TECHNICAL REPORT
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NITROSO RUBBER HANDBOOK

by

Malcolm C. Henry and Charles B. Griffis

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January 1966

UNITED STATES ARMY
NATICK LABORATORIES
Natick, Massachusetts 01760

Clothing and Organic
Materials Division
C&OM-15

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NITROSO RUBBER HANDBOOK

by

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FOREWORD

Military operations conducted on a global scale require a variety of equipment that must operate under all climatic conditions. This imposes severe requirements on construction materials, particularly rubber whose properties are severely affected by temperature extremes. To assure that rubber materials are available that meet requirements, a continuing Army research program is maintained. Out of this research, new rubbers are developed. Work both in-house and under Army contract has contributed to the availability of these new types of rubbers, the result of many and varied efforts of a number of persons. This report deals with such a new product, "nitroso" rubber, which is not a single polymer but rather a family of many rubbery polymers.

The story of nitroso rubber development is spread over a number of contractor reports, published and unpublished papers, scientific meeting presentations and laboratory notebooks. This handbook summarizes in one convenient volume all of the work performed on this subject. It is designed for the use of materials engineers looking for specific applications and for research scientists interested in synthesizing new materials.

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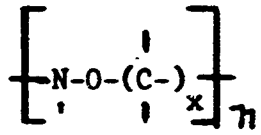
ABSTRACT

"Nitroso" rubber is the generic name for a family of rubbery high polymers having the common structural denominator of a repeating nitrogen-oxygen-carbon atomic sequence as follows:



$$\left[-\underset{|}{N}-O-\left(\overset{|}{\underset{|}{C}}-\right)_x- \right]_n$$

Architecturally these nitroso polymers are the first of a whole new class of materials. Nitroso polymers, as currently known, are highly fluorinated or completely fluorinated and as such are members of a specialty type of elastomer since only a limited number of fluorinated elastomers are known. It is becoming increasingly evident, however, that the combination of "nitroso" groups in the highly fluorinated linear polymer chain is responsible for the introduction of interesting and novel combinations of properties. Thus, nitroso elastomers have good low temperature properties, solvent resistance, stability to corrosive environments, and flame resistance.

Nitroso polymers have been developed to their present state by the cooperative effort of Army scientists and contractors. Over the past eight years, considerable insight has been gained as to the nature and potential uses of nitroso rubbers. This handbook is an attempt to assemble a summary of this accumulated knowledge. It is hoped that the contents so compiled will aid in the future development of this new family of specialty elastomers.

NITROSO RUBBER HANDBOOK

I. Introduction

The foundation upon which the U. S. Army's Research and Development Program is based rests upon the requirements of its tactical and support forces. As a result of these requirements a continuing program is carried out in an attempt to develop new and improved materials.

Materials required by the Army often must have properties or combinations of properties not required by others. Military operations are routinely carried out in environments presenting severe stress upon both personnel and equipment. Arctic operations at -65°F and lower are typical of the low temperatures met in Army operations. On the other hand, extremes of ground temperatures may reach 120°F while 1000°F is a common temperature encountered in operating components of military equipment.

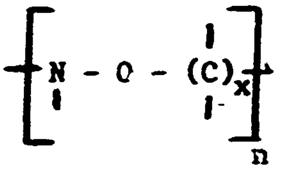
Experience has shown that commercially available rubbers, both natural and synthetic, are unsatisfactory in many cases. One specific requirement for improved elastomers is that of low temperature flexibility and petroleum fluid resistance. Elastomers are not commercially available that have the combined properties of low temperature flexibility and gasoline or oil resistance. Elastomers having these combined properties are required for many military items such as fuel lines, pump diaphragms, rubber covered cables and wire, chemical warfare protective clothing, gas masks, gaskets, flexible containers and liners.

Additional properties required in elastomers in addition to those already cited are ozone resistance, flame resistance, resistance to high thermal flux and radiation and both acid and oxidizer resistance. In short, elastomers are required having combinations of properties that will maintain their integrity in a wide range of temperature and corrosive environments.

The development of new elastomers with the best possible combination of properties has thus been the goal of the U. S. Army Natick Laboratories research program since its inception some years ago. Nitroso rubbers were recognized to belong to a unique system both as a generalized chemical structure and as a material with desirable combinations of properties that have potential use in military operations. This report is the story of the development of nitroso rubber to its present state. Many people have contributed to the nitroso rubber program that has been carried out by the U. S. Army Natick Laboratories. It is hoped that recognition of individual efforts have been made within the text of this report.

II. Terminology and Nomenclature

The terminology for the class of polymeric structures now commonly known as nitroso rubber has evolved primarily as a result of convenience. In one sense this is unfortunate since the implication is to a single structure. In reality, it is a generalized class of structures. Nitroso rubber is derived from material having a common structural denominator, namely a repeating trivalent nitrogen-oxygen-carbon sequential atomic arrangement of the following type:



$$\left[\overset{|}{\underset{|}{N}} - O - \overset{|}{\underset{|}{(C)}}_x \right]_n$$

As currently known, it is highly or completely fluorinated. However, many structural variations are theoretically possible and a large variety of structures have been prepared all having in common the repeating nitrogen-oxygen-carbon linkage.

Many structures containing this repeating unit are not elastomeric. Depending upon other incorporated structural features, these products may range from viscous oils to resinous plastics. From a structural point of view nitroso elastomers are unique as the only known example of a nitroso group entering into a polymer chain as an integral entity.

III. Historical Development

The history of the development of nitroso rubbers began in 1955 when Barr and Hazeldine[1-3] reported the discovery of a reaction between tetrafluoroethylene and trifluoronitrosomethane. One of the reaction products was reported to be a viscous polymeric oil. Subsequent work established the elastomeric nature of one of the reaction products[4] and extended the scope of the reaction.

In 1956 the first patent was issued to Rose[5] for the product resulting from the reaction of tetrafluoroethylene and trifluoronitrosomethane.

A summary report by Fitt[6] was also published in 1957 on both the preparation of nitroso compounds and the addition reactions of nitroso compounds to olefins.

Published reports in the early literature described nitroso elastomers as having novel combinations of properties. Resistance to the action of corrosive chemical environments such as solvents, oxidizing chemicals and ozone coupled with good low temperature properties were typical of the properties that created the initial interest for Army scientists. In 1957 the U. S. Army Natick Laboratories (then the Quartermaster Research and Development Command) funded its first contract to investigate the possibilities of developing these nitroso polymers into useable or practical elastomeric materials for military use. Complimentary interest in these unique elastomers has resulted in further investigations by Hazeldine[7,8] and Rose[9]. Since that time to the development of the present state of the art the following industrial and academic laboratories under contract to the U. S. Army Natick Laboratories, have contributed considerable data toward the development of these nitroso containing elastomers: The Central Research Laboratories of the Minnesota Mining and Manufacturing Company; Thiokol Corporation; Peninsular Chemical Research Corporation; Monsanto Research Corporation; University of Florida and the University of Colorado. Throughout this report repeated references will be found relating to these contractors and the results obtained under their research programs with the U. S. Army. For convenience these references have been abbreviated using a sequence of a capital letter indicating the company, a number indicating the report number and finally a page reference thus: T7-p-32 indicates Thiokol Corporation, Report #7, page 32.

Contractors referenced in this report are as follows:

1. U. S. Army Contract DA19-129-QM-1043, 15 October 1957 - 15 August 1960.
   Minnesota Mining and Manufacturing Company, Arctic Rubber, G. H. Crawford, et. al. Final Research Report 1960.

2. U. S. Army Contract DA19-129-QM-1684, 24 August 1960 - 23 December 1962.
   Minnesota Mining and Manufacturing Company, Arctic Rubber, H. A. Brown, et. al. Final Research Report 1962.

3. U. S. Army Contract DA19-129-AMC-69(X)0.19044, 27 February 1963 - 28 February 1965. Nitroso Rubber, Research Development and Production, Thiokol Chemical Corp., Trenton, N. J. J. Green, et. al. Final Research Report 1965.

4. U. S. Army Contract DA19-129-AMC-151(N) O.I. 9115, Physical and Rheological Properties of Nitroso Rubbers, Monsanto Research Corp., Everett, Mass., G. L. Ball, et. al, 1963 - present; 9 reports.

5. U. S. Army Contract DA19-129-AMC-152(N) O.I. 9116, Synthesis and Polymerization of Fluorinated Sulfur Modified Nitroso Rubber, Peninsular Chemical Research, Inc., Gainesville, Florida, G. Stump, et. al. 1963 - present; 8 reports.

6. U. S. Army Contract DA19-129-QM-1926 O.I. 6028-62, Synthesis of Special Fluorine Containing Monomers, University of Colorado, Boulder, Colorado, J D. Park and J R. Lacher, 1964 - 1966 period.

7. U.S. Army Contract DA19-129-AMC-79(N) Research on Synthesis of Unsaturated Fluorocarbon Compounds, University of Florida, P. Tarrant, et. al. April 1 1963 - 1966 period.

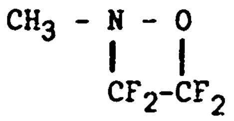
Abbreviations:

a.	Minnesota Mining and Manufacturing Company	3M
b.	Thiokol Chemical Corporation	T
c.	Monsanto Research Corporation	M
d.	Peninsular Chemical Research, Inc.	P
e.	University of Florida	F
f.	University of Colorado	C

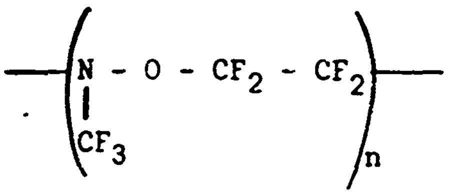
IV. Nitroso Rubber Chemistry

In 1957 the U. S. Army Natick Laboratories funded a program with the Central Research Laboratories of the Minnesota Mining and Manufacturing Company to begin to investigate the potential of nitroso polymers as a military elastomer.

Early work was substantiated that trifluoronitrosomethane, CF_3NO, reacts with tetrafluoroethylene to form an oxazetidine as the main product,



at temperatures above 100°C. At temperatures below 0°C a linear polymer predominates containing alternating CF_3NO and CF_2CF_2 groups.



$$\left(\underset{\displaystyle CF_3}{\overset{|}{N}} - O - CF_2 - CF_2 \right)_n$$

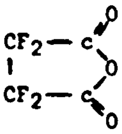
Both the polymer and the oxazetidine were found to be stable towards acids as well as oxidizing and reducing agents. Additionally the polymer had good low temperature properties. From this initial study it became apparent that methods of synthesizing nitroso-containing monomers and other potentially useful fluorocarbon comonomers was of some importance.

A. Monomer Syntheses

The course of this investigation has resulted in the syntheses of innumerable monomers. Only those monomers most pertinent will be discussed in detail. A number of the synthesized nitroso monomers are shown in Table I along with reference to information concerning their syntheses.

Table I

SYNTHESIS OF NITROSO MONOMERS

MONOMER	METHOD	REFERENCE
1. p-BrC_6F_4NO	$HC_6F_4NH_2 + Br_2 \xrightarrow{CH_3COOH} BrC_6F_4NH_2$ 70% $BrC_6F_4NH_2 + HCOOOH \xrightarrow{CH_2Cl} BrC_6F_4NO$ 64%	T7,p10
2. C_6F_5NO	$C_6F_5NH_2 + HCOOOH \xrightarrow{CH_2Cl_2} C_6F_5NO$	T3, p11 G.M. Brooke et. al. Chem & Industry 1961, 832
3. C_6H_5NO	Commercially available	Chemical Procurement Laboratories
4. CH_3CF_2NO	$CF_2 = CH_2 + HI \longrightarrow CH_3CF_2I$ $CH_3CF_2I + NO \xrightarrow[u.v.]{Hg} CH_3CF_2NO$	3M Final Report 1962
5. $H(CF_2)_4NO$	$H(CF_2)_4I + NO \xrightarrow[u.v.]{Hg} H(CF_2)_4NO$	3M Final Report 1962
6. $ClCF_2CF_2NO$	$F_2C = CF_2 + NOCl \longrightarrow ClCF_2CF_2NO$	3M Final Report 1962 Pierce Chemical Co.
7. $NO_2CF_2CF_2NO$	$C_2F_4 \xrightarrow{3NO} O_2NCF_2CF_2NO$	3M Final Report 1960
8. $C_8H_{17}NO$	$C_8F_{17}I + NO \xrightarrow[u.v.]{Hg} C_8H_{17}NO$	3 M Final Report 1960
9. C_3H_7NO	$C_3F_7I + NO \xrightarrow[u.v.]{Hg} C_3H_7NO$	3M Final Report 1960
10. $CF_2ClCFClNO$	$CF_2 = CFCl + NO \xrightarrow{FeCl_3} CF_2ClCFClNO$	3M Final Report 1960 Pierce Chemical Co.
$CH_3O_2C(CF_2)_2NO$	 $+ CH_3NO_2 \longrightarrow CH_3O_2C(CF_2)_2COONO$ $CH_3O_2C(CF_2)_2COONO \xrightarrow{pyrolysis} CH_3O_2CCF_2CF_2NO$	P8,p7

1. Tetrafluoroethylene, C_2F_4

Tetrafluoroethylene may be obtained commercially as a compressed gas (Peninsular Chemical Research Corporation, Gainesville, Florida) or by the debromination of Freon 114-B_2, tetrafluorodibromomethane, in the presence of activated zinc dust in methanol.

$$CF_2BrCF_2Br + Zn \xrightarrow{CH_3OH} CF_2 = CF_2 + ZnBr_2.$$

The synthesis of nitroso compounds is somewhat restrictive. The more successful procedures usually involve one of the following methods: pyrolysis of acetylnitrites; oxidation of amino groups under selective conditions and the addition of nitrosyl halides or nitric oxide to olefins. Typical syntheses that have been used for preparing nitroso compounds are described in the following paragraphs and in Table I. A recent review by Gowenlock and Luttke describes the general structure and properties of C-nitroso compounds[10].

2. Trifluoronitrosomethane, CF_3NO

Trifluoronitrosomethane is a deep blue gas with a boiling point of -84°C. It was first prepared by Ruff and Giese[11] by the fluorination of silver cyanide in the presence of silver nitrate. Barr and Hazeldine[1] synthesized it from the reaction of trifluoroiodomethane, CF_3I or CF_3Br[12] and nitric oxide, NO, in the presence of ultraviolet light using mercury as a catalyst. The pyrolytic decarboxylation of trifluoroacetylnitrite[13] has been the most successful procedure used to date.

Trifluoroacetylnitrite is formed by the reaction of trifluoroacetic anhydride with dinitrogen trioxide by mixing equivalent quantities of the two reactants, using autogeneous pressure or a reflux condenser to maintain the N_2O_3 in the liquid phase. The reaction is complete in a few minutes and may be followed by the change in color from blue (N_2O_3) to amber (CF_3COONO).

$$(CF_3CO)_2O + N_2O_3 \longrightarrow 2CF_3COONO$$

$$CF_3COONO \longrightarrow CF_3NO + CO_2$$

The pyrolysis is carried out in refluxing FC-43, tri(perfluorobutyl) amine. The overall yield is approximately 30%. Trifluoronitrosomethane obtained this way is amenable to scale up and can be purified readily to a state satisfactory for participation in polymerization reactions (See Sec. IVC).

Trifluoronitrosomethane may currently be obtained commercially from Peninsular Chemical Research Corporation, Gainesville, Florida.

3. p-Bromotetrafluoronitrosobenzene (p-Br C_6F_4NO) (Table I)

A bromine-glacial acetic acid solution was added to a solution of 2,3,5,6-tetrafluoroaniline at room temperature. The product 4-bromo-2,3,5,6-tetrafluoroaniline was obtained as colorless crystals, mp 57-80°C, and was characterized by infrared spectra and elemental analysis. The brominated product was refluxed together with a mixture of 98% formic acid and 90% hydrogen peroxide for five hours followed by a chromatographic separation on acid washed alumina. The pure 4-bromo-2,3,5,6-tetrafluoronitrosobenzene was obtained as colorless crystals that melted to a green liquid at 39-40°C. Thermochromism of this type is common in aromatic nitroso compounds due to dimer formation in the solid state.

4. Methylperfluoronitrosopropionate (Table I)

Equimolar amounts of methyl nitrite and perfluorosuccinic anhydride were condensed in a Fisher Porter tube and allowed to come to room temperature for 1-1/2 hours. Unreacted material was removed at reduced pressure. Yield, practically quantitative.

Analysis for $CH_3O_2CCF_2CF_2NO$: %C, 25.76; %H, 1.29; %F, 32.60
Found: %C, 25.84; %H, 1.33, %F, 36.91.

A two-neck flask fitted with a Vigreaux column and an addition funnel was connected to an air cooled condenser vented through a 183°C trap. A vacuum was maintained while the nitrite was dropped into the flask heated to 200°C. After the pyrolysis had been going for several minutes a blue liquid collected in the -183°C trap. The blue product was separated and distilled twice. GLC and an infrared spectrum showed it to be pure $CH_3O_2C(CF_2)_2NO$.

5. β-Nitrosoperfluoropropionic Acid, $HOOCCF_2CF_2NO$[14]

One preparation of $HOOCCF_2CF_2NO$ was carried out by the photolysis of dinitrosyl perfluorosuccinate utilizing a quartz

$$\begin{tikzcd}(CF_2COONO)_2 \arrow[r, "h\nu"] & ONOOC\ CF_2CF_2NO + CO_2 \arrow[d] \\ HOOCCF_2CF_2NO & H_2O \arrow[l]\end{tikzcd}$$

ampoule kept at 0°C with irradiation from a sunlamp. The reaction rate was very slow and in all cases considerable N_2O_3 was formed indicating decomposition of the dinitrite as follows:

$$(CF_2COONO)_2 \longrightarrow (CF_2CO)_2O + N_2O_3$$

The rate of decomposition was increased at higher temperatures. Varying conditions did not result in improved yields which were in all cases very low.

6. γ-Nitrosoperfluorobutyric Acid, $HOOC(CF_2)_3NO$[14]

The photolysis of dinitrosyl perfluoroglutarate, $(CF_2)_3(COONO)_2$, derived from the reaction product of perfluoroglutaric anhydride and N_2O_3, proceeded at a much faster rate with less reversion to N_2O_3. The reaction product γ-nitrosoperfluorobutyric acid, $HOOCCF_2CF_2CF_2NO$, could be purified by distillation.

7. Miscellaneous

Alternative methods may also be used for the syntheses of nitroso-containing compounds such as those described by Andreades[15] and Park[16] utilizing addition reactions of nitrosyl halides to fluoroolefins and fluoroketones.

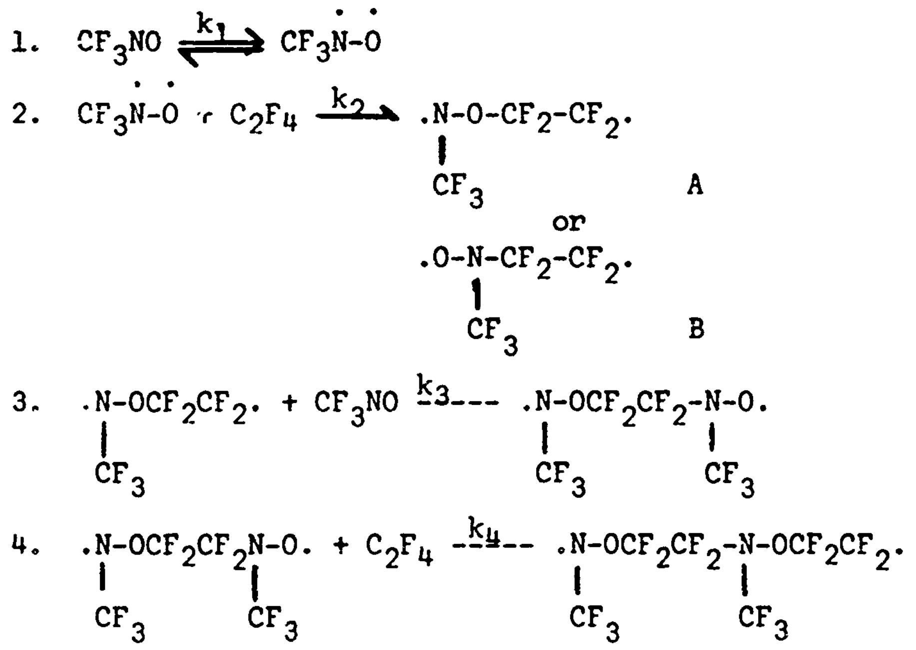
B. Polymerizations

Nitroso elastomers may be prepared using standard bulk, solvent or water emulsion polymerization techniques. Hazeldine[17,18] has also reported the formation of high molecular weight elastomers containing the nitroso group as an integral part of the elastomer. Both bulk and solution polymerizations of CF_3NO/C_2F_4 have the disadvantage of poor heat transfer (leading to uncontrolled reactions) or low molecular weight product when used on a larger scale. Methods of carrying out these polymerizations in aqueous medium indicated that satisfactory conditions could be obtained when using low temperatures. Thus an aqueous suspension system employing an organic suspending agent such as magnesium carbonate and a soluble inorganic salt such as lithium chloride or lithium bromide as a freezing point depressant was found to be a good polymerizing medium. Using this system the polymer is obtained in the form of small particles. The polymer is separated from the water phase by filtration and freed of suspending agent by acid treatment. The resultant molecular weight of the product compares favorably with that obtained by small scale bulk polymerizations. As will be seen (IVC) this polymerization system was found to be the most advantageous for "scale-up" and was used in the pilot plant facility when larger quantities of nitroso rubber copolymers were being prepared. Materials obtained via this method have been shown to have intrinsic viscosities of greater than one, indicating molecular weights over one million.

1. Kinetics and Postulated Mechanisms

The mechanisms involved in the copolymerization of nitroso monomers have as yet not been resolved to any degree of certainty. The dependence of initial polymerization rate on the concentration of CF_3NO and C_2F_4 was determined approximately by polymer isolation techniques. The rates obtained best fit a reaction which is first order in CF_3NO concentration and one-half order in C_2F_4 concentration. Experiments have shown rather conclusively that mechanism of initiation is not due to impurities being present in the monomers. Rather, the initiation is probably due to the radical character of the nitroso compound itself.

A partial scheme for this mechanism might be:



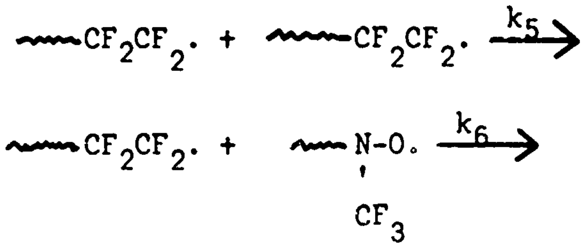
1. $CF_3NO \overset{k_1}{\rightleftharpoons} CF_3\dot{N}-\dot{O}$

2. $CF_3\dot{N}-\dot{O} + C_2F_4 \xrightarrow{k_2} \cdot\underset{CF_3}{\underset{|}{N}}-O-CF_2-CF_2\cdot$ A or $\cdot O-\underset{CF_3}{\underset{|}{N}}-CF_2-CF_2\cdot$ B

3. $\cdot\underset{CF_3}{\underset{|}{N}}-OCF_2CF_2\cdot + CF_3NO \xrightarrow{k_3} \cdot\underset{CF_3}{\underset{|}{N}}-OCF_2CF_2-\underset{CF_3}{\underset{|}{N}}-O\cdot$

4. $\cdot\underset{CF_3}{\underset{|}{N}}-OCF_2CF_2\underset{CF_3}{\underset{|}{N}}-O\cdot + C_2F_4 \xrightarrow{k_4} \cdot\underset{CF_3}{\underset{|}{N}}-OCF_2CF_2-\underset{CF_3}{\underset{|}{N}}-OCF_2CF_2\cdot$

Termination steps might include:



$$\sim CF_2CF_2\cdot + \sim CF_2CF_2\cdot \xrightarrow{k_5}$$

$$\sim CF_2CF_2\cdot + \sim\underset{CF_3}{\underset{|}{N}}-O\cdot \xrightarrow{k_6}$$

A biradical mechanism is reasonably plausible based on existing data, the stability of CF_3NO and the formation of oxazetidine under conditions of elevated temperatures. (3M-Final Report 1960).

A number of interesting features concerning the nitroso copolymers have been observed that are of interest. As shown in reaction step No. 2 there are theoretically two different ways in which the nitroso group can attach to the C_2F_4. In a polymeric species one might expect to find either a random sequence or a regular preferred orientation. W. T. Flowers[19] has done considerable work having to do with the thermal degradation of nitroso polymers and in particular the CF_3NO/C_2F_4 copolymer. Inside a mass spectrometer volatile fragments with molecular weights up to 6000 have been produced. There is nothing to suspect that the structure is other than a regular one. These mass spectrometric results also show a repeating regular pattern for every molecular weight of the monomer, that is 199. If one were to have a unit in the reverse sequence with fragmentation occurring at the N-O bond (which it does being the weakest link in the polymer) then one would get molecular weights which do not correspond to the 199 difference and these have not been seen.

Another interesting feature, also having to do with the direction of addition of the nitroso group to an olefinic carbon bond, has been noted by Sutcliffe[20]. Using unsymmetrical olefins the direction of addition of the N=O group of CF_3NO to a C=C bond in oxazetidine formation is opposite to that involved in formation of the predominant copolymer. This can be explained by postulating that copolymerization occurs by a free radical mechanism and that oxazetidine is produced by either a free radical or molecular process preceded by formation of a 1:1 complex of nitroso compound with olefin[21].

Finally, the effect of small amounts of chain transfer agents on the polymerization rate and molecular weight were determined. The transfer agents used had no significant effect on the polymerization rate, which is normal for a radical type polymerization provided the radical formed after transfer is capable of initiating new chains. In all cases the transfer agents significantly lowered the molecular weight of the polymer. Initial polymerization rates in $CF_2ClCFCl_2$ solutions were determined and found to be lower than in $(C_4F_9)_3N$. The rate dependency on monomer concentrations was found to be the same in $CF_2ClCFCl_2$ as in $(C_4F_9)_3N$. These results also seem to be consistent with the polymerization mechanism already proposed earlier in this section (3M-Final Report 1962).

2. Copolymerizations

A variety of nitroso copolymer systems have been studied under a variety of conditions. Both laboratory scale and pilot plant scale procedures have been worked out in considerable detail. The pilot plant copolymerizations are described in section IVC of this report. Typical laboratory procedures for bulk polymerizations are described by Crawford[22] and Brown (3M-Final 1962) for trifluoronitrosomethane and tetrafluoroethylene.

The monomers are condensed into pyrex ampoules, sealed and the reaction carried out at subambient temperatures. Unreacted monomers are vented and the solvent, if any, removed.

Copolymerization systems that have been prepared are noted in Tables II and III and are referenced within the table for source information.

3. Terpolymerizations

In contrast to copolymerizations the experimental procedures for terpolymerizations are relatively undeveloped. Terpolymerizations studies to date have been primarily bulk polymerizations using nearly molar equivalent quantities of comonomers with a relatively small molar proportion of added termonomer. Experimentally the reaction conditions are essentially similar to copolymerization conditions. Table IV describes and references the variety of terpolymer systems that have been studied thus far. Termonomers are usually selected as participating members of the polymerization based on structural considerations for subsequent compounding studies.

The termonomer selected must have a reactivity such that the reactive groups will be distributed randomly along the polymer chain. Very few olefinic compounds then qualify as termonomers. Nitroso compounds containing functional groups in the side chain are suitable termonomers since all nitroso compounds have about the same reactivity towards C_2F_4 provided the nitroso group is adjacent to a $-CF_2-$ group.

C. Pilot Plant Scale-Up

The requirement for extensive compounding studies concomitant with the requirement for relatively large quantities of the trifluoronitrosomethane/tetrafluoroethylene copolymer suggested a need for a pilot plant facility. In 1963 the U. S. Army funded an extensive program with Thiokol Chemical Corporation (T-Final 1965) to produce a sizeable quantity of this copolymer for the purpose of carrying out extensive compounding evaluations. Thiokol reports to the U. S. Army reflect this effort.

One of the main efforts in this work deal with the scale-up synthesis of the trifluoronitrosomethane as well as determining the hazard involved in the synthesis and handling of this relatively unexplored chemical compound. Thiokol's past experience in propellants was recognized as being somewhat unique as a result of the many procedures that have been developed for the evaluation of potentially hazardous materials. Both the art and the science of those skilled in these safety tests were made available to the program.

The preferred route for trifluoronitrosomethane production was through the formation and decarboxylation of trifluoroacetylnitrite, CF_3CO_2NO[15]. Nothing to date has been uncovered that has resulted in any change in this approach. Trifluoroacetylnitrite can be prepared by the interaction of dinitrogen trioxide, N_2O_3, or with nitrosyl chloride, NOCl, with the former method being preferred because of superior yields.

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

The N_2O_3 was obtained from the Matheson Company, Inc., and used as received. The purity was greater than 99 percent. Since N_2O_3 dissociates readily it was removed from the storage cylinders as the liquid phase. Trifluoroacetylnitrite was decomposed to CF_3NO by pyrolytic techniques. In Trauzl block tests trifluoroacetylnitrite could be detonated although the detonation was not very brisant. Additional detonation testing by a card gap test to ascertain whether or not this material will propagate a detonation wave (and at what rate) showed that the critical diameter of trifluoroacetylnitrite is greater than 11/16 inch with metallic confinement. Ignition limits of the vapors were determined over the range of 25-100°C as a function of concentration in nitrogen. No detonations were experienced. The data from these tests indicated that CF_3CO_2NO ignites on initiation at concentrations greater than 50 percent up to about 65°C and at lower concentrations at higher temperatures. The lower temperature limit for the ignition of CF_3CO_2NO vapor appears to be about 40°C. Thermal decomposition rate of CF_3CO_2NO were determined up to 184°C at which temperature the time required for complete decomposition is of the order of 5 - 6 minutes. Spark tests indicated that dilution of the CF_3CO_2NO vapors by FC-43 (3M product-perfluorobutyl tertiary amine isomer mixture) had resulted in a process operable without undue hazard (Thiokol Reports Nos. 1 and 3).

Satisfactory completion of the safety tests along with studies of the pyrolysis of CF_3CO_2NO resulted in a unitized operation capable of producing one pound/hour of the deep blue gaseous CF_3NO which could ultimately be stored in gas storage bottles. Thus it became

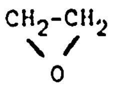
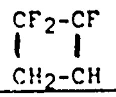
Table II

COPOLYMERS WITH CF_3NO

	CoMonomer	System	Time, hr	Temp. °C	Reactant Ratio(Molar)	Conversion %	Product	Remarks	Reference
1.	SO_2	Bulk	4 days	-25	1/1	--	--	No reaction	P6,p9
2.	$F_2C=S$	Bulk	2 days 4 days	-78 -20	1/1	--	--	No reaction	P1, p18
3.	$F_3CN=SF_2$	Bulk	20	-38	--	--	--	No reaction	P2,p15
4.	$F_2C=CFCl$	Bulk	20-1/4 days	-30	1/1	75	Elastomer	--	P8,p9
5.	$F_2C=CFBr$	Bulk	4	-30	1/1	81	White hard elastomer		P8,p10
		Bulk	3	-78	1/1	--	Tough sticky gum		
		Bulk	2	Ambient	1/1	--	Fluid liquid		
		Bulk	18	-20	1/1	60	White tough elastomer		
6.	$F_2C=CFI$	Bulk	15	-30	1/1	--	--	Dark brown solid	P8,p9
7.	$FHC=CHF$	Bulk	30 days	-30				No reaction	P8,p12
8.	$F_2C=CF_2$	Sol'n	1 week 2 weeks	10 Ambient	1/1 1/1		No change No change	$AlBr_3/VCl_3/Ph_4Sn$ catalyst	P4,p16
9.	$CH_2=CH_2$	Bulk	3 weeks	-15 to 20	--	--	--	No product	1960 3M Final
10.	$F_2C=CH_2$	Bulk	3 weeks	-15 to 20	1/1	37	Grease		1960 3M Final
11.	$F_2C=CCl_2$	Bulk	24	-20	2/1	100	Friable Thermoplastic		1960 3M Final
12.	$FHC=CH_2$	Bulk	2 days 1 day	-16 to 20 20	2/1	--	Unknown Unknown	No polymer No polymer	1960 3M Final 1960 3M Final
13.	$FHC=CF_2$	Bulk	3 days	-20	1/1	73	Elastic gum		1960 3M Final

Table II (continued)

COPOLYMERS WITH CF_3NO

CoMonomer	System	Time, hr	Temp. °C	Reactant Ratio(Molar)	Conversion	Product	Remarks	Reference
14. $CF_2=CFBr$	Bulk	18	-78 to 25	1/1	89	Tough white gum Tg=3°, Insol. FC-43		P7,p9
15.  CH_2-CH_2 O		4 days	-15	1/1			No reaction	P6,p9
16. $CF_2=CFCl$	Bulk	2 days	-15	1/1	100	Elastic gum		1960 3M Final
17. $CF_2=CFSF_5$	Bulk						No reaction	P3
18. $CF_2=CFCF_3$	Bulk	75	20	1/2.5	20	Elastic gum		1960 3M Final
19. $FClC=C(F)OCH_3$	Bulk	12	-15	1/1	100	Plastic		1960 3M Final
20. $F_2C=CFSCF_3$	Bulk Bulk Bulk	65 72 48	-30 -38 Ambient	1/1 1/1 1/1	20 -- --	Gum -- Possible polymer	Tg = -48 No reaction - Cobalt 60 irradiation	P7,p9 P2,p15
21. $(CF_3)_2C=S$	Bulk	360	-78	1/1	--	--	No polymer	P2,p15
22. $CF_3CH_2OCH=CH_2$	Bulk	48 24	-65 +20	2/1 2/1	0 0	-- --	Product unknown Product unknown	1960 3M Final 1960 3M Final
23. $CF_3CF_2CH=CH_2$	Bulk	48	-20	2/1	0	--	Product unknown	1960 3M Final
	Bulk	24	20	2/1	0	--	Product unknown	1960 3M Final
24. $CF_3CF_2CF=CH_2$	Bulk Bulk	48 24	-16 to 20 +20	2/1 2/1	0 0	-- --	Product unknown Product unknown	1960 3M Final
25.  CF_2-CF CH_2-CH	Bulk	48	-20	2/1	0	--	Product unknown	1960 3M Final

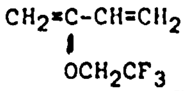
26. $CF_2=CHCF=CH_2$	Bulk					Diels Alder adduct		
27. $CF_2=CFCH=CH_2$	Sol'n		-20	1/1	50	Elastomer	Tg= -55°C	1960 3M Final
28. $CH_2=CHCH=CH_2$	Bulk						Diels Alder Adduct	1960 3M Final
29. $CF_2=CFCF=CF_2$	Bulk Suspension	48 48	-30 -30	1/1 1/1	34 16.7	Gum Tough gum		P7,p9
30. $CF_2CF=CFCF_2$	Bulk	72	-20	1/1	--	--	No reaction	P5
31. $CF_3CF_2CF_2CHO$	Bulk	3 weeks	-15 to 20	1/1	--	--	Product unknown no polymer	1960 3M Final
32. $CH_2=C(CH_3)C(CH_3)=CH_2$	Bulk						Diels Alder adduct	1960 3M Final
33. $CH_3CH=CHCH=CH_2$	Bulk						Diels Alder adduct	3M Final
34. $CH_2=C(CH_3)CH=CH_2$	Bulk						Diels Alder Adduct	3M Final
35. $CF_2=CFCH_2CH=CH_2$	Sus-pension	48	-20	1/1	20	Gum	Brown tacky product	P5,p11
36.  $CH_2=C(OCH_2CF_3)-CH=CH_2$							Diels Alder Adduct	3M Final
37. $CH_3CH=CHCH=CHCH_3$							Diels Alder Adduct	3M Final
38. $(CN)_2C=C(CN)_2$	Bulk	96	Ambient				No reaction	
39. $C_6H_5CH=CH_2$	Bulk	24	-15	1/1	Unknown	Oil		3M Final
40. $CH_2=C(CH_3)COOC_4H_9$		24	-15	1/1	80	Oil		3M Final

Table III

NITROSO COPOLYMERS OTHER THAN CF_3NO

	Monomers	System	Time,(hr) Temp(°C)	Molar Ratio	Conversion %	Product	Remarks	Reference
1.	$CF_3CF_2NO/F_2C=CF_2$	Bulk	24/16	2/1	100	Gum rubber		1960 3M Final
2.	$CF_3CF_2CF_2NO/F_2C=CF_2$	Bulk	24/-20	2/1	100	Gum rubber		1960 3M Final
3.	$(CH_3)_2NNO/F_2C=CF_2$						No reaction	1960 3M Final
4.	$BrCF_2CF_2NO/F_2C=CF_2$	Bulk	12/-78 to 25	1/1	84	Clear elastomeric gum		P8,p12
5.	$C_8F_{17}NO/F_2C=CF_2$	Bulk	24/-20	1/1.5	50	Gum rubber		1960 3M Final
6.	$CF_2ClCFClNO/CF_2=CFCl$	Bulk	1-wk/20	1/1	60	Gum		1960 3M Final
7.	$O_2NCF_2CF_2NO/F_2C=CF_2$	Bulk	24/-20		90	Gum rubber		1960 3M Final
8.	$O_2NCF_2CF_2NO/F_2C=CCl_2$	Bulk	5-day/-25		95	Brittle-short		1960 3M Final
9.	$O_2NCF_2CF_2NO/F_2C=CFCl$	Bulk	24/-25		92	Brittle-short		1960 3M Final
10.	$O_2NCF_2CF_2NO/F_2C=CFH$	Bulk	24/-25		80	Gum-stiff		1960 3M Final
11.	$O_2NCF_2CF_2NO/CF_3CH_2OCH=CH_2$	Bulk	24/-25		98		Brown fuming oil	1960 3M Final
12.	$O_2NCF_2CF_2NO/F_2C=CHCl$	Bulk	24/-25	--	--	--	No product	1960 3M Final
13.	$O_2NCF_2CF_2NO/F_2C=CH_2$	Bulk	24/-25				No product	1960 3M Final
14.	$O_2NCF_2CF_2NO/SO_2$	Bulk	24/-25				No product	1960 3M Final
15.	$O_2NCF_2CF_2NO/F_2C=CF_2$	Emulsion	17/20		95	Gum		1960 3M Final
16.	$O_2NCF_2CF_2NO/F_2C=CF_2$	Bulk	24/-25		82	Gum		1960 3M Final
17.	$ClCF_2CF_2NO/F_2C=CF_2$	Bulk	20/-20			Transparent rubber		1960 3M Final

18. $ClCF_2CF_2NO/F_2C=CF_2$	Bulk	8-day/ -65 to -35		82	Elastomeric gum		1960 3M Final
19. $ClCF_2CF_2NO/F_2C=CFCl$	Bulk	20/-20			Very short rubber		1960 3M Final
20. $ClCF_2CF_2NO/F_2C=CFH$	Bulk	20/-20				Transparent thermoplastic	1960 3M Final
21. $ClCF_2CF_2NO/F_2C=CH_2$	Bulk	20/-20				Transparent thermoplastic	1960 3M Final
22. $ClCF_2CF_2NO/F_2C=CCl_2$	Bulk	20/-20				Transparent thermoplastic	1960 3M Final
23. $ClCF_2CF_2NO/CF_3CF=CH_2$	Bulk	20/-20					1960 3M Final
24. $ClCF_2CF_2NO/CF_3CH_2OCH=CH_2$	Bulk	20/-20			Polymer	Decomposed on drying	1960 3M Final
25. $ClCF_2CF_2NO/CF_3CH=CH_2$	Bulk	20/-20			Polymer	Decomposed on drying	1960 3M Final
26. $HCF_2(CF_2)_3NO/F_2C=CF_2$		35 day/ -65		58	Elastomeric gum		1962 3M Final
27. $CH_3CF_2NO/F_2C=CF_2$		3 day/ -20		10	Elastomeric gum	Tg = -35°C	1962 3M Final
28. $HCF_2CF_2NO/F_2C=CF_2$		24/-20		40	Tacky gum		1962 3M Final
29. $HCF_2CF_2NO/F_2C=CF_2$		20/-25		72	Elastomeric gum		1962 3M Final
30. $C_6H_5NO/F_2C=CF_2$	Solution	18/-35			Polymer	Black powder	1962 3M Final
31. $C_6F_5NO/F_2C=CF_2$	Solution	20/-20	1/1		Semi-solid	Tacky benzene solvent	P1,p19
32. $C_6F_5NO/F_2C=CF_2$	Solution	48/-20	1/1.25		Polymer	Yellow tacky powder CH_2Cl_2 solvent	P1,p19
33. $C_6F_5NO/F_2C=CFCl$	Solution	24/-40 (3 day/-20)	1/1			Hard white-yellow solid	P1,p19
34. $BrC_6H_4NO/F_2C=CF_2$	Solution	1-25	1/1		Polymer	Hard resin, rubbery 55-130°C; 1/1 copolymer CH_2Cl_2 solvent	T7,p10

Table IV

NITROSO TERPOLYMERS ($CF_3NO/F_2C=CF_2/A$)

Monomer A	System	Time,hr/ Temp°C	Molar Ratio	Conversion %	Product	Remarks	Reference
1. SO_2	Bulk	96/-25	.5/1/.5		Tacky polymer		P6,p10
2. $F_2C=S$	Bulk	20 day/ -78 to -20	1/1/.001		Polymer	Copolymer of CF_3NO + $F_2C=CF_2$	P1,p19
3. CF_3OF	Bulk	18/-25	1/1/.2		Tacky gum		P6,p9
CF_3OF	Bulk	--	1/1.4		--	Exploded after 5 min.	P6,p9
4. CCl_3Br	Bulk	(96/-15 48/ambient)	1/1/ trace		Viscous gum		P6,p11
5. CF_2Br_2	Bulk	96/ambient	1/1/1		Viscous liquid		P6,p11
6. $F_2C=CH_2$	Bulk		1/1/.6	80	Elastomeric gum		T8,p12
			1/1/.5	84	Elastomeric gum		T8,p12
7. $CFH=CFH$	Bulk	96/-30		62	Polymer	No$CFH=CFH$ in polymer	P8,p12
8. $CF_2=CFH$	Suspension		1/.99/.01	40	Rubber		T7
9. $CF_2=CFH$	Suspension		1/99.01	--	Rubber		T7
10. $CF_2=CFH$	Suspension		1/96/.04	70	Rubber		T7
11. $CF_2=CFH$	Suspension		1/-/1	--		No reaction	T7
12. $CF_2=CFH$	Suspension		1/.5/.5	45	Gum		T7
13. $CF_2=CFH$	Suspension		1/.25/.75	63	Rubber		T7
14. $CF_2=CFH$	Suspension		1/.125/.875	71	Rubber		T7
15. $CF_2=CFH$	Suspension		1/.96/.04	79	Rubber		T7
16. $CF_2=CFBr$	Bulk	48/-30	.12/.14/.024	70	Elastomeric gum η = 0.36		P8,p10

17. $CF_2=CFBr$	Bulk	38/-30	.14/.095/.047	61	Elastomeric gum $\eta = 0.10$		P8,p10
18. $CF_2=CFBr$	Bulk	48/-30	.14/.095/.047	90	Elastomeric gum $\eta = 0.11$		P8,p10
19. $CH_2=CHCOOH$	Bulk	(24/-65 (120/-25	1/-/1		No reaction	(Copolymerization)	T8,p16
20. $CH_2=CHCOOH$	Bulk	(24/-65 (120/-25	1/.5/.5		Gum	No -COOH in polymer	T8,p16
21. $CH_2=CHCOOH$	Bulk	(24/-65 (120/-25	1/.9/.1		Gum	No -COOH in polymer	T8,p16
22. $CH_2=CHCOOH$	Bulk	20/10-20	1/.9x's		Polymers	Liquid + gum products	T8,p16
23. $CH_2=CHCOOH$	Bulk	20/0	1/.9/.1		Terpolymer		T8,p16
24. $CH_2CHCOOH$	Bulk	20/0 3/50	1/.9/.1		Terpolymer		T8,p16
25. $CH_2=CHCOOH$	Solution	23/-25	1/.9/.1		Soft gum	No -COOH in polymer CH_2Cl_2 solvent	T8,p16
26. $CH_2=CHCOOH$	Solution	-/25	1/-1.1			Exploded, overpressure CH_2Cl_2 solvent	T8,p16
27. $CH_2=CHCOOH$	Solution	-/25	1/.5/.5			Exploded, overpressure CH_2Cl_2 solvent	T8,p16
28. $CH_2=CHCOOH$	Solution	-/25	1/.9/.1			Exploded, overpressure CH_2Cl_2 solvent	T8,p16
29. $CH_2=CHCOOH$	Solution	20/25	1/.5/.5		Liquid polymer	CH_2Cl_2 solvent	T8,p16
30. $CH_2=CHCOOH$	Solution	(24/-65 (120/-25	1/-1		No reaction	Freon 113 solvent	T8,p16
31. $CH_2=CHCOOH$	Solution	(24/-65 (120/-25	1/.5/.5		Liquid polymer	Freon 113 solvent	T8,p16
32. $CH_2=CHCOOH$	Solution	(24/-65 (120/-25	1/.9/.1		Liquid polymer	Freon 113 solvent	T8,p16
33. CH_2CH_2O	Bulk	96/-25	2/1/1		Tacky gum		P6,p4
34. $F_2C=CFBr$	Bulk	12/-78 to 25	1/1/.25	92	Elastomer	Terpolymer, 9.4 mole % $CF_2=CFBr$ Tg=-45°C	P7,p10

Table IV

NITROSO TERPOLYMERS ($CF_3NO/F_2C{=}CF_2/A$ (continued)

Monomer A	System	Time,hr/ Temp°C	Molar Ratio	Conversion %	Product	Remarks	Reference
35. $F_2C{=}CFBr$	Bulk	12/-78 to 25	1/1/.50	84	**Elastomer**	**Terpolymer, 21.7 mole % CF_2CFBr Tg=-35°C**	**P7,p10**
36. $F_2C{=}CFBr$	Bulk	12/-78 to 25	2/1/1	89	**Elastomer**	**Terpolymer 31 mole % CF_2CFBr Tg=-21°C**	**P7,p10**
37. $NOCF_2CF_2COOH$							**3M Final**
38. $CH_2{=}CHCN$	Bulk	72/-30			**Gum**	No $CH_2{=}CHCN$ in polymer	P8,p12
39. $CF_3SCF{=}CF_2$	Bulk	48/-38	.01/.009/.001		Polymer	**Viscous, Pale blue thioether recovered**	**P2,p15**
40. $CF_3SCF{=}CF_2$	Bulk	65/-30	5/5/1		White gum		**P7,p10**
41. $CF_2{=}CFCH{=}CH_2$	Suspension	48/-30	.22/.17/.05	17	Elastomeric gum		**P8,p11**
42. $CF_2{=}CFCF{=}CF_2$	Suspension	48/-30	.08/.06/.02	50	Elastomeric gum		**P8,p11**
43. $CF_2{=}CFCF{=}CF_2$	Bulk	48/-30	1/1/.2	33	Gum	$[\eta] = 0.355$	**P7,p10**
44. $CF_2CFCF{=}CF_2$	Bulk	48/-30	1/-/1	17	Elastomeric gum	(Copolymerization)	**P8,p11**
45. $CF_2{=}CFCF{=}CF_2$	Suspension	72/-20	2/1/1	47	Polymer	**Viscous sticky liquid**	**P5,p11**
46. $CF_2{=}CFCF{=}CF_2$	Suspension	2/1/1		37	Polymer	Viscous sticky liquid	**P5,p11**
47. $\underbrace{CF_2CF{=}CF}CF_2$	Bulk	72/-20	2/1/1	14	Viscous liquid	No monomer A incorporated	**P5,p12**
48. $CH_2{=}CHCH{=}CH_2$	Bulk	48/-30	.043/.037/.005	88	Viscous liquid	Decomposes rapidly in air	**P8,p11**
49. $CF_2{=}CFCF_2CFCl$	Suspension	24/-20	11/8/3	17	Viscous liquid		**P5,p12**

50. $CF_2=CFCH=CH_2$	Suspension	72/-20	2/1/1	39	Polymer	Viscous sticky liquid	P8,p11
51. $CF_2=CFCH=CH_2$	Suspension	24/-20	3/2/1	38	Polymer	Viscous sticky liquid	P5,p11
52. $CF_2=CFCH=CH_2$	Suspension	20/-20	2/1/1	33	Polymer	Viscous sticky liquid	P5,p11
53. $CF_2=CFCH=CH_2$	Suspension	0/-20	2/1/1	--	Polymer	Exploded after 5 mins.	P5,p11
54. $CF_2=CFCH=CH_2$	Bulk	12/-30	1/1/2	39	Gum	$[\eta] = 0.14$	P7,p10
55. $CF_2=CFCH=CH_2$	Bulk	0/-78	2/1/1	--	--	Exploded	P7,p10
56. $CF_2=CFCH=CH_2$	Bulk	0/-78	2/1/1	--	--	Exploded	P7,p1
57. $NO(CF_2)_3COOH$						See VB	
58. $CH_2=CHOC_2H_5$	Bulk	144/-20	2/1/1	50	Polymer	Clear viscous liquid	P5,p12
59. $CF_2=CFSi(CH_3)_2Cl$	Bulk	48/-25	2/1/1	--	--	Clear liquid, no silane incorporated	P6,p10
60. $CF_2=CFCH=CH_2$	Bulk	72/-30	3/2/1		Gum	Clear elastomer	P6,p10
61. $CF_2=CFCH_2CH=CH_2$	Suspension	48/-20	2/1/1	33		Brown viscous liquid	P5,p11
62. $CF_2=CFCF_2COOCH_3$	Bulk	48		77	Elastomeric gum	No ester incorporated	P8,p12
63. $NO(CF_2)_3COOCH_3$	Bulk	48/-30		50	Elastomeric gum	Ester incorporated	P8,p12
64. $CH_2=C(CH_3)CH=CH_2$	Bulk	-10	.04/.025/.025	--		Exploded	P7,p11
65. $CH_2=C(CH_3)CH=CH_2$	Bulk	-10	.03/03/01	--		Exploded	P7,p11
66. $CH_2=C(CH_3)CH=CH_2$	Bulk	24/-78	.03/.02/.01	53	Gum	Tacky, turns brown	P7,p11
67. $CF_2=CFCF_2COOEt$	Bulk	48/-30			Elastomeric gum	No ester incorporated	P8,p12

Table IV (continued)

NITROSO TERPOLYMERS ($CF_3NO/F_2C{=}CF_2/A$)

Monomer A	System	Time,hr/ Temp°C	Molar Ratio	Conversion	Product	Remarks	Reference
68. C_6H_5NO	Solution					Black non-elastomeric solid	T4,p9
69. C_6F_5NO	Solution		.9/1/.1	76	Elastomer		T4,p9
70. C_6F_5NO	Solution		.8/1/.2	78	Elastomer		T4,p9
71. C_6FNO	Solution		.5/1/.5	86	Stiff elastomer		T4,p9
72. C_6F_5NO	Solution		.2/1/.8	58	Resin		T4,p9
73. C_6F_5NO	Solution		0/1/1	50	White powder	(Copolymerization)	T4,p9
74. BrC_6H_4NO	Solution		-1/1/1	42	Brittle solid	Rubbery 55°C CH_2Cl	T7,p11
75. BrC_6H_4NO	Solution		Trace/1/1	40	Brittle solid	Rubbery 55°C CH_2Cl_2	T7,p11
76. BrC_6H_4NO	Solution		.3/1/.7	43	Brittle solid	Rubbery 50°C	T7,p11
77. BrC_6H_4NO	Solution		.5/1/.5	40	Elastomer		T7,p11
78. BrC_6H_4NO	Solution		.7/1/.3	85	Elastomer		T7,p11
79. BrC_6H_4NO	Solution		.9/1/.1	79	Elastomer		T7,p11
80. BrC_6H_4NO	Solution		.9/1/.1	82	Elastomer		T7,p11
81. NOC_6H_4COOH	Solution	24/-25	-/1/1		Resin	Solvent CH_2Cl_2:Et_2O	T8,p17
82. NOC_6H_4COOH	Bulk	24/-25	.9/1/.1		Gum	40% Terpolymer	T8,p17
83. NOC_6H_4COOH	Bulk	24/-25	.9/1/.1		Gum	60% Terpolymer	T8,p17

84. NOC_6H_4COOH	Solution	24/-25	.9/1/.1		Liquid	Solvent CH_2Cl_2:Et_2O	T8,p17
85. NOC_6H_4COOH	Solution	24/-25	.5/1/.5		Gum	Solvent CH_2Cl_2:Et_2O	T8,p17
86. NOC_6H_4COOH	Solution	24/-25	.9/1/.1		Soft rubber	Solvent CH_2Cl_2: $(CH_3)_2CO$ Product soluble in FC43; Freon 113 mixture	T8,p17
87. C_6F_5NO	Solution	24/-40	9/10/1		Semi-elastomeric tacky gum	Solvent CH_2Cl_2	P1,p20
88. $CF_2{=}CFS:(CH_3)_2OEt$	Bulk	240/-35	2/1/1	53	Clear liquid	No silane incorporated	P5,p12
89. NOC_6F_4COOH							T8,p12
90. $CH_2{=}CHO(CH_2)_2OCH_2CH{=}CH_2$	Bulk	144/-78	2/1/1	52	Brown gum		P5,p12
91. $(CF_2{=}CFCF_2)_2CFCl$	Bulk	48/-30	038/027/011	52	Viscous liquid	Some diene incorporated	P7,p12
92. $CF_2{=}CFC_6H_4CH_3$	Bulk	48/-30	.03/.025/.005	63	Viscous liquid	Styrene incorporated	P7,p12
93. $CF_2{=}CFC_6H_4COOH$	Solution	48/-30	.03/.025/.005	62	Viscous liquid	No acid incorporated	P7,p12
94. $CF_2{=}CFC_6H_4COONa$	Suspension	72/-30	.03/.025/.005	62	Gum	No acid incorporated	P7,p12
MISCELLANEOUS TERPOLYMERIZATIONS							
95. $CF_2{=}CFCH{=}CH_2/CF_2{=}CFCF{=}CF_2/CF_3NO$			1/12			Exploded at -25° bulk system	P6,p9
$CF_2{=}CFCH{=}CH_2/CF_2{=}CFCF{=}CF_2/CF_2{=}CF_2/CF_3NO$	Bulk	18/-25	.005/.005/.055/.032		Tacky gum		P6,p9
$CF_3\underset{O}{CF{-}CF_2}/CF_3CF{=}CF_2/CF_3NO$	Bulk	48/-25	/1/2		Tacky gum		P6,p9

possible to continuously produce CF_3NO of at least 99 percent purity by metering trifluoroacetylnitrite into a reactor containing an inert diluent at reflux. Decarboxylation is affected in the vapor phase and the CF_3NO swept continuously from the reactor zone through a purification train into traps at liquid nitrogen temperature where it is condensed. The inert diluent (triperfluorobutylamine-FC-43) is returned to the reactor by a condenser. CF_3NO purification is affected by a 5 percent caustic scrubber to remove CO_2 and NO_2, a drying tower and finally a molecular sieve column at -100°C to remove non-acidic nitrogen oxides and CF_3NO_2. This unitized operation was capable of producing one pound per hour of pure CF_3NO which could be stored in gas storage bottles for extended periods of time at -20°C without change or detrimental effect on its use in polymerizations.

Figure 1 illustrates the equipment flow chart for CF_3NO production. Tetrafluoroethylene, C_2F_4, for the scaled up production of nitroso rubber was manufactured in the Thiokol TFE facilities in Moss Point, Mississippi. For the initial polymer program tetrafluoroethylene was prepared by the debromination of tetrafluorodibromoethane. This was accomplished by a refluxing suspension of activated zinc in methanol. The efficient vapors were precooled by a cold water condenser and then passed through a -35°C condenser to remove any dimethyl ether which might have been produced by the reaction of zinc and methanol. The product was then condensed at liquid nitrogen temperatures under a slight helium pressure to preclude contamination by atmospheric oxygen. When the reaction was complete the condensate was warmed to -76°C transferred in vacuum to a stainless steel storage cylinder containing an inhibitor. The Equipment Flow Chart for the tetrafluoroethylene preparation is shown in Figure 2.

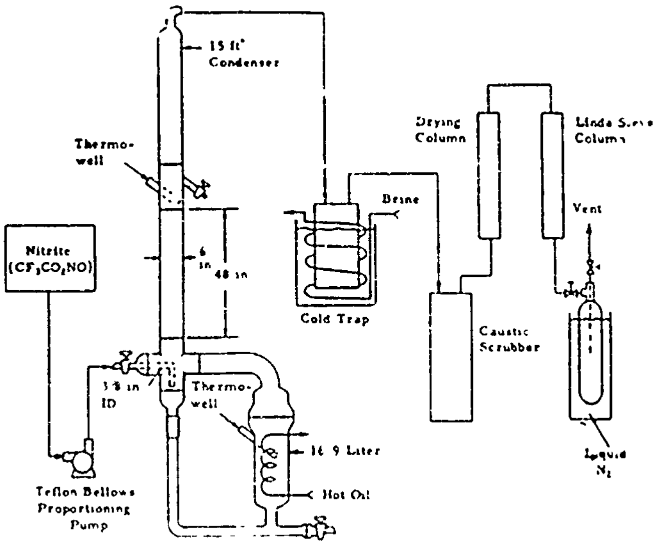


Figure 1. Equipment flow chart for CF_3NO production

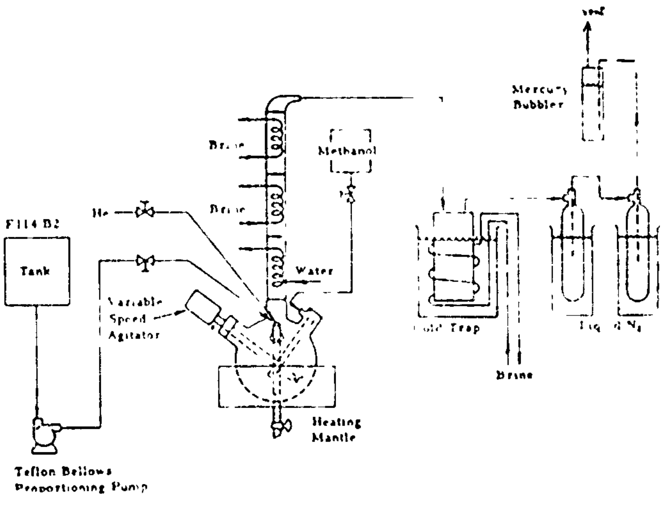


Figure 2. Equipment flow chart for C_2F_4 production

Thiokol's copolymer facility consisted of two reinforced concrete bays in which the glass monomer production equipment and the 25 gallon stainless steel polymerization reactor were housed. A circulating brine system cooled by direct injection of CO_2 furnished refrigeration for the polymerization and necessary cold traps. This was accomplished by a 100 gallon tank equipped with a stainless steel 7-1/2 HP brine pump. A 12 kw oil heating system was piped to the pyrolysis unit. The equipment flow chart is given in Figure 4.

In evaluating the reaction variables which could have significant effect upon the product it was found that the purity of the CF_3NO was critical. In addition certain solvents could act as chain transfer agents as for example, carbon disulfide or those containing hydrogen or chlorine. The optimum polymerization time at -25°C was found to be about 24 hours. The purity of lithium bromide used as a freezing point depressant was found not to be critical. The quantity of magnesium carbonate used did not particularly effect better suspensions or yield significantly variable products. The heat of polymerization was determined to be 74.8 ± 0.5 K cal/mole using the CF_3NO/C_2F_4 monomer ratio.

Since the nitroso monomer is itself the initiator in the polymerization of the nitroso rubber, very special polymerization conditions are required to assure the formation of a high molecular weight polymer. Suspension, bulk and solution polymerizations have been investigated. The suspension procedure described herein is typical of one that has consistently produced high molecular weight nitroso rubber: a 150 cc. stainless steel cylinder is charged with 70 cc. of Li Br solution (53g. Li Br/100g. H_2O, freezing point -45°C), 2.0g. $MgCO_3$ and 8.0g. each of CF_2CF_2NO. The cylinder is agitated at a temperature of -25°C for 20 hours. At the end of this time, the unreacted monomers are vented and the contents of the cylinder removed. The resulting suspension is allowed to settle and the supernatant liquid decanted. The precipitate is washed in water and then stirred in concentrated HCl until no further reaction is noticed. The conversion may be as high as 86 percent of the expected high molecular weight polymer. The material flow chart for the scale-up of this process is given in Figure 3. Two hundred pounds of CF_3NO/CF_2CF_2 copolymer have been produced in this facility in lots of approximately 30 pounds. Yields run as high as 85 percent.

D. Basic Polymer Property Studies

In 1962 the U. S. Army Natick Laboratories began funding a program with Monsanto Research Corporation to carry out certain physical and rheological properties on the CF_3NO/CF_2CF_2 copolymer gumstock. The goal of this program was to obtain basic information about the chemical structure of this polymeric systems in order to have a fuller understanding of its potential.

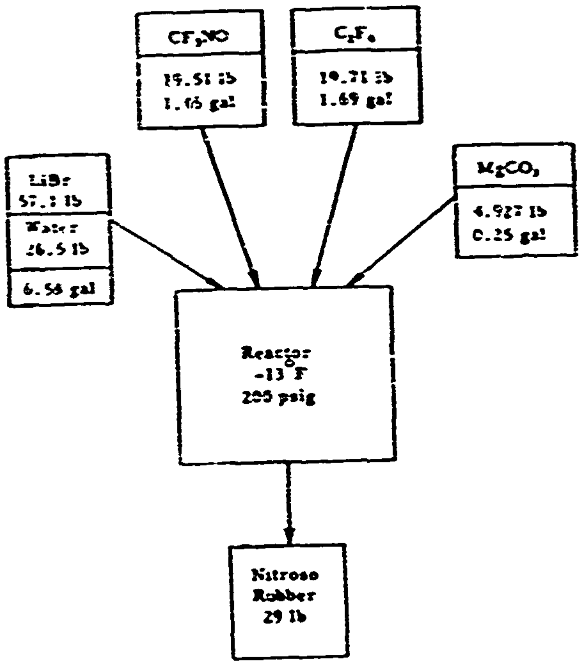


Figure 3. Material flow chart for nitroso rubber

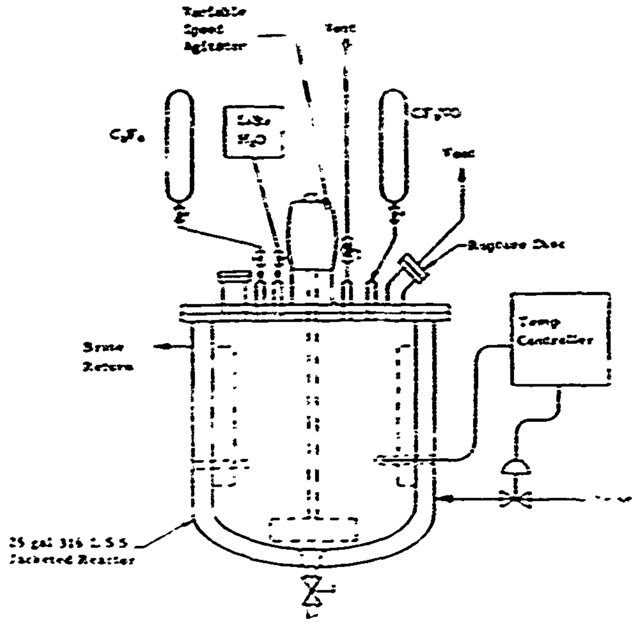


Figure 4. Equipment flow chart for nitroso rubber production

1. Solvent Properties

Useful solvents for measuring physical and rheological properties of CF_3NO/CF_2CF_2 gumstock were found to be FC-75, (a mixture of isomers of perfluorocyclic ether, $C_8F_{16}O$, manufactured by 3M Co.), Freon 113, trichlorotrifluoro ethane and perfluorotributylamine, FC-43.

2. Infrared Spectroscopy

Inasmuch as no infrared frequency assignments were found for the perfluorocarbons in standard sources, only tentative conclusions have been drawn. Absorptions for CF_3NO/CF_2CF_2 copolymer gumstock appear at 830 cm^{-1} believed due to $-CF_2-CF_2-$ bend, at 745 cm^{-1} due to either $-CF_2-CF=$ or $=CF-CF=$ either of which appear in the idealized average structure obtained by NMR. Significantly, no $-CF(CH_3)_2$ which would appear at 730 cm^{-1}, was seen nor was $-CF_2CF_3$ present which would appear at 735 cm^{-1}. Figure 5 shows a typical CF_2NO/CF_2CF_2 spectrum.

3. Nuclear Magnetic Resonance Spectroscopy

Shown in Figure 6 is a typical NMR spectrum obtained for a CF_3NO/CF_2CF_2 nitroso rubber gumstock. Listed in the following table are these peaks and their assignments. The structure is defined as

$$-\left[N(CF_3)CF_2CF_2O\right]_x-$$

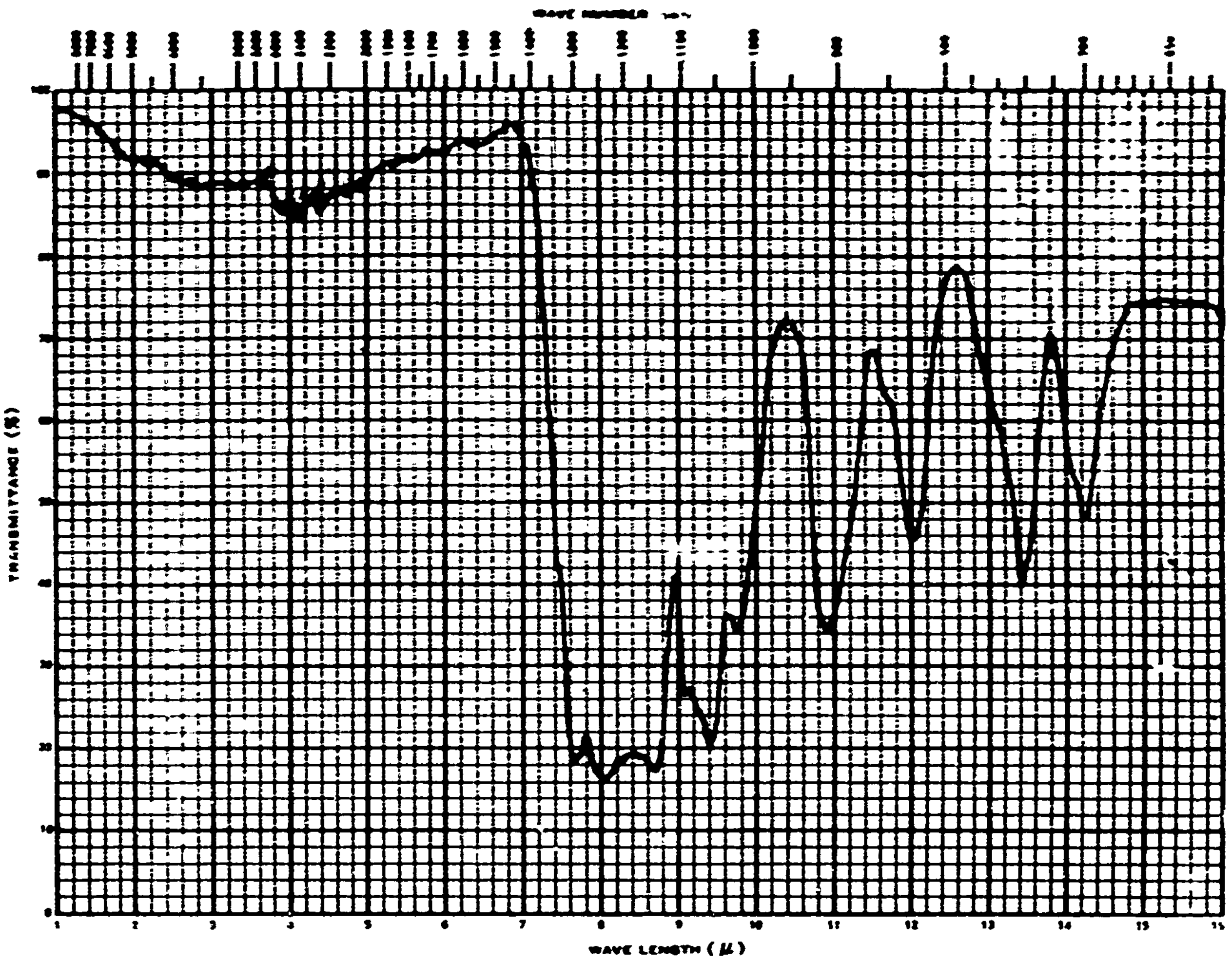
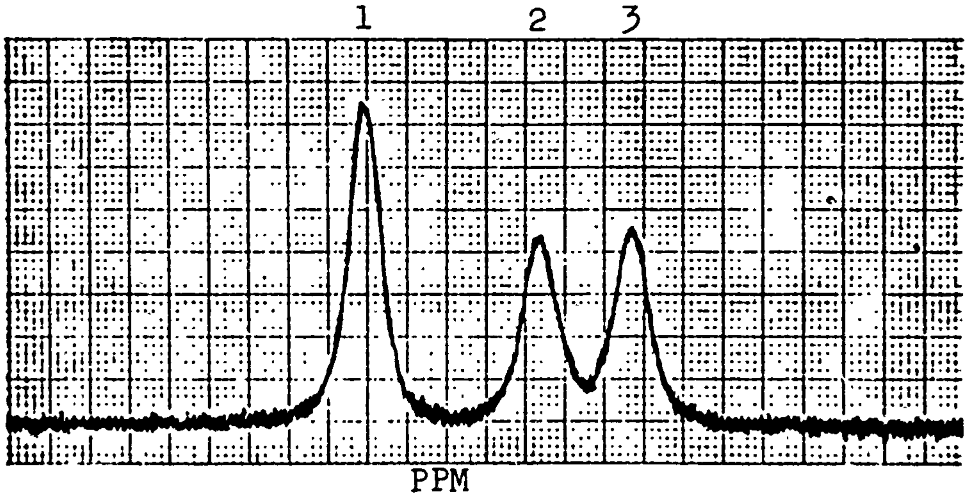


Figure 5. Infrared spectrum (2-15u) of 56703-3 nitroso gum

RF Frequency: 40.0 Mc
Nuclei: F^{19}
Reference: Trifluoro acetic acid



Peak		1		2	3				
PPM		-11.6		+11.6	+24.0				
Area Ratio		3		1.8	1.8				

Figure 6. Nuclear magnetic (F^{19}) resonance spectrum of 56703-3 nitroso gum

Table V

NMR SPECTROSCOPY OF NITROSO RUBBERS*

Sample No	Chemical Shift of Peaks, ppm			Area Ratio of Peaks		
	1	2	3	1	2	3
XP5675	-11.4	+11.5	+24.0	3.0	1.9	2.0
XP5702	-11.4	+11.7	+24.2	3.0	2.0	1.9
XP5812	-11.3	+11.7	+24.8	3.0	1.9	2.0
XP5887	-11.5	-11.5	+24.0	3.0	2.0	1.9

$-N(CF_3)-$ $-N-CF_2CF_2-$

$-OCF_2CF_2-$

---

*F19 Resonance @ 40 Mc
Reference trifluoro acetic acid

4. X-ray Diffraction

All samples of CF_3NO/CF_2CF_2 were found to be non-crystalline as shown by their diffuse diffraction patterns

5. Glass Transition Temperature (rebound method)

Figure 7 shows the rebound tester used to determine the glass transition of a material at 1000 cps by measuring the rebound of a small ball bearing from the surface of the specimen The percent rebound correlates to the logarithmic decrement since this decrement goes through a maximum where the elastic modulus decreases rapidly from a glassy state to a rubbery state Data of percent rebound versus temperature for a typical CF_3NO/CF_2CF_2 copolymer is shown in Figure 8. The specimen was tested from -100°C up to 40°C. The minimum rebound region of -18°C is the 1000 cps glass transition temperature Using an equivalence of 7°C per decade of frequency (approximation) the 0.1 cps glass transition (such as determined by the torsion pendulum) would be -46°C.

6. Thermogravimetric Analyses

A TGA in helium and in air was conducted on cured CF_3NO/CF_2CF_2 samples, the results of which are shown in Figure 9. In air the rubber violently decomposed at 270°C.

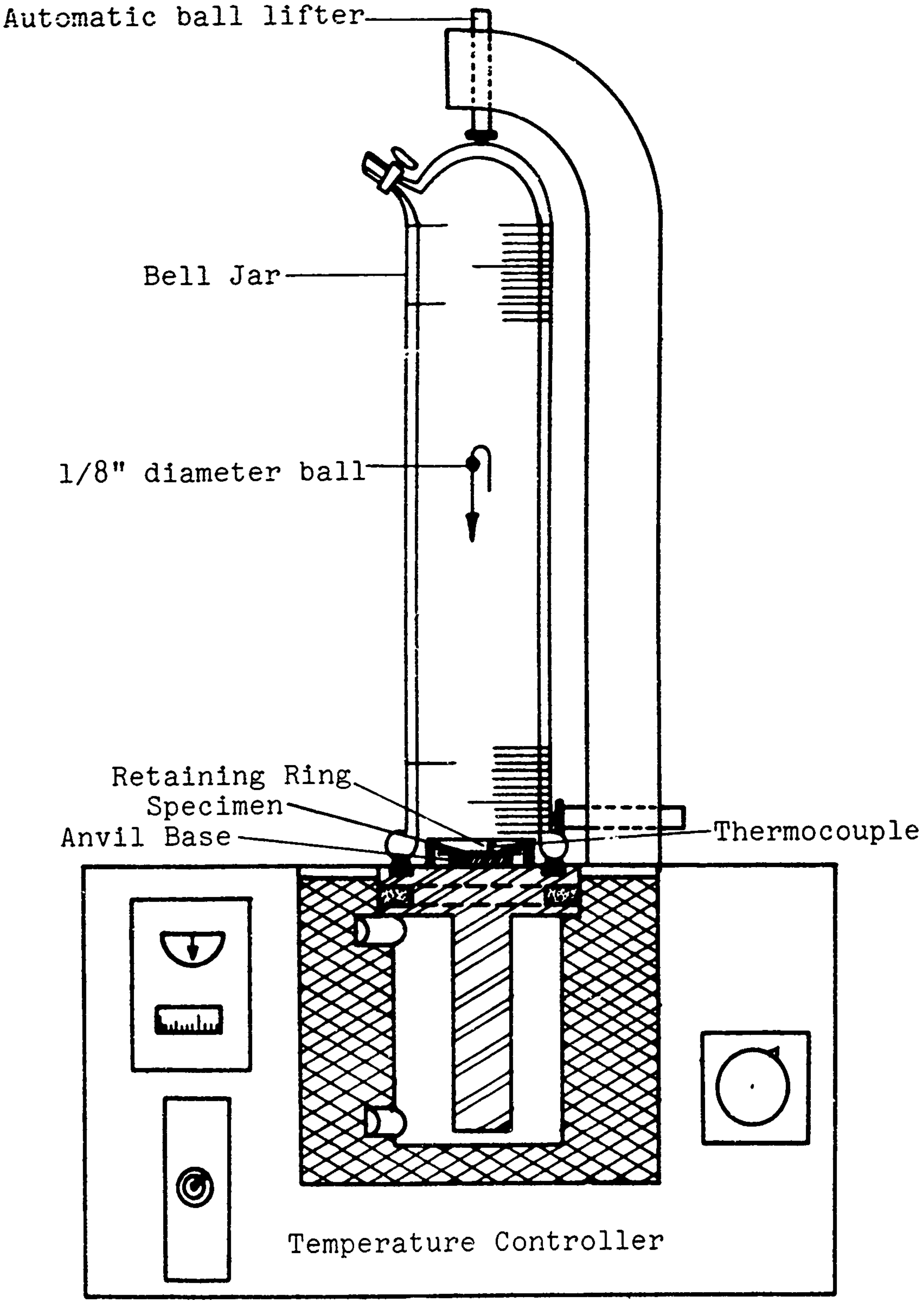


Figure 7. Rebound tester for 1000 cycles per second modulus

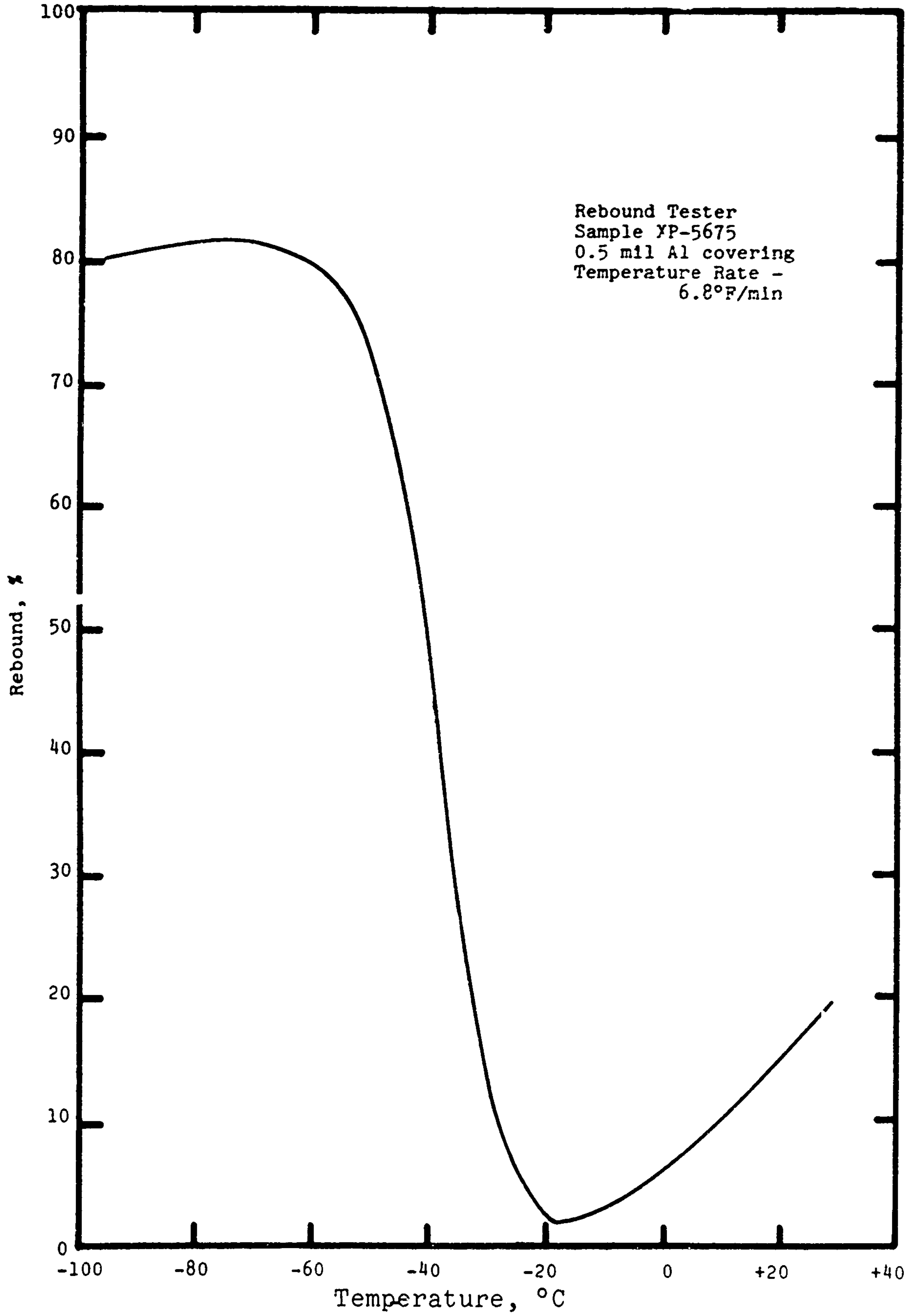


Figure 8. 1000 cycle per second modulus by rebound on sample XP5675

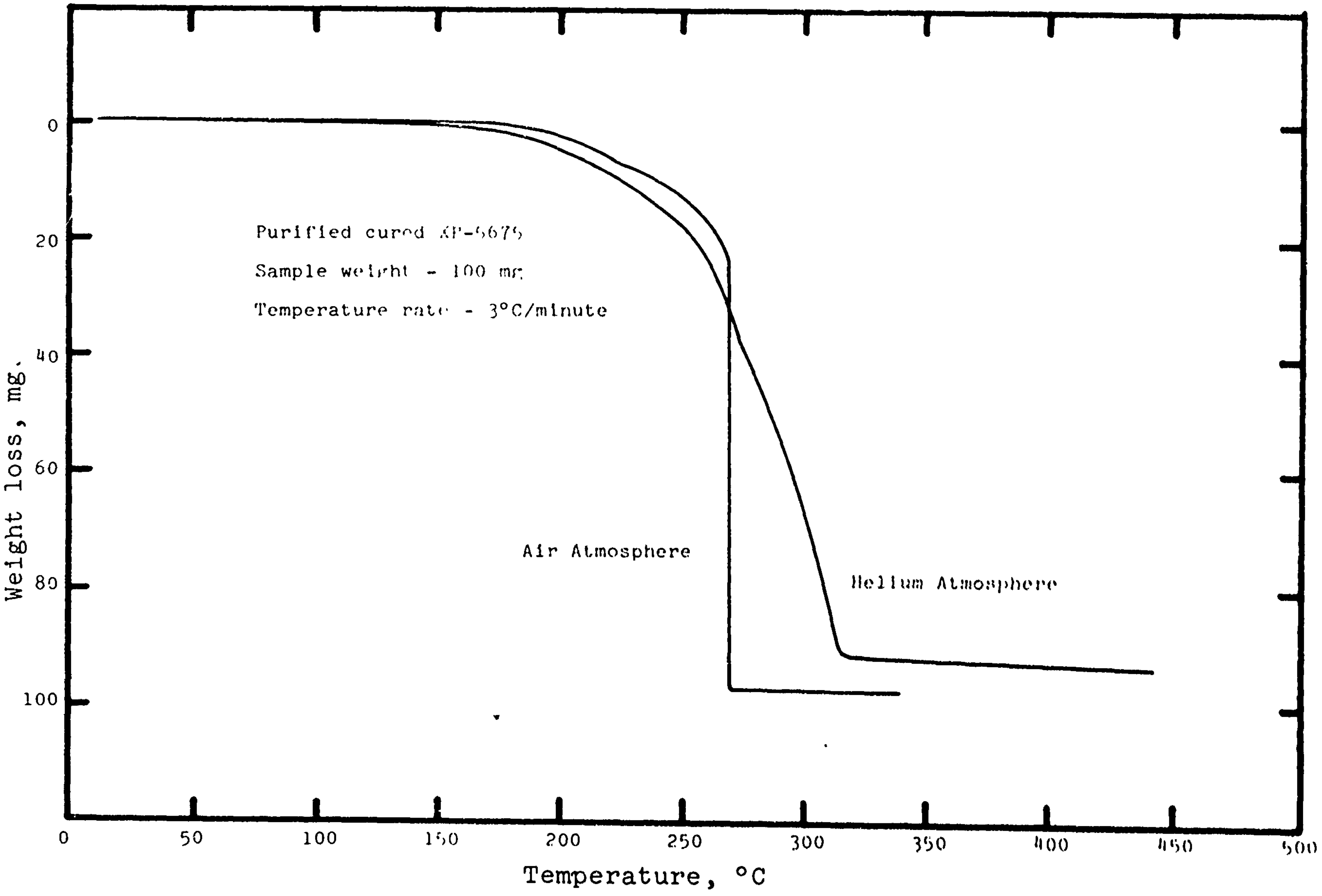


Figure 9. **Thermogravimetric analysis in air and helium of an amine-cured nitroso copolymer**

7. Linear Thermal Expansion Coefficients (apparent)

Coefficients of linear thermal expansion by means of a dynamic modification of ASTM-D596-44 were conducted on samples of CF_3NO/CF_2CF_2 gumstock. A quartz dilatometer was used. The dynamic modification consisted of periodic determinations of expansion as a function of temperature at a rate of 1°C/min. The term "apparent" is used because of the non-equilibrium nature of these determinations. A temperature range of -75°C up to about 10°C above the glass transition temperature was covered. Glass transition temperatures Tg, where $(\partial \Delta l/\partial T)=0$ were determined as a result of expansion measurements and is shown in Table VI.

Table VI

APPARENT LINEAR THERMAL EXPANSION COEFFICIENTS

OF CF_3NO/CF_2 NITROSO GUMS

Sample	Apparent Linear Expansion Coefficient °C-1	Temperature Range	Tg^{b}0°C	Tg,^{c}0°C
XP5675^d	(7.2 x 10-5)	-67 to -52	-46	-60^c
	(1.2 x 10-4)	-52 to Tg		
XP5702	(8.2 x 10-5)	-67 to -52	-46	-45
	(1.2 x 10-4)	-52 to Tg		
XP5812	(7.6 x 10-5)	-72 to Tg	-49	--
XP5887	(5.7 x 10-5	-72 to -62	-48	--
	(8.8 x 10-5)	-62 to Tg		

a. "Apparent" due to temperature use of 1°C/min.
b. From thermal expansion data
c. From Clark-Berg determinations
d. Devolatilized 16 hr at 80°C and 3 mm Hg
e. Sample contained volatiles

V. Properties of Nitroso Rubber

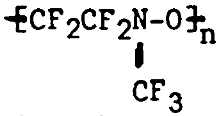
For the great majority of nitroso elastomers prepared to date only mininal data has been compiled. Certain selected systems have been subjected to intensive investigations and considerable data has been accumulated. This is particularly true for the CF_3NO/CF_2CF_2 copolymer system and to a lesser extent the $CF_3NO/CF_2CF_2/NO(CF_2)$ (3 or 4) COOH terpolymer systems. The properties of fluorinated elastomers have received considerable attention and reviews by Montermoso[22,23] and others[24-26] describe their properties in some detail. Summations of various phases of the U. S. Army sponsored Nitroso Rubber Program have been described in publications by Montermoso[27-29]. Recent results describing the chemical and physical properties of nitroso rubber co- and terpolymers have been reported by Griffis and Henry[30,31].

A. Copolymers

The properties of the raw polymer of nitroso rubber obtained from the reaction of CF_3NO and $CF_2{=}CF_2$ are described in Table VII. As an equimolar copolymer it is a colorless, transparent rubber that can be processed on regular rubber compounding equipment. The rubber is completely nonflammable. When directly exposed to a flame, some gas is evolved which tends to put out the flame; however, no charring of the rubber takes place.

Table VII

NITROSO RUBBER (raw polymer)

Structure	 $\left[CF_2CF_2\underset{\overset{\mid}{CF_3}}{N}-O\right]_n$
Crystal structure	Amorphous
Mol. Wt.	Approx. $1.3X10^6$
Specific gravity	1.93
Dielectric constant	2.41 @ 60 cycles
Tg	-51°C
Solubility	- soluble in - fluorocarbons, FC-43, Freon 113 insoluble and unaffected in hydrocarbons

Reaction: aliphatic and aromatic amines degrade or crosslink.

Thus far, the only successful cure has been with triethylenetetramine and even this cure requires extended periods of time at temperatures near the decomposition temperature of the copolymer. Higher molecular weight copolymer samples are definitely more difficult to cure, using the amine treatment, than lower molecular weight materials. Above 212°F. sponging occurs rather rapidly.

The properties of the compounded rubber and the recipe used for compounding is given in Table VIII.

Table VIII

NITROSO RUBBER (compounded)

Recipe:	
Polymer	100
Hi Sil 303	15
TETA	1.25
HMDA	2.5
Properties:	
Tensile strength, (Psi)	1230
Stress at 300% Elongation, (Psi)	410
Ultimate elongation, %	640
Hardness, Shore A	60
Tensile set at break, %	34
Low temperature properties:	
Temperature retraction, TR50	-36°C
Gehman stiffness, T_5	-41°C
Chemical resistant properties, volume swell, % in following:	
70/30: isoctane/toluene	2
MEK, ether	2
Perchloroethylene	3
Nitrogen Tetroxide	1

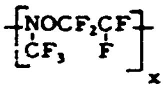
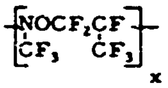
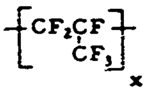
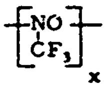
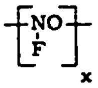
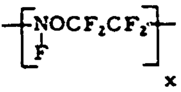
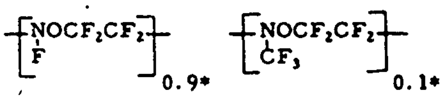
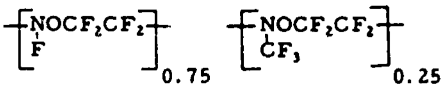
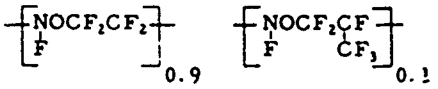
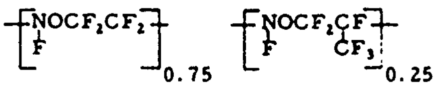
Ozone resistance: after 24 hrs @ 175 ppm @ 150°F. No cracks
Flammability: will not ignite

In its uncompounded state nitroso rubber copolymer is a white to amber colored dense elastomer with a fluorine content of 66.8%. Its low glass temperature results from the low attractive forces between chains and to free rotation about the -N-O bonds in the repeating unit. A study of the glass transition temperatures for various nitroso and fluorocarbon polymers has been compiled by Thiokol (T-1) and as shown in Table IX.

Hypothetical Tg values such as those found in Table IX are subject to considerable variation. The Tg of tetrafluoroethylene for example has been calculated to be anywhere from -112°C to 130°C. Stump[32] and Boyer[33], believe it to be -50°C based upon experimental evidence and subsequent use of the Fox equation ($Tg_{1,2} = {}^{w1}/Tg, + {}^{w2}/Tg_2$). The values as shown in Table IX, in a relative manner, do indicate the theoretical potential for developing lower temperature flexible fluoroelastomers.

Table IX

GLASS TRANSITION TEMPERATURES FOR VARIOUS NITROSO AND FLUOROCARBON POLYMERS

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

---

* weight fractions

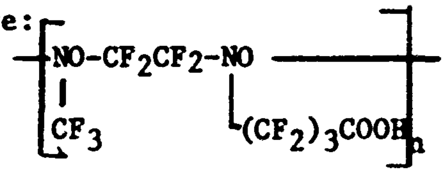
B. Properties of Nitroso Rubber Terpolymer (carboxyl-nitroso rubber)

Properties of the carboxyl-nitroso raw polymer are given in Table X. The beginning of a family of these terpolymers have been synthesized, in which nitrosoperfluoropropionic acid and nitrosoperfluorobutyric acids have been used in varying mole ratios of 0.5 to 2.

Table X

CARBOXYL-NITROSO RUBBER

Chemical Structure:



$$\left[\begin{array}{ll}\text{NO-CF}_2\text{CF}_2\text{-NO} & \\ | & \quad | \\ \text{CF}_3 & \quad (\text{CF}_2)_3\text{COOH}\end{array}\right]_n$$

Mole Ratio: 48/50/2

Crystal Structure: Amorphous

Molecular Weight: 0.62 (FC43); - 0.81 X 10^6

Solubility: Soluble in fluorocarbons, FC43 and Freon 113

The compounding recipe and the properties of the vulcanized carboxyl-nitroso rubber are given in Table XI. The incorporation of the acid termonomer into the nitroso polymer has resulted in decided improvement of tensile strength properties, while retaining the excellent chemical, low temperature and flammability characteristics. It is interesting to note the increased volume swell of this compound in methyl ethyl ketone over the copolymer.

Nitroso rubber gumstock appears to be resistant to chlorine trifluoride ClF_3. Amine cured vulcanizates of nitroso rubber copolymer and metal salt vulcanizates of carboxyl-nitroso rubber terpolymer, are converted by chlorine trifluoride, to substances resembling the original gumstock, with losses of weight approximately corresponding to the amount of curing agent present. The rate of degradation appears to depend upon the metal salt used in the vulcanization and upon the temperature[34].

Nitroso elastomer gumstocks containing no hydrogen atoms (completely fluorinated) are extremely resistant to corrosive environments. Of particular note are the resistance to strong oxidizing agents such as N_2O_4 or fuming acids. In the presence of strong bases the elastomer degrades. Table XIA indicates the stability of nitroso elastomers to a variety of atmospheres.

Table XI

CARBOXYL-NITROSO RUBBER (compounded)

Compounding Recipe:	Polymer - 100 Silstone 110-20 Chromium triperfluoroacetate 8
Properties of compounded polymer:	
Tensile strength, psi	2170
Ultimate elongation, %	720
Set at break (10 min.), %	30
Hardness, Shore A	57
Low temperature properties:	
Temperature retraction, TR-50	-41°C
Gehman stiffness, T_5	-44°C
Chemical resistance:	
Volume swell, %, in following:	
70/30: isooctane/toluene	2
MEK	52
Dichloroethane	4
Nitrogen tetroxide	6
Flammability - will not ignite	

C. Properties of Special Interest

Storable Oxidizers:	Nitrogen tetroxide, N_2O_4, has no effect.* Elemental Fluorine: unaffected by fluorine at room temperature.
Ozone Resistance:	No cracks after 24 exposure to 175 ppm @ 150°F.
Sunlight Resistance:	No cracks after 2 months of exposure @ 20% elongation.

*Various nitroso elastomers have been evaluated for N_2O_4 resistance. The nitroso rubber copolymer gum has shown no indication of degradation after 60 days immersion in liquid N_2O_4 at 150°F. Carboxy-containing nitroso terpolymers cured with chromium triperfluoroacetate appear to be unaffected after three weeks in liquid N_2O_4 at 100°F[35]. A summation of these results with carboxyl nitroso elastomers is shown in Tables XIB, C and D. It was noted that although the cured carboxyl nitroso elastomers swelled in many liquids, in most cases the liquid was a solvent of the curing agent $(CF_3COO)_3Cr$. It was thus possible to speculate that the solvation of the $(CF_3COO)_3Cr$ caused the swelling.

Table XIA

NITROSO RUBBER COPOLYMER CF_2NO/CF_2CF_2

(Unvulcanized Gumstock)

Solvents and chemical agents having no significant affect, solvation, swell or degradation.

	Temperature
50:50 xylene hexafluoride:chloroform	steam bath
2-Butanone (MEK)	steam bath
Trichlorobenzene	steam bath
1,4-Dioxane	steam bath
3:1 Heptane:MEK	steam bath
Chlorocyclohexane	steam bath
3:1 MEK:Heptane	steam bath
50:50 MEK:Heptane	steam bath
Xylene Hexafluoride (XHF)	steam bath
1,4-dichlorobutane	steam bath
Benzotrifluoride (BTF)	steam bath
Trifluoroethanol (TFE)	steam bath
Carbon tetrachloride	steam bath
Diethyl Ether	steam bath
n-Butyl Chloride	steam bath
Tetraethyl orthosilicate (TEOS)	steam bath
para-chloro-benzotrifluoride	steam bath
Chlorobenzene	steam bath
Trichloroethylene	steam bath
Chloroform	steam bath
Methyl chloroform	steam bath
β,β -dichloroethyl ether	steam bath
Methyl Perfluoro Butyrate (MFB)	steam bath
Distilled water	212°F
Conc. ammonium hydroxide	reflux
Furfural	212°F
Skydrol	212°F
Skydrol 500	212°F
JP6 Fuel	212°F
ASTM ref. oil #1	212°F
ASTM ref. oil #3	212°F
MIBK	212°F
Xylene	212°F
10% aq. acetic acid	212°F
10% aq. sulfuric acid	212°F
Conc. hydrochloric acid	158°F
Conc. nitric acid	158°F

Table XIB

RESISTANCE TO ClF_3 GAS OF VARIOUS VULCANIZATES(*) OF CARBOXYL-NITROSO ELASTOMERS

Elastomer(**) (100 p. by wt.)	(1)	(0)	(4)	(2)	(0)	(0)	(2)	(5)
Silstone 110, p. by wt.	-	-	-	-	25	25	-	20
Curing Agent, formulae	ZnO	MnO	CdO	Cd(OH)	BPA Epoxy	$HO(CH_2)_2OH$	$HO(CH_2)_2OH$	$Cr(CF_3COO)_8$
Curing Agent, p. by wt.	5	4	8	2	3	3	5	8
Press-Cure	1 hour at 200°F							
Oven-Cure (post-cure)	Stepwise to the indicated temperatures:							
hours/°F	22/350	1/400	0.5/350	0.25/350	21/225	23/350	1/350	1/300
Resistance to ClF_3:	Observations after 4 hours exposure at indicated temperatures:							
at 25°C, appearance	No ch.	No ch.	No ch.	No ch.	Degraded	Warped	No ch.	No ch.
weight	-	-1.8%	+0.8%	0.0	-42.7%	-21.4%	-4/1%	-19.2%
at 50°C, appearance	No ch.	-	-	No ch.	-	-	Melted	-
weight	-	-	-	-0.6%	-	-	-5.5%	-
at 100°C, appearance	Sl. Flow	-	-	-	-	-	-	Melted
weight	-	-	-	-	-	-	-	-19.3%
at 120°C, appearance	-	-	-	No ch.	-	Gumstock	-	-
weight	-	-	-	-2.2%	-	-27.6%	-	-
at 135°C, appearance	-	Melted	-	-	Gumstock	-	-	-
weight	-	-8.7%	-	-	-42.8%	-	-	-
at 150°C, appearance	Melted	-	Sl.Flow	-	-	-	-	-
weight	-	-	-6.2%	-	-	-	-	-

Notes: (*) Approx. 2 gm. samples were compounded on a Micro-Mill

(**) --(0) Terpolymer: $C_2F_4/ONCF_3/ONCF_2CF_2COOH$, mole ratio = 100/97/3

--(1) " : $C_2F_4/ONCF_3/ONCF_2CF_2CF_2COOH$, mole ratio = Unknown

--(2) " : " / " / , mole ratio = 100/48/2

--(4) " : "/ " / " , mole ratio = 100/99.5/0.5

--(5) " : "/ " / " , mole ratio = 100/98.6/1.4

Table XIC

RESISTANCE TO ClF_3 GAS OF CARBOXYL-NITROSO ELASTOMERS(*) CURED WITH $Cr(CH_3COO)_3$ OR WITH $Cr(CF_3COO)_3$

Elastomer(**)(100p.by wt.)		(5)	(5)	(2)	(5)	(5)	1F4 Rubber(**)	Fluorel 2140	Teflon Film
Silstone 110, p. by wt.		20	-	-	-	-	Compounded	and	
Curing Agent, formulae		$Cr(CF_3COO)_3$	$Cr(CF_3COO)_3$	$Cr(CH_3COO)_3$	$Cr(CH_3COO)_3$	$Cr(CF_3COO)_3$		Cured	
Curing Agent, p. by wt.		8	8	4	4	4	(3M Co.)	(3M Co.)	(duPont)
Press-Cure		1 hour at 200°F							
Oven-Cure (post-cure)		Step-wise to the indicated temperatures:							
	hours/°F	1/300	1/300	0.5/350	12/300	12/200	-	-	-
Resistance to ClF_3		Observations after 4 hours exposure at the indicated temperatures:							
at 25°C,	appearance	No. ch.	No. ch.	No. ch.	No. ch.	No. ch.	No. ch.	No. ch.	No. ch.
	weight	-19.2%	-	-1.5%	-	-	+6.2%	+3.8%	+0.1%
at 50°C,	appearance	-	-	-	-	-	No. ch.	No. ch.	No. ch.
	weight	-	-	-	-	-	+7.1%	+4.7%	+0.3%
at 100°C,	appearance	Melted	-	-	-	-	-	-	-
	weight	-19.3%	-	-	-	-	-	-	-
at 120°C,	appearance	-	-	-	Melted	Melted	v.brittle	No. ch.	No. ch.
	weight	-	-	-	-8.1%	-7.9%	+6.7%	+8.3%	+0.3%
at 135°C,	appearance	-	Gumstock	-	-	-	-	-	-
	weight	-	-8.7%	-	-	-	-	-	-
at 150°C,	appearance	-	-	Sl.Flow	-	-	-	-	-
	weight	-	-	-6.0%	-	-	-	-	-

Notes: (*)--(2) Terpolymer: $C_2F_4/ONCF_3/ONCF_2CF_2CF_2COOH$, mole ratio = 100/98/2
(5) " : " / " / " , mole ratio = 100/98.6/1.4

(**)--Poly-(1,1-Dihydro-Perfluorobutyl Acrylate (Commercial Chemicals Div., 3M Co.)
A gasket made from this material was used effectively in presence of ClF_3 gas at room temp. for approx. 3-1/2 years (at intermittant exposure).

Table XID

FLUID RESISTANCE OF CARBOXYL-NITROSO ELASTOMERS(*) CURED WITH $Cr(CF_3COO)_3$

(8 p. by wt. $Cr(CF_3COO)_3$/100 p. by wt. ELASTOMER)

Original Properties	Appearance	-	Strength	Elong.
	Dk. Green	-	330 psi	600%

Aging Conditions: Samples (small dumbells) were placed in 50 ml. of liquids in 100 ml. single neck flasks fitted with the reflux condensers. All flasks were kept in an oil bath for 7 days at 110°C.(**)

Testing: Aged samples were tested wet (ASTM D471-57T)

	Liquids (Samples were aged in)	Appearance	Weight Change, %	Strength Retained, %	Elong. Retained,
1	Distilled water	No change	+26	70	92
2	Skydrol-500	Swollen	+109	-	-
3	JP-4 Fuel	Brown	0	109	107
4	FC-43 Solvent, Tech.	Swollen	+500	-	-
5	NH_4OH, 10% aq. soln.	Degraded	-	-	-
6	DMF Solvent, Tech.	Bleached	Swollen	Weak	-
7	Xylene, Tech.	Bleached	Swollen	Weak	-
8	Carbon-Tetrachloride, Reag.	Sl. Bleach	+4	67	72
9	Heptane, Tech.	Brown	0	127	110
10	Trifluoro-Ethanol, Tech.	Swollen	+39	56	78
11	H_2SO_4, 30% aq. soln.	No change	-2	285	132
12	NaOH, 10% aq. soln.	No change	+6	164	130
13	DMSO solvent, Tech.	Bleached	Swollen	Weak	-
14	Phenol, 5% aq. soln.	Swollen	+25	58	73
15	Ethylene Glycol, Reag.	No change	0	141	125
16	1,2-Dichloroethane, Reag.	No change	+4	83	87
17	Ethyl Alcohol, 50% aq.	No change	+8	73	88
18	Acetic Acid, 10% aq.	Swollen	+33	39	92
19	Ethyl Acetate, Tech.	Swollen	+53	36	66
20	MEK, Tech.	Swollen	+52	42	65
21	Benzene, Tech.	No change	+3	64	60
22	HCl, 10% aq. soln.	No change	+12	71	88
23	HNO_3, 10% aq. soln.	No change	+15	79	95
1	N_2O_4, at room temp.(1)	No change	-	194	131
2	N_2O_4, at 5-15°C	No change	+6	186	136
3	UDMH, at room temp.	Degraded	-	-	-

Notes: (*) Terpolymer: $C_2F_4/ONCF_3/ON(CF_2)_3COOH$, mole ratio = 100/99.5/0.5
(1) Under pressure.
(**) Liquids boiling at lower temperatures refluxed.

VI. Compounding Studies

Although nitroso elastomers have interesting combinations of properties it was clear from the initial studies that certain physical properties, such as tensile strength, have to be improved before they become useful items. Accordingly work was initiated with the Thiokol Corporation to develop techniques for producing nitroso rubber in pilot plant quantities. This was successfully carried out by Thiokol as already described in earlier sections of this report. The following paragraphs report the work concerned with the research compounding of nitroso elastomers.

A. Materials and Test Methods

The Thiokol Chemical Corporation produced six batches of nitroso rubber that were used in this study. These rubbers, all copolymers of trifluoronitrosomethane and tetrafluoroethylene, were made in the pilot plant of the company.

Compounding studies have been conducted on only two of the batches. Their physical properties and the test methods used are as follows:

Property	ASTM Test Method Number
Tensile strength) Ultimate elongation) Stress at 300% elongation)	D412-62T
Hardness	D676-59T
Mooney viscosity	D1646-63

The differential thermal analysis data were obtained with a DuPont Model 900 differential thermal analyzer under the following conditions:

Sample size:	4mm	Atmosphere:	AR$_2$ @ 760 mm
Reference:	glass beads	Temperature scale:	50
Program mode:	heat	Temperature scale:	0.5
Rate of heating:	10°/min	Base line slope:	0

B. Results and Discussion

It was noted early in the compounding studies that the properties of the vulcanizates produced from the pilot plant facility were not similar to those of the compounds from the laboratory produced rubber (Minnesota Mining and Mfg. Co.) even though the compounding recipe used was the same. For example, while tensile strengths of 1000 psi or more had readily been obtained from the earlier rubber (3M), tensile strengths of 300 psi represented the maximum obtainable from the Thiokol rubber. There were differences in curing characteristics (scorch time, time of cure, and cure index) as well. To compensate for these differences, a series of amine cure studies were made.

The compounding and curing recipes, cure times and temperatures, and subsequent physical properties of various compounds of batch 5702 are given in Tables XII and XIII, and of batches 5702 and 5675 in Tables XIV and XV. Table XII gives the test results of amine-cured, HiSil 303-filled vulcanizates and Table XIII the results with amine-cured, carbon black-filled vulcanizates. Table XIV lists the vulcanizates with amine cures and amine and filler variations, and Table XV those with other than amine cures.

In the Table XII series (HiSil 303 filler) the triethylenetetramine (TETRA) was varied from 1.25 to 5 pphr (parts per hundred rubber) and the hexamethylenediamine carbamate (Diak #1) from 1 to 2.5 pphr. Press cure temperatures varied from 220° to 260°F. The Thermax black filler (MT), which had been found to increase the rate of cure of the Thiokol rubber, was tried in combination with the HiSil 303 in compound 57. This vulcanizate proved to be too weak to test. Compound 79, which had the smallest amount of TETA (1.75 pphr), was the best of this series but even this showed a tensile strength of only 245 psi.

In the second series using the amine cure Table XIII, various carbon black fillers were used: medium thermal (MT) furnace black "Thermax", an easy-processing channel (EPC) black, and a high-abrasion furnace (HAF) black. Press cure temperatures varied from 180° to 250°F. None of the black fillers gave vulcanizates that were superior to those using HiSil 303 Table XII or to those using Linde silicone-treated HiSil 233 or Silstone 101. **When the curing time was kept below 250°F, only the HAF black among the black-filled compounds did not sponge but it failed to cure.**

Table XII

COMPOUNDING RECIPES AND TEST RESULTS
AMINE CURES - HiSIL 303 FILLER

Ingredient Parts by Weight	Compound Number 79	50	51	51	57	58	60	64	65
Nitroso, Thiokol 5702	100	100	100	100	100	100	100	100	100
Triethylenetetramine	1.25	2	3	3	3	1.5	5	1.5	1.5
Hexamethylenediamine carbamate	2.5	2	1.25	1.25	1	2	1	1	
HiSil 303	15	20	15	15	15	15	15	7.5	10
Mg O					5				
Zn Silicate Fluoride					3				
MT Black					15				
Sodium Borate								7.5	
Press Cure, Time min/Temp °F	60/250	60/220	60/260	60/230	60/220	60/260	60/220	60/220	60/220
Oven Cure, Time hrs/Temp °F	16/212	16/212				64/212			
Tensile Strength, psi	245	200				100	175		
Ultimate Elongation, %	380	100				300	260		
Stress at 300% Elong. psi	230	-				100	-		
Hardness, Shore A	57	80				60	67		

Table XIII

COMPOUNDING RECIPES AND TEST RESULTS
AMINE CURES - CARBON BLACK FILLERS

Ingredient Parts by Weight	Compound Number 9*	10	11	13	17	18	19	22	23	31	32
Nitroso, Thiokol 5702	100	100	100	100	100	100	100	100	100	100	100
Silstone 101										20	20
Triethylenetetramine	3	3	3	3	1.5	1.5		2	3	2.5	2.5
Hexamethylenediamine Carbamate	1	1	1	1	1	1	2		1	1	1
1,4 Cyclohexane Bis(Methylamine)	1	1	1	1	1	1	1	1	1		
ZnO	3	3	3	3	3	3		3	3	3	3
Zinc Fluoride	1	1		1							
HAF Black				15	25	17	17	17	17		
MT Black	15	15	15			8	8	8	8		
Linde Silicone Treated HiSil									10		
Press Cure, Time, min/Temp °F	60/250	60/210	60/210	60/220	60/200	60/200	60/200	60/200	60/200	60/240	60/210
Oven Cure, Time, min/Temp °F	16/212							16/200	16/200		
Tensile Strength, psi	125	100	140	100	210	200	160	90	200	250	220
Ultimate Elongation, %	290	400	490	370	100	160	225	490	350	750	650
Stress @ 300% Elong, psi	-	90	100	-	-	-	-	-	-	100	100
Hardness, Shore A	36	30	28	40	62	50	35	38	50	37	41

*Sponged

Table XIII (continued)

COMPOUNDING RECIPES AND TEST RESULTS
AMINE CURES - CARBON BLACK FILLERS

Ingredient Parts by Weight	Compound Number 33	34	35	36	37	38	39	40	41	42
Nitroso, Thiokol 5702	100	100	100	100	100	100	100	100	100	100
Silstone 101	20	10	10	10	10	10	10	10	10	10
Triethylenetetramine	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Hexamethylenediamine Carbamate	1	1	1	1	1	1	1	1	1	1
ZnO	3	3	3	3	3	3	3	3	3	3
MT Black		10	10	10						
EPC Black					10	10	10			
HAF Black								10	10	10
Press Cure Time, min/Temp °F	60/180	60/240	60/210	60/180	60/240	60/210	60/180	60/240	60/210	60/180
Tensile Strength, psi	50	150	200	100	100	150	150			
Ultimate Elongation, %	950	500	600	950	500	550	600			
Hardness, Shore A	33	26	26	22	28	37	29			

Table XIV

COMPOUNDING RECIPES AND TEST RESULTS
AMINE CURES - AMINES AND FILLER VARIATIONS

Ingredient	Compound Number											
Parts by Weight	1	2	3	14	4	5	6	7	15	8	21	24
Nitroso, Thiokol 5675	100	100	100	100								
Nitroso, Thiokol 5702					100	100	100	100	100	100	100	100
ZnO	3					5				3	3	
Triethylenetetramine	2	3	3	1	3			2	3	2	1	3
Hexamethylenediamine Carbamate			2	0.33	1	2		2	3	1	1	1
Diethylene Glycol			1									
Diphenylguanidene			2									
1,4 Cyclohexane Bis (Methylamine)							5	2	3	3	1	
HiSil 233	15		15									
Cab-O-Sil		15										
Silstone 101				10	15	15	15	10	12.5	12.5		15
DyPhos						10						
Nitroso Treated HiSil 233											12.5	
Press Cure, Time, min/Temp °F	60/240	90/210	60/210	240/212	60/190	60/280	60/280	60/280	60/230	60/250	60/200	60/200
Oven Cure, Time, hrs/Temp °F	16/212	16/212	16/212	24/195	16/190	16/300	16/212	-	-	16/212	16/200	16/212
Tensile Strength, psi	sponged	sponged	sponged	300	sponged	no cure	100	sponged	no cure	200	100	180
Ultimate Elongation, %				500			170			700	950	340
Stress at 300% Elong, psi				150			-			-	-	-
Hardness, Shore A				34			60			16	21	53

Table XIV (continued)

COMPOUNDING RECIPES AND TEST RESULTS
AMINE CURES - AMINE AND FILLER VARIATIONS

Ingredient Parts by Weight	70	71	72	73	74	75	76	77	78	79	88	81
Nitroso, Thiokol 5702	100	100	100	100	100	100	100	100	100	100	100	100
Triethylenetetramine	2	4	8	1	2					1	5	2
Hexamethylenediamine Carbamate	2	5	5			3			2		1	
Ethylenediamine Carbamate								3				
Sulfur					1.5	2	2	2	2	1		0.5
Pyrometallicanhydride				5								
Methylene Bis (phenyldi-isocyanate)				1								
Sodium Bicarbonate				3								
DyPhos	5	5	5									
HiSil 303				15	15	20	20	20	20	20	20	
N,N'-Dicinnamylidene-1,6 Hexanediamine							3					3
ZnO										3		
Cadmium Stearate										1.5		
Diphenylnitrosoamine											2	
HiSil 233												15
Diethylene Glycol												2
Press Cure, Time, min/Temp °F	60/220	60/230	60/230	180/212	30/250	30/250	30/250	30/250	30/250	30/250	60/250	60/240
Oven Cure, Time, Hrs/Temp °F	-	-	-	-	-	-	-	-	-	1	1	16/212
Tensile Strength, psi	100	100	150	No cure	No cure	No cure	No cure	No cure	150	No cure	No cure	No cure
Ultimate Elongation, %	900	400	225						395			
Stress at 300% Elong, psi	-	-							-			
Hardness, Shore A	26	32	42						60			

Table XV

COMPOUNDING RECIPES AND TEST RESULTS OTHER THAN AMINE CURES

Ingredient Parts by Weight	Compound Number 82	 83	 84	 85	 86	 87	 88
Nitroso, Thiokol 5675	100						
Nitroso, Thiokol 5702		100	100	100	100	100	100
Chromium triperfluoroacetate	5						
CaO	2						
Cab-O-Sil		15					
Hexamethylenediamine Carbamate		1					
Diethylthiourea		2					
MAPO		5					
HiSil 303			15	15	15	15	15
$Bu_2SN\ Cl_2$			3				
DiCup 40c				9			
Trimethylolpropane trimethacrylate				3			
Pyrometalicanhydride					1		
MDI					1	1	
MgO							5
Cadox BSG Paste							3
Press Cure, Time, min/Temp °F	60/240	60/250	60/300	60/300	60/250	60/250	60/250
Tensile Strength, psi	no cure	no cure	no cure	no cure	no cure	no cure	no cure
Ultimate Elongation, %							
Stress @ 300% Elong, psi							
Hardness, Shore A							

Table XIV describes the compounds made with a variety of amine crosslinking agents, fillers, and stabilizers. It had been found that the addition of more than 2 pphr of triethylenetetramine usually produces sponging and this always lowers the tensile strength. Sponging often is not readily discernible; sometimes it can be detected only by means of a microscope. To ensure against sponging, compound 14 was made using only 1 pphr of triethylenetetramine and 0.33 pphr of hexamethylenediamine carbamate. To achieve maximum cure with this low level of curative, the compound was press-cured for 240 minutes at 210°F and then oven-cured for 24 hours at 195°F. The tensile strength of this compound (300 psi) was the highest obtained with the Thiokol nitroso rubber. Compound 14 showed no signs of sponging. None of the other variations produced a vulcanizate with more than 200 psi tensile strength.

Table XV shows the results when compounds were vulcanized with other than amine crosslinking agents. None of these vulcanizates could be tested; from visual examination none appeared to have been cured.

To determine the curing characteristics of the nitroso rubber, the viscosity, not only of batches 5702 and 5675 but also of the remaining four batches, was determined on the Mooney viscometer Table XVI. Batch 5675 gave the lowest result, a viscosity of only 22. The curing characteristics of a variety of compounds are given in Table XVII. Compounds 12 and 13, which represent 3M and Thiokol nitroso rubbers, respectively, showed great differences in curing characteristics. Compound 7 is a compound in which 1 pphr of 1.4 cyclohexane bis (methylamine) replaced 1 pphr triethyletramine and then 3 pphr of zinc oxide stabilizer was added. This compound gave the best curing characteristics, hence the same formula was used in a series of compounds (8,9,11, and 12) in which the fillers were varied by the use of different carbon blacks and the effect of zinc fluoride was investigated.

Table XVI

MOONEY VISCOSITY OF VARIOUS
BATCHES OF NITROSO RUBBER

Thiokol Chemical Corporation Batch Identification	Mooney Viscosity (ML-4+1 @ 212°F)
5702	35
5812	35
5812 (9/14/64)	36
5812 (9/15/64)	35
5812 (Part #3)	36
5675	22

Table XVII

CURE CHARACTERISTICS AS DETERMINED WITH MOONEY VISCOMETER (LARGE ROTOR)

Ingredient Parts by Weight	Compound Number 12	13	7	8	9	11	12	13	14	15
Nitroso, MMM 9690		100								
Triethylenetetramine	3	3	2	2	3	3	3	3	3	3
Hexamethylenediamine Carbamate	1	1	1	1	1	1	1	1	1	1
Silicone treated HiSil 233	10	10	12.5							
Nitroso, Thiokol 5702	100		100	100	100	100	100	100	100	100
Zinc Fluoride					1		1	1		1
Thermax					15	15				
ZnO			3	3	3	3	3	3	3	3
1,4, Cyclohexane Bis(Methylamine)			1	3	1	1	1	1	1	1
HAF Black								15	15	12.5
Temp. of Test, °F	215	215	250	250	250	250	250	250	250	250
Minimum Viscosity	11.5	70	56	13	20	8	9	68	54	55
Scorch Time, t_5, min.	50	10	5	14.5	2.75	4.2	11.5	7	7.2	4.3
Time of Cure, t_{35}, min.	100	26.5	18	-	5.5	-	14.5	19.2	14.3	-
Cure Index, $t\ 30=t_{35}-t_5$	50	16.5	13	-	2.75	-	3	12.2	7.1	-

NOTE: Serrated, large rotor used.

Table XVII (continued)

CURE CHARACTERISTICS AS DETERMINED WITH MOONEY VISCOMETER (LARGE ROTOR)

Ingredient Parts by Weight	Compound Number 16	19	20	21	24	32	35	38	41	50	51
Nitroso, Thiokol 5702	100	100	100	100	100	100	100	100	100	100	100
Triethylenetetramine	3			1	3	2.5	2.5	2.5	2.5	2	3
Hexamethylenediamine Carbamate	1	2	2		1	1	1	1	1	2	1.25
1,4 Cyclohexane Bis(Methylamine)	1	1		1							
ZnO	3	3	3	3		3	3	3	3		3
MT Black		8	8		4		10				
HAF Black		17	17						10		
Ethylenediamine Carbamate				1							
Nitroso treated HiSil 233				12.5							
Silicone treated HiSil					15	20	10	10	10		
EPC Black								10			
HiSil 303										20	15
Temp. of Test, °F	250	200	200	200	200	210	210	210	210	212	212
Minimum Viscosity	7	66	10	48	66	53	40	54	50	55	50
Scorch Time, t_5, min.	11.2	10	-	-	2	5	3	1.5	1.75	-	4.75
Time of Cure, t_{35}, min.	16	-	-	-	11	8	9	4.2	4.25	-	-
Cure Index, $t\ 30=t_{35}-t_5$	4.8	-	-	-	9	3	6	2.7	2.50	-	-

With Thermax black as a filler, compound 9, the zinc fluoride improved the curing characteristics of the nitroso rubber, as is shown below.

No.	Compound	Time for Cure (beyond 35 min) min
8	No filler, no zinc fluoride	no cure
9	Thermax black with zinc fluoride	5.5
12	No filler with zinc fluoride	no cure
11	Thermax black, no zinc fluoride	14.5

Zinc fluoride in HAF black filler systems (compounds 13, 14, and 15) did not change the curing characteristics of these compounds to the same degree that it did with the Thermax black and it did not improve the physical properties of the vulcanizates. In compounds 38 and 41, 2.5 pphr of triethylenetetramine and mixtures of carbon black and silicone-treated fillers were used and the temperature was reduced to 210°F (to eliminate sponging). The cure characteristics produced were excellent but the physical properties were poor.

Results of attempts to identify crosslinking of the nitroso rubber by the use of differential thermal analysis techniques are given in Table XVIII. Triethylenetetramine was the only material tested that indicated crosslinking, and this occurred at 60°C. Using this method of analysis, the second order transition of -50°C compares with that previously reported on the 3M rubber. Table XVII shows that the addition of triethylenetetramine reduced the temperature for the onset of deterioration from 220°C to 200°C. The addition of Diak #1 (hexamethylenediamine carbamate) significantly reduced the temperature for the onset of deterioration. This was also true when other amines were used, and when dicumylperoxide was added.

Table XVIII

DIFFERENTIAL THERMAL ANALYSIS RESULTS

Sample Identification	Tg°C	Tc°C	Td°C
Thiokol 5702	-50	--	220
Thiokol 5702 with TETA	-49	60	200
Thiokol 5702 with Diak #1	--	--	155
Thiokol 5702 with H_2N F F NH_2	--	--	168
Thiokol 5702 - TETA and UROTROPIN	--	--	137
Thiokol 5702 - dicumylperoxide	--	--	133
Thiokol 5702 - TETA, Diak #1, DPG, CAB-O-SIL	--	--	138

Tg = Second order transition temperature
Tc = Onset of crosslinking temperature
Td = Onset of degradation temperature

C. Conclusions

The Thiokol Chemical Corporation nitroso rubber has different curing characteristics from that made by the Minnesota Mining and Manufacturing Company.

The physical properties of the compounds made and reported here, using the Thiokol Chemical Corporation nitroso rubber, were extremely poor.

The reinforcing fillers HiSil 303 and the silicone-treated HiSil 233 were superior to the medium thermal furnace blacks, the high-abrasion furnace blacks, and the easy-processing channel blacks.

VII Future and Potential Uses of Nitroso Rubber

The future of nitroso rubbers depends upon the types of uses that can be developed for this unique elastomer. These uses, in turn, are largely dependent upon the specific combinations of properties that can be evolved from this architecturally unique molecular system. Undoubtedly nitroso elastomers are to be considered specialty rather than general purpose elastomers.

Nitroso rubbers appear to have potential utility for applications where corrosive environments are found, such as in the aerospace industry, use in expulsion bladders and for valves exposed to rocket fuels and oxidizers. As a low temperature elastomer whose petroleum resistance is required, nitroso elastomers may also have practical utility. As a metal coating material nitroso elastomer may have practical advantages in certain areas where extremely corrosive environments predominate.

VIII Summary

The syntheses of nitroso monomers and the practicability of carrying out pilot plant syntheses of nitroso polymers has been demonstrated. Nitroso elastomers have unique combinations of properties not held by an elastomer to date. These elastomers are the only completely fluorinated "rubber" materials known and indeed the only known case where a nitroso group enters into a polymerization reaction to yield a -N-O-chain sequence in a linear polymer. To retain these desirable properties and at the same time develop yet new elastomer systems with high tensile strengths is the goal of the present effort. Current applications require materials having tensile strength superior to those now currently known in the nitroso elastomer systems.

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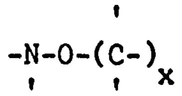
13 ABSTRACT

"Nitroso" rubber is the generic name for a family of rubbery high polymers having the common structural denominator of a repeating nitrogen-oxygen-carbon atomic sequence as follows:



$$-\underset{|}{N}-O-(\overset{|}{\underset{|}{C}}-)_x$$

Architecturally these nitroso polymers are the first of a whole new class of materials. Nitroso polymers, as currently known, are highly fluorinated or completely fluorinated and as such are members of a specialty type of elastomer since only a limited number of fluorinated elastomers are known. It is becoming increasingly evident, however, that the combination of "nitroso" groups in the highly fluorinated linear polymer chain is responsible for the introduction of interesting and novel combinations of properties. Thus, nitroso elastomers have good low temperature properties, solvent resistance, stability to corrosive environments, and flame resistance.

Nitroso polymers have been developed to their present state by the cooperative effort of Army scientists and contractors. Over the past eight years, considerable insight has been gained as to the nature and potential uses of nitroso rubbers. This handbook is an attempt to assemble a summary of this accumulated knowledge. It is hoped that the contents so compiled will aid in the future development of this new family of specialty elastomers.

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