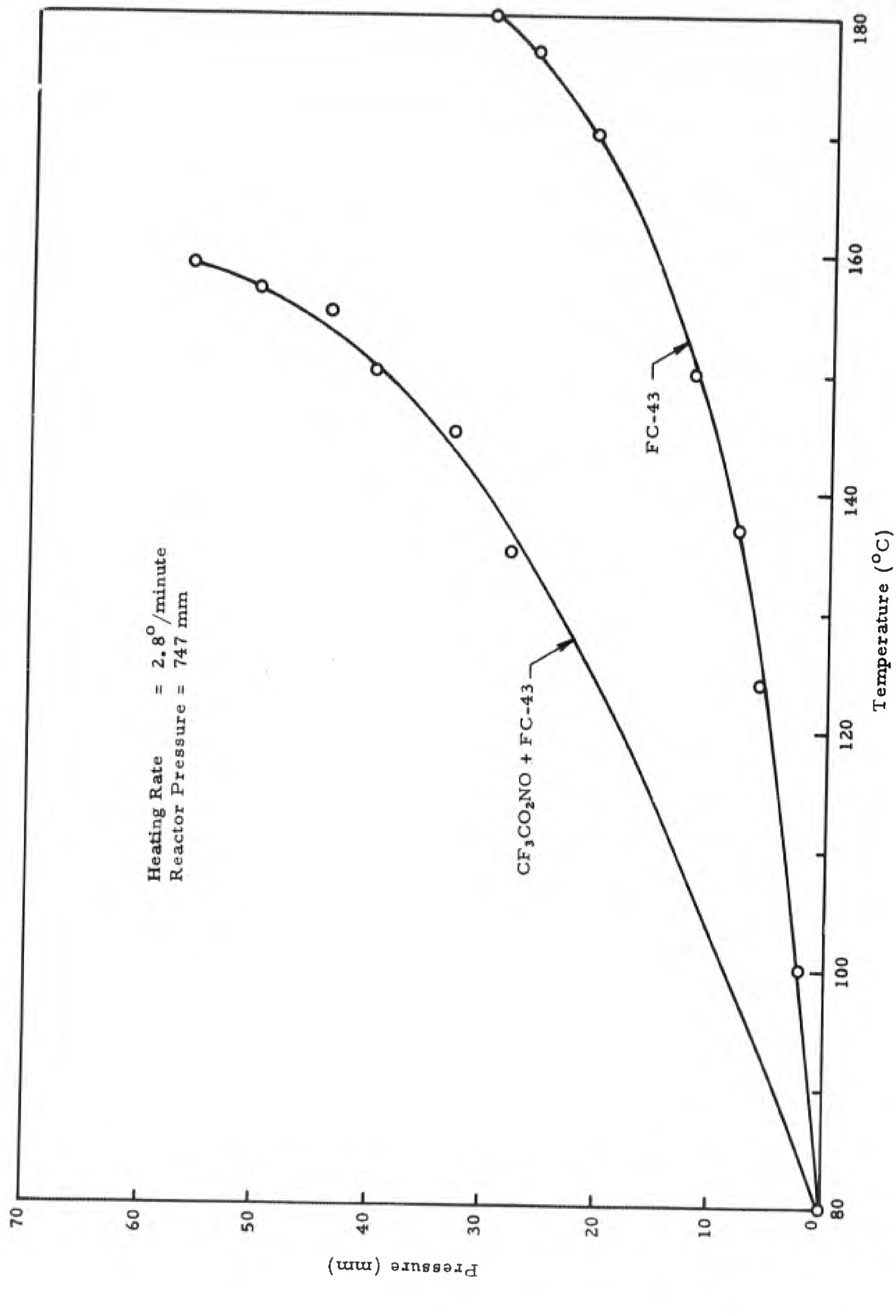


Figure 2. Pressure Change with Increasing Temperature, CF_3CO_2NO/FC-43

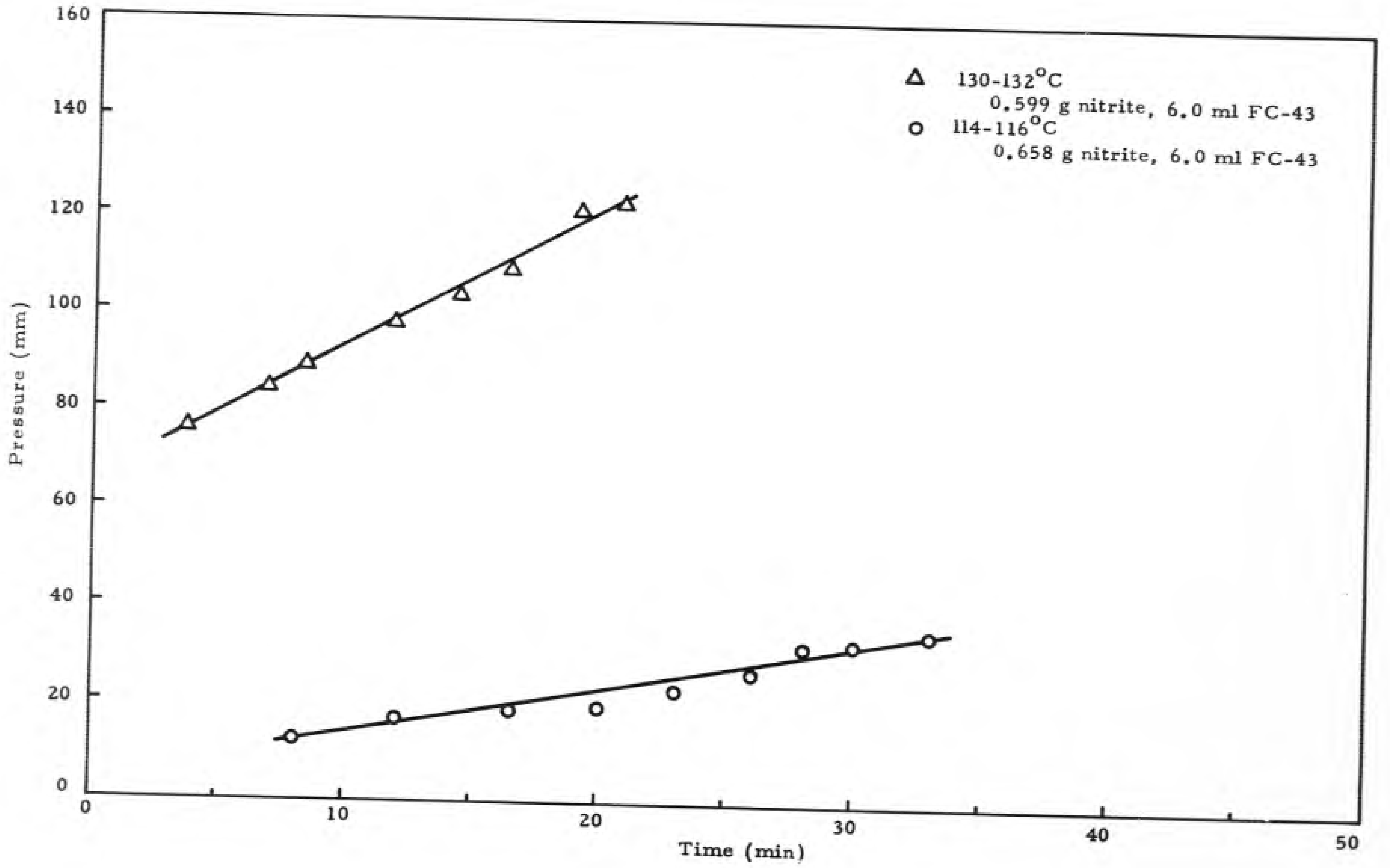


Figure 3. Pyrolysis of CF_3CO_2NO in FC-43

Experiments at higher temperature, e.g., 140°C, could not be maintained at an initial pressure high enough to preclude CF_3CO_2NO reflux.

The apparatus used for these experiments has volume limitations and is not suitable for the bench scale preparation of CF_3NO. Another apparatus is being constructed for this purpose and will be put into operation as soon as data have been obtained on the detonability of FC-43/CF_3CO_2NO mixtures. It would also be desirable to pursue alternate routes to CF_3NO which completely bypass the acetyl nitrite route and such studies have been initiated.

Task 2 - Preparation of Tetrafluoroethylene (C_2F_4)

The objective of this task is to prepare or procure sufficient tetrafluoroethylene initially for research studies and then for polymer production.

Tetrafluoroethylene has been found to be unavailable in small quantities at the present time, but large quantities will be made available when required for the later phases of the program. The amounts required for the initial polymer development tasks will be prepared by the debromination of tetrafluorodibromoethane, Freon 114-B2.

$$CF_2Br\text{-}CF_2Br + Zn \xrightarrow[\Delta]{CH_3OH} CF_2{=}CF_2 \uparrow + ZnBr_2$$

An apparatus for this reaction has been assembled.

Task 3 - New Nitroso Monomers

The objective of the task is to investigate the preparation of new fluorinated nitroso monomers for improved low temperature properties of nitroso rubbers and also to prepare fluorinated nitroso monomers that contain functional groups capable of acting as cross-linking sites for the vulcanization of the nitroso rubber.

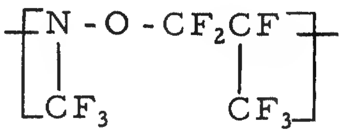
Since low temperature serviceability is one of the prime objectives of this program the glass transition temperatures (Tg) of various nitroso rubbers were analyzed. The Tg (in °K) for an amorphous polymer can be predicted approximately if the glass transition temperatures, Tg_1 and Tg_2, of both homopolymers are known. One of the empirical formulas that has been found to apply fairly well in many cases is:

$$1/Tg = \frac{w_1}{Tg_1} + \frac{w_2}{Tg_2}$$

where w_1 and w_2 are the weight fractions of each of the components of the copolymer. This formula can be extended to terpolymers.

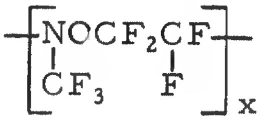
To demonstrate the validity of this equation in the nitroso-fluorocarbon polymer system, the Tg of the theoretical homopolymer $\left[\underset{CF_3}{\underset{|}{NO}}\right]$ was calculated using the experimental data for the polymers CF_3NO/CF_2CF_2 and $CF_3NO/CF_2CF(CF_3)$ and the literature values of 80°C for $\left[CF_2CF_2\right]_x$ and 165° for $\left[CF_2CF(CF_3)\right]_x$. The Tg values thus obtained for $\left[CF_3NO\right]_x$ were -111° and -108°C. These data are in excellent agreement indicating the validity of this equation for the polymer systems under discussion. As a result this equation was used to obtain approximate Tg data for the new systems.

The Tg of CF_3NO/CF_2CF_2 has been reported as -51°C and the experimental results show that increasing the length of the nitroso-fluorocarbon side chain has a comparatively small effect. Copolymerization of CF_3NO with fluorocarbon olefins containing pendant fluorocarbon groups results in polymers of higher Tg, presumably due to interference of the two pendant groups in rotation around the polymer backbone. This effect has been adequately demonstrated with the polyacrylates. Side chain branching increases the bulk of the polymer close

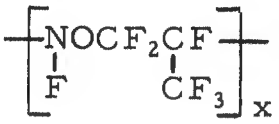

$$\left[\underset{CF_3}{\underset{|}{N}}-O-CF_2\underset{CF_3}{\underset{|}{CF}}\right]$$

to the main polymer chain, increasing the volume required by a rotating segment, thus stiffening the polymer chain and raising the Tg. Extending this thought further it becomes obvious that one method of reducing the Tg of the CF_3NO/CF_2CF_2 polymer is to reduce the volume of the pendant group on the nitroso portion of the polymer.

The use of nitrosyl fluoride (FNO) has been considered for copolymerization with CF_2CF_2. To demonstrate by calculation the advantage in low temperature properties, the assumption was made that the polymers


$$\left[\underset{CF_3}{\underset{|}{N}}OCF_2\underset{F}{\underset{|}{CF}}\right]_x$$

and


$$\left[\underset{F}{\underset{|}{N}}OCF_2\underset{CF_3}{\underset{|}{CF}}\right]_x$$

(where CF_3 and F are interchanged in the comonomers) have the same Tg, and since the Tg of the former is known, then Tg for $\left[\underset{F}{\underset{|}{NO}}\right]_x$ could be calculated.

Calculations show that FNO/CF_2CF_2 has a theoretical Tg of -95°C as compared to -51°C for CF_3NO/CF_2CF_2. This is a substantial improvement in the low temperature properties of the nitroso rubbers. These data are summarized in Table III.

In anticipation of close packing and resultant polymer crystallization, terpolymers containing pendant CF_3 groups were considered. The use of CF_3NO or $CF_2CF(CF_3)$ as a termonomer, up to 25 percent in their respective systems, still yielded polymers of substantially improved low temperature properties (Table III).

During this report period the preparation of nitrosyl fluoride (FNO) for improved low temperature nitroso rubbers was initiated. Nitrosyl fluoride can be prepared by the direct fluorination of nitric oxide (Ref 8), by the pyrolysis of nitrosyl salts in the presence of sodium or potassium fluoride (Ref 9, 10, 11), by the reaction of nitrosyl chloride with silver fluoride (Ref 12), or by the reaction of nitric oxide and silver difluoride under pressure (Ref 13). It is reported that the most convenient laboratory method (Ref 9) is by the pyrolysis of nitrosyl fluoroborate-sodium fluoride mixtures.

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

Nevertheless, the successful synthesis of pure nitrosyl fluoride by any method is dependent upon the care with which air and moisture are excluded from the apparatus, and the materials used to construct the apparatus. At elevated temperatures, only fluorinated nickel or high nickel content alloys such as Monel are satisfactory for handling nitrosyl fluoride. Nickel reacts with nitrosyl fluoride to form a film of NiF_4 on the surface which prevents further attack. Stainless steel is unsatisfactory because the iron fluorides do not adhere to the metal surface. At moderate temperature, Teflon, Kel-F, or polyethylene apparatus are satisfactory. Glass must be avoided because of the formation of a volatile fluorosilicate with FNO.

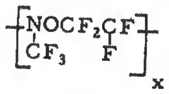
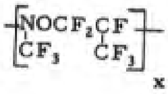
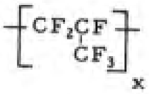
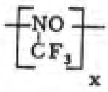
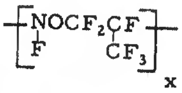
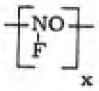
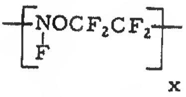
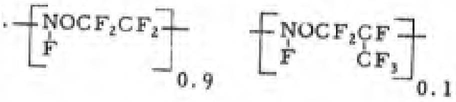
$$6\ FNO + SiO_2 \longrightarrow (NO)_2SiF_6 + 2\ NO + 2\ NO_2$$

The most common impurity in nitrosyl fluoride is N_2O_3 which is usually formed by reaction with moisture.

$$2\ FNO + H_2O \longrightarrow 2\ HF + N_2O_3$$

TABLE III

GLASS TRANSITION TEMPERATURES FOR VARIOUS NITROSO AND FLUOROCARBON POLYMERS

Polymer	Tg, °C	Comments
1.  $\left[\underset{CF_3}{N}OCF_2\underset{F}{C}F\right]_x$	-51	literature
2.  $\left[\underset{CF_3}{N}OCF_2\underset{CF_3}{C}F\right]_x$	-9	literature
3.  $\left[CF_2CF_2\right]_x$	80	literature
4.  $\left[CF_2\underset{CF_3}{C}F\right]_x$	165	literature
5.  $\left[\underset{CF_3}{N}O\right]_x$	-108	calculated based on 1 and 2
6.  $\left[\underset{F}{N}OCF_2\underset{CF_3}{C}F\right]_x$	-51	Assumption - same as 1
7.  $\left[\underset{F}{N}O\right]_x$	-184	calculated
8.  $\left[\underset{F}{N}OCF_2CF_2\right]_x$	-95	calculated
9.  $\left[\underset{F}{N}OCF_2CF_2\right]_{0.9^*}\left[\underset{CF_3}{N}OCF_2CF_2\right]_{0.1^*}$	-90	calculated
10.  $\left[\underset{F}{N}OCF_2CF_2\right]_{0.75}\left[\underset{CF_3}{N}OCF_2CF_2\right]_{0.25}$	-86	calculated
11.  $\left[\underset{F}{N}OCF_2CF_2\right]_{0.9}\left[\underset{F}{N}OCF_2\underset{CF_3}{C}F\right]_{0.1}$	-91	calculated
12.  $\left[\underset{F}{N}OCF_2CF_2\right]_{0.75}\left[\underset{F}{N}OCF_2\underset{CF_3}{C}F\right]_{0.25}$	-86	calculated

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* weight fractions

The pyrolysis of $NOBF_4$-NaF was chosen as the method of preparation. The $NOBF_4$ was purchased from Ozark-Mahoning Company and on the basis of infrared its spectrum contains no NO_2BF_4. The pyrolysis experiments were carried out in a Monel vacuum rack. The reactor was loaded in a dry atmosphere with a 2:1 molar ratio of NaF and $NOBF_4$, respectively, and then attached to the vacuum rack. The system was evacuated and the reactor heated to 75°C for one hour to remove residual moisture. The temperature of the reactor was then raised to 250°C and the resultant products were condensed in traps maintained at -110°C and -196°C; nitrosyl fluoride was trapped in the latter trap.

To date the FNO prepared by this method has been contaminated with NO_2. In the earlier runs the occurrence of small leaks during the pyrolysis was the probable cause of this contamination; however, the vacuum system has now been thoroughly checked for leaks and is believed to be air tight. The only remaining source of NO_2 must be trace amounts of water in one or both of the starting reagents and measures are being taken to eliminate this possibility. Trap B was maintained at -110°C during the run to remove any NO_2 ($NO_2 \leftrightharpoons N_2O_4$ equilibrium pressure is less than 1 mm at -80°C) formed during the pyrolysis. Nevertheless, NO_2 was present in trap C along with FNO. It appears that ordinary fractionation procedures are not sufficient for the separation of NO_2 and FNO. Therefore the preferred solution is to prevent the formation of NO_2 during the preparation.

PHASE II - POLYMERIZATION STUDIES

The objectives of this phase of work are (1) to conduct polymerization studies to develop capabilities of producing the CF_3NO/CF_2CF_2 copolymer in quantities of 10 to 50 pounds per 24 hour period and (2) to conduct polymerization studies with the new monomers developed under this project, purchased, or supplied by the Government. Polymerization studies are to begin June 15.

PHASE III - PRODUCTION OF NITROSO RUBBER

The objective of this phase of work is to supply the Government with 700 pounds of nitroso rubber. All or a part of this nitroso rubber may be the copolymer CF_3NO/CF_2CF_2. Production is scheduled to begin about February 1, 1964. Nevertheless, in order to allow time for the design and purchase of equipment, it is necessary to define monomer processes by mid-August and polymer processes by October 1963.

PHASE IV - COMPOUNDING AND CURING STUDIES

The objective of this phase of work is to conduct studies and evaluations to establish by compounding the best methods of realizing the unusual properties of nitroso rubber. Curing and compounding studies are scheduled to begin around October 1963 when sufficient polymer will be 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, molding and proofed goods and (2) to produce gaskets, reinforced hose and coated fabric. This phase is scheduled to begin around August 1964.

III. SUMMARY

1. Trifluoroacetyl nitrite has been prepared by replicate, small scale batches by the interaction of trifluoroacetic anhydride and dinitrogen trioxide. According to infrared analysis this material is equivalent to that prepared at 3M.

2. Lab-scale production at a 100 g/day level has been set up.

3. Trauzl block tests indicate that CF_3CO_2NO can be detonated by a No. 8 blasting cap; its brisance is low.

4. Exploratory solution pyrolyses of trifluoroacetyl nitrite indicated that decarboxylation occurs at a significant rate at temperatures of 145°C or greater; trifluoronitrosomethane was the major product.

5. Apparatus for a larger scale decarboxylation reaction has been assembled.

6. Apparatus for the preparation of tetrafluoroethylene by the debromination of tetrafluorodibromoethane has been assembled.

7. Nitrosyl fluoride (FNO) has been prepared by the pyrolysis of nitrosylfluoroborate ($NOBF_4$) and sodium fluoride at 250°C. This monomer is of interest for improving the low temperature properties of the nitroso rubbers.

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THIOKOL CHEMICAL CORPORATION, CHEMICAL OPERATIONS, TRENTON, N.J. AND REACTION MOTORS DIVISION, DENVILLE, N.J., NITROSO RUBBER RESEARCH, DEVELOPMENT AND PRODUCTION, by M. Fein, J. Green, and J. Paustian, 27 Feb 1963 to 31 May 1963, 25 pp. incl. figs., tables and refs. (Trenton Project No. RD-343-Q1, RMD Project No. 8576, QMC Project No. 7X93-15-004), U.S. Army Contract No. DA-19-129-AMC-69(X)O.I. 9044.

Unclassified Report

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