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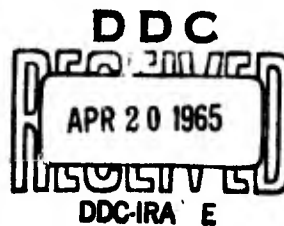
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RMD 8576-Q6

Report Period:

1 June 1964 to 31 August 1964



NITROSO RUBBER

RESEARCH
DEVELOPMENT
And
PRODUCTION

CHEMICAL CORPORATION
CHEMICAL OPERATIONS TRENTON, NEW JERSEY

Thiokol

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NITROSO RUBBER
RESEARCH, DEVELOPMENT AND PRODUCTION.

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FOREWORD

This report was prepared by Thiokol Chemical Corporation under U.S. Army Contract No. DA-19-129-AMC-69(X) O.I. 9044, QMC Project No. 7X93-15-004 with Mr. Frank Babers as project engineer. This report covers work conducted from 1 June 1964 through 31 August 1964. The overall project leader is Mr. Joseph Green; the divisional project leader at Trenton is Mr. Warren Helmer. Other contributors to the program are Messrs. John Paustian, Joseph Castellano, Nathan Levine, Ernest Cottrill, David Kennedy, and Richard Crooker at Denville and Messrs. Robert Hoffman and Malcolm Reynolds at Trenton.

ABSTRACT

Additional CF_3NO and $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ copolymer production lots were successfully completed although detonations were experienced in two CF_3NO runs. An additional 138 pounds of CF_3NO and 87 pounds of copolymer were prepared. Modifications of laboratory bulk copolymerizations resulted in products with inherent viscosities up to 2.88 indicating molecular weights to $> 3,000,000$. Vulcanizates obtained from production copolymer were of low strength. Terpolymerization and termonomer studies were continued.

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I. INTRODUCTION

Army-sponsored research oriented toward the development of a chemical and fuel resistant arctic rubber has resulted in the preparation of a 1:1 copolymer of trifluoronitrosomethane and tetrafluoroethylene, generally referred to as nitroso rubber (Ref 1 and 2). The nitroso rubber gum stock exhibits excellent solvent resistance, is nonflammable and is resistant to most solvents except those which are halogenated. The glass transition temperature (T_g) is -51°C . This low T_g value is attributed to rotation of the chain about the N-O bond.

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

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

The goals of the present program are threefold:

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

Thiokol Chemical Corporation has initiated a five-phase R and D program to meet these goals:

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

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

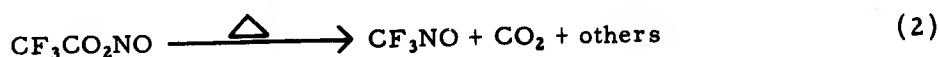
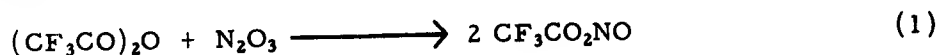
1. Preparation of nitroso monomer containing a carboxy functional group for terpolymerization studies
2. Polymerization studies to attain high molecular weight polymer
3. Production of monomer and polymer
4. Polymer curing studies.

II. TECHNICAL WORK

PHASE I - MONOMER SYNTHESIS

Task 1. Process Development for Trifluoronitrosomethane (CF₃NO)

The objective of this task was the development of a process capable of operation at a production level of 10 to 50 pounds of CF₃NO per 24-hour period. The process which has been investigated for the attainment of this goal involved the preparation and the pyrolytic decarboxylation of trifluoroacetyl nitrite.



The development of processes for these two preparative reactions had been essentially completed during previous report periods (Ref 5) and operation of these processes at the production level has been successfully effected (cf. Phase III, below); thus, the only experimentation conducted during this report period was designed to aid the production operations.

During operation of the CF₃NO production reactor, a gradual formation of a solid material in the FC-43 solvent was observed. Since this material had not been observed in the laboratory operations, characterization of this material and the determination of its effect on the pyrolysis was desired. A sample was obtained from the production facility and submitted for infrared and elemental analyses. Exact identification has not yet been obtained but it has been established that the material is essentially inorganic (C = 1.4%; H < 1%; N = 0.9%). Fluorine is present although quantitative data are not available. The infrared spectrum is typical of an inorganic salt. The solid is not impact sensitive.

Task 2. Preparation of Tetrafluoroethylene (C₂F₄)

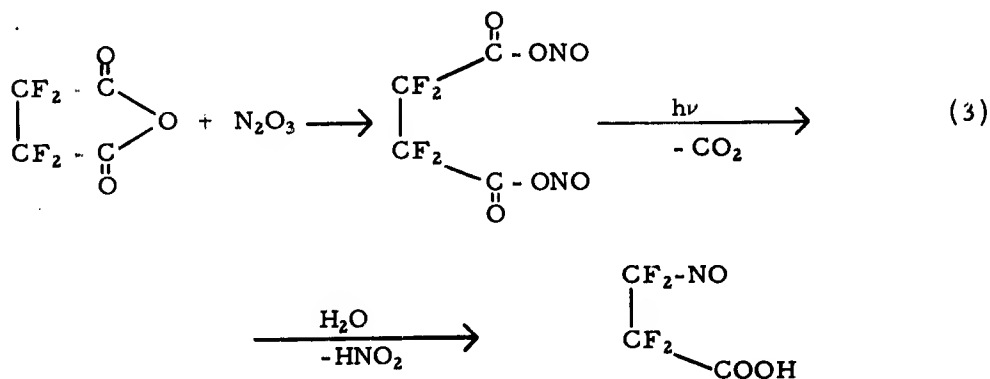
Tetrafluoroethylene is being received from the Thiokol production facility at Moss Point, Mississippi. No production runs were completed at either the Reaction Motors or Trenton facilities during this report period.

Task 3. New Nitroso Monomers

The objective of this task is the preparation of new monomers that improve the low temperature properties of nitroso rubber or provide functionalities which could become crosslinking sites for improved mechanical properties. Current work is concerned with the preparation of nitroso perfluoroaliphatic and perfluoroaromatic compounds containing carboxyl groups as cure sites.

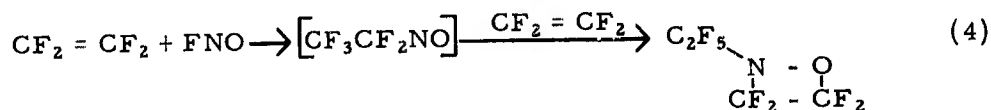
A. Aliphatic Nitroso Compounds

The preparation of 3-nitrosoperfluoropropanoic acid and 4-nitrosoperfluorobutanoic acid has been described (Ref 1, 3 and 6). They reacted N_2O_3 with perfluoroglutaric and perfluorosuccinic anhydrides and subjected the resulting acylnitrites to ultraviolet radiation in order to produce the desired nitroso compounds (equation 3). Yields were low, however, and the preparative methods were not amenable to scaleup.

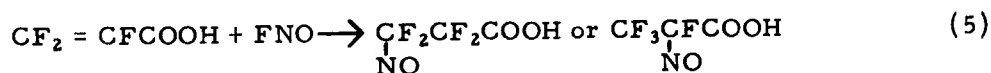


It was decided, therefore, to investigate new methods of preparing carboxy-substituted nitroso compounds. The first method chosen, the preparation and pyrolysis of hydroxamic acids (Ref 7), did not yield any of the desired compounds. Although some nitroso compounds appeared to form when a mixture of NOCl and perfluoroglutaric acid was irradiated with ultraviolet light (Ref 8), this method was abandoned because the low yield reaction did not appear to be amenable to scaleup.

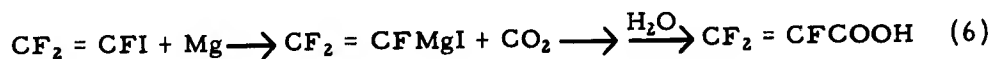
The reaction of FNO with perfluoroolefins has been used successfully to prepare perfluoronitroso compounds (Ref 9). Although tetrafluoroethylene and FNO appear to give mainly oxazetidine (equation 4) (Ref 9, 10 and 11),



nitroso compounds were obtained from the reaction of FNO with perfluoropropene and perfluoroisobutylene. The addition of FNO to trifluoroacrylic acid and perfluoro-4-pentenoic acid might yield the desired nitroso compounds via this route (equation 5). The addition of ClNO to perfluoroolefins has been accomplished (Ref 12) and this may afford an alternate route to nitroso compounds.



The preparation of trifluoroacrylic acid has been described by Knunyants and his coworkers (Ref 13). The acid was obtained in 37% yield by a simple Grignard reaction (equation 6). This procedure will be used to prepare the acid.

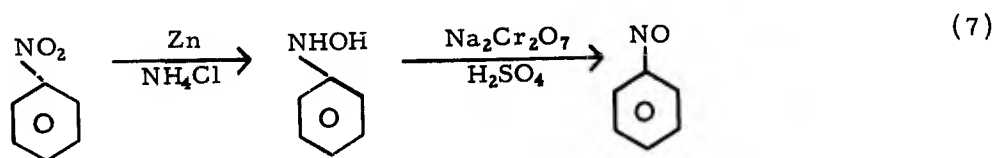


The oxidation of 2,2,3,3,4,4,5,5-octafluoropentanol was carried out with potassium permanganate and a 25% yield of the hydrated acid - $\text{CHF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{COOH} \cdot 15 \text{H}_2\text{O}$, bp 164-6°C - was obtained. The compound was identified by elemental and infrared spectral analysis. The boiling point of the pure acid is reported (Ref 14) to be 155-60°C. This material will be dehydrofluorinated in an effort to produce the desired perfluoro-4-pentenoic acid and subsequently allowed to react with FNO.

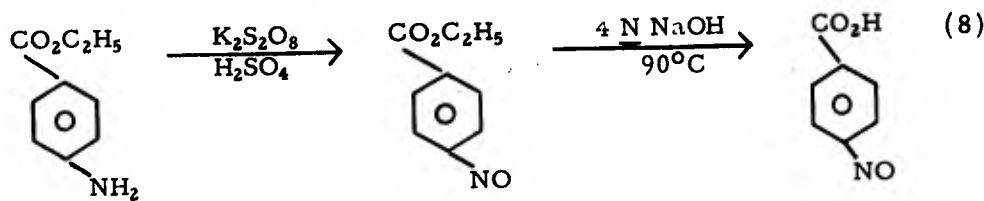
B. Aromatic Nitroso Compounds

The preparation of *p*-aminotetrafluorobenzamide was described in the last quarterly report (Ref 15). This compound was prepared in 20% yield by the reaction of ammonia/methanol with pentafluorobenzamide at 100°C and 130 psig. When the preparation of *p*-aminotetrafluorobenzamide was treated

with performic acid at room temperature for one hour, no evidence for the formation of the nitroso compound was observed (absence of blue color). Upon heating the mixture at 80°C for 5 hours, however, a 31% yield of pure *p*-nitrotetrafluorobenzamide, mp 110-2°C, identified by elemental and infrared analysis, was obtained. The complete oxidation of *p*-aminotetrafluorobenzamide under relatively mild conditions indicates the difficulty of obtaining the nitroso-compound by this route. An alternate route to the desired compound may be the reduction of *p*-nitrotetrafluorobenzamide by the method of Coleman, et al. (Ref 16).



Schors and his coworkers (Ref 17) oxidized ethyl *p*-aminobenzoate with persulfuric acid at room temperature to give 20-60% yields of the *p*-nitroso compound. Subsequent hydrolysis of the ester produced *p*-nitrosobenzoic acid (equation 8). The same procedure should be applicable to the corresponding 2,3,5,6-tetrafluoro compound and work directed toward this objective was therefore started. The preparation of 8 gm of ethyl pentafluorobenzoate, bp 92-3°C/14.5 mm, was carried out by simply refluxing pentafluorobenzoic acid with absolute ethanol in the presence of a catalytic quantity of H₂SO₄. The ester will now be treated with sodium amide in liquid ammonia in an effort to produce the desired amine.



PHASE II - POLYMERIZATION STUDIES

The effort on this phase is composed of two tasks: (1) the development of the process for producing $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ copolymer in 10 to 50 pound quantities per 24-hour period and (2) research toward preparation of other nitroso polymers with improved properties. The production of copolymer in the production facility has been successfully effected in replicate batches during this report period and there has been a corresponding reduction in the copolymer development effort.

Task 1. Process Development and Improvement

The emphasis on this task during previous report periods had been the development of a suspension process for the copolymerization of CF_3NO and C_2F_4 . With the successful utilization of this process in the production facility, Task 1 was reoriented to studies of the lower-temperature bulk copolymerization.

The $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ bulk copolymerization has been characterized by long reaction times (up to 60 days). During this report period, studies of the effect of reaction time on molecular weight were initiated which resulted in copolymers of the highest molecular weight yet produced (inherent viscosities to 2.88, molecular weights to 3,500,000, Table I). These reactions were conducted at -65°C in heavy-walled, glass "Y" tubes. The monomers were condensed at a 1:1 mole ratio into one leg of the "Y" tube, then placed in a -65°C environment and maintained without agitation for periods of 6 to 16 days. During this period, the transfer of the majority of the monomer mixtures to the other leg of the "Y" tubes occurred, possibly because of thermal gradients in the refrigerated chamber. Polymerization in both legs occurred, the extraordinarily high molecular weight polymer was formed from the transferred monomers. That polymer which formed from the residual monomers was of low molecular weight, about 400,000. It is postulated that impurities capable of initiating and/or terminating the chain copolymerization remained behind and effected low molecular weights while uncontaminated monomers transferred and polymerized to the extremely high molecular weight products. Cure studies (see Phase IV below) have shown the superiority of vulcanizates obtained from these high molecular weight products.

Task 2. Experimental Nitroso Polymers

Seven additional laboratory batches of the $\text{C}_6\text{F}_5\text{NO}/\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ terpolymer were prepared during this report period. These polymerizations were effected

TABLE I
CF₃NO/C₂F₄ BULK COPOLYMERIZATIONS

Reaction No. 212091-	<u>2H</u>	<u>3H</u>	<u>4H</u>	<u>5H</u>
Reaction time (days)	6	9	12	16
Conversion (%)	72.6	88.3	88.3	91.0
High mol. wt fraction (% of total polymer)	69.5	63.2	63.2	86.3
Inherent viscosity ⁽¹⁾ of high mol. wt fraction	2.06	2.88	2.70	1.39
Molecular weight ⁽²⁾ (x 10 ⁶)	2.5 h	3.5 t	3.3 h	1.5 h

(1) 0.5 gm polymer/100 ml Freon 113.

(2) h - By extrapolation from inherent viscosity datum point.
t - From intrinsic viscosity.

in methylene chloride solution as previously reported (Ref 5), the ratio of $C_6F_5NO:CF_3NO$ was 1:9. A total of 120 gm of product was obtained representing an overall conversion from monomer of 82%. These products will be used for cure studies.

No additional FNO/ C_2F_4 copolymerizations were attempted during this report period. Previous attempts (Ref 7 and 15) were conducted in a Monel and Kel-F apparatus which had been utilized on other programs and the possibility of residual contaminants effecting the observed FNO decomposition was considered. For this reason, another apparatus is being constructed from new materials. Upon completion, FNO copolymerization studies will be resumed.

PHASE III - PRODUCTION OF NITROSO RUBBER

The production of nitroso rubber and its precursors, CF_3CO_2NO and CF_3NO , was continued during this report period. Details of the facilities and equipment have been given in previous reports (Ref 5 and 8). Production of C_2F_4 has not been initiated on this program since this material is being received from the Thiokol production facility at Moss Point, Mississippi.

A. Production of Trifluoronitrosomethane

Nine production runs were initiated during this report period from which approximately 138 pounds of purified CF_3NO was obtained. Experimental details for these runs are summarized in Table II; analyses of the products are given in Table III.

Although most of the runs were completed without incident, a sudden pressure increase in the purification section caused significant product loss in one run. In two others, minor explosions were experienced in the nitrite feed section of the pyrolysis column. In neither case did the explosions propagate back to the CF_3CO_2NO reservoir, an effect predicted by the safety testing completed early in the program (Ref 8). The first incident occurred after a change in the feed rate of the CF_3CO_2NO to the reactor resulting in destruction of the column feed section and a one-month production delay. It was hypothesized that the neat CF_3CO_2NO superheated in the tubing section adjacent to the pyrolysis unit. Therefore, provisions for dilution of the nitrite with helium were incorporated into the system. Despite this, another explosion was experienced during a subsequent run. This explosion occurred at the same place but with less force and less equipment damage.

TABLE II
PRODUCTION OF CF_3NO

Experiment No.	5658	5674	5678	5703	5705(1)	5706	5707	5808	5809(1)
$(CF_3CO)_2O$ Charge (lb)	41.6	35.5	35.3	70.6	70.6	70.6	70.6	70.6	70.6
$N_2O_2/(CF_3CO)_2O$ (mole ratio)	0.66	0.70	0.73	0.73	0.73	0.73	0.73	0.73	0.73
			<u>CF_3CO_2NO Preparation</u>						
			<u>CF_3CO_2NO Pyrolysis</u>						
Reactor Temp ($^{\circ}F$)	340-373	360	360	353-360	360-365	360-370	355-363	359-362	358-362
Reboiler									
Condensate	220-350	300-350	320-340	295-340	320-350	300-310	290-340	296-340	310-340
Reaction Time (hr)	18	12	30	15	1.6	25	21	13.5	30
CF_3NO Yield % Based on $(CF_3CO)_2O$	15	31	23	27.4	---	37	14.7	29.9	42.9
Weight (lb)	6	10	12.5	20.5	3.8	25	10	20.4	30.2

(1) Explosion in nitrite feed section during pyrolysis

TABLE III
CF₃NO ANALYSES

Batch No.	5674	5678	5703	5706	5707	5808	Combined 5809 + 5707	5810 ⁽¹⁾	5811 ⁽²⁾
CF ₃ NO	94	90.5	80	97.5	96	97.5	94.5	99	99
CF ₃ NO ₂	--	--	2	1.5	1	1.7	3.6	0.4	< 1
CF ₃ NO ₂ /NO ₂	< 1	--	--	--	--	--	--	--	--
C ₂ F ₆	--	4.5	3	--	--	--	--	--	--
C _x F _y	--	--	1	--	1	0.5	0.6	0.4	< 1
COF ₂	1	--	--	--	--	--	--	--	--
Air ⁽³⁾	--	5	10	1	2	0.3	1.3	0.2	Trace
CO ₂	4	--	4	5	--	--	--	--	--

NOTE: All figures in mole percent

- (1) Repurified XP 5808 plus part of combined 5809 and 5707
- (2) Remainder of combined 5809 and 5707 repurified
- (3) Air is believed to have been introduced during sampling.

It was noted that the total utilization time of the FC-43 before explosion was the same in each case (88 hours and 89 hours, respectively). Thus, there may be a concentration of some relatively nonvolatile impurity in the FC-43 over a prolonged period which sensitizes the $\text{CF}_3\text{CO}_2\text{NO}$ or is itself sensitive. Salvage of the FC-43 after the second incident was possible; this will be checked for contamination. Other possible reasons may include a buildup of the solid material in the FC-43 (see Phase I, Section 1, above) to the point where temporary blocking of the feed tube and, therefore, uncontrolled feed, could occur.

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

The first copolymerization of CF_3NO and C_2F_4 in the production facility was reported (Ref 15). This polymerization was at -25°C with the monomers in aqueous suspension. Three additional polymerizations were successfully completed during this report period; another is in progress. Total polymer production to date is 100.5 pounds. The polymerization conditions and polymer properties are summarized in Table IV. The molecular weights of the products of the latter two batches (XP-5704 and XP-5807) were lower than those of the preceding batches; this is attributed to a higher concentration of CF_3NO_2 in the CF_3NO batches utilized.

PHASE IV - COMPOUNDING AND CURING STUDIES

The objective of this phase is to establish the best methods of realizing the unusual properties of nitroso rubber through formulation studies. The first production lot of nitroso rubber (XP-5676) was extensively studied during this report period.

Initial cures with this batch were made with the standard formulation (Hi-Sil 303, 15 phr; Diak No. 1, 2.5 phr; and triethylenetetramine, 1.25 phr) and cure conditions (press for one hour at 250°F plus 18 hours at 212°F in oven). The initial cures were porous, however, and as a comparison laboratory prepared nitroso rubber was cured under the same conditions. The physical properties of the vulcanizates are shown in Table V. All except that of the 3,500,000 molecular weight stock (138 D) were characterized by low strength and in the samples from production stock, by porosity. Therefore, an intensive study of possible process and cure modifications was undertaken.

TABLE IV
 CF₃NO/C₂F₄ COPOLYMERIZATIONS

<u>Batch No.</u>	<u>5702</u>	<u>5704</u>	<u>5807</u>	<u>5812</u>
CF ₃ NO Charged (Batch No.)	5678	5703	5706	5810
(lb)	21	19	25	23
C ₂ F ₄ Charged (lb)	20.9	19	24.4	22.7
C ₂ F ₄ Addition time (hr)	4	1	1	1
Reaction time (hr)	25	22	27	24
Polymer yield (%)	66.8	66	68	in
(lb)	28	25	34	process
Inherent viscosity $[\eta]$ (1)	1.15	0.6	0.6	--
Extrap. mol. wt ($\times 10^6$)	1.4	0.6	0.6	--

 (1) 0.5 gm polymer/100 ml Freon 113

TABLE V
 PHYSICAL PROPERTIES OF CF_3NO/C_2F_4 COPOLYMER VULCANIZATES^{(1), (2)}

Formulation	<u>183E</u>	<u>183A</u>	<u>183B</u>	<u>183D</u>
Nitroso rubber batch No.	XP-5676	XP-5676	212063	212091-3H
Source and treatment	Production, as received	High mol. wt fraction	High mol. wt fraction, RMD	Bulk copolymer, RMD
Tensile strength (psi)	140	380	540	1165
Elongation (%)	100	300	300	650
Modulus (psi at 200%)	---	290	405	355
Comments	Porous	Slightly porous	Nonporous	Nonporous

(2) Cure Time: 1 hr at 250°F in press
 18 hr at 212°F in oven

(1) Rubber - 100
 Hi-Sil 303 - 15
 Diak No. 1 - 2.5
 TETA - 1.25

A. Copolymer Treatment

Several methods of copolymer pretreatment were evaluated in an attempt to effect improved physical properties of the cured products. These included coacervation of polymer solutions followed by wash cycles and drying in vacuo at temperatures up to 257°F. These techniques did not benefit the copolymer in that improved cures were not obtained. Solvent fractionation of the copolymer did, however, yield a higher molecular weight gum with cured properties (183 A, Table V) superior to that obtained from unfractionated copolymer vulcanizates (183 E, for example).

B. Modifications of Process and Cure Conditions

Processing techniques and conditions frequently have a significant effect on the properties of an elastomer vulcanizate. The effect of milling temperatures was investigated (between 60 and 220°F, 100-120°F standard) and it was found that when a hot mill (>200°F) was used nonporous vulcanizates were obtained, presumably because of loss of volatile material. These vulcanizates, however, exhibited low strength (Table VI).

One formulation, compounded with standard conditions, was press-cured at a lower temperature (185°F) and a nonporous product was obtained. Physical properties were again poor (Table VI).

C. Formulation Studies

Variations of the standard formulations as well as additional curing agents were evaluated in attempts to improve vulcanizate physical properties. The elimination of Diak No. 1 (hexamethylenediamine carbamate) from an otherwise standard formulation resulted in a nonporous but low strength vulcanizate. Variations in TETA and filler concentrations were also unsuccessful except for one formulation, an unfilled TETA cure, which had a tensile strength of 465 psi, the highest of the series (Table VII). Other unfilled (or with decreased filler) formulations containing Diak were more porous than the standard, possibly due to the reduced viscosity of the system. Little or no cure with Diak was obtained when TETA was eliminated.

Calcium oxide and barium hydroxide were added in an attempt to improve cures by the elimination of any residual acid. These formulations were nonporous but of low strength (Table VII).

Other materials of potential use as curatives, such as, MAPO {tris [1-(2-methyl)aziridinyl] phosphine oxide}, zinc oxide, triallylcyanurate, disodioresorcinol, and benzoyl peroxide, were evaluated but none resulted in a suitable cure.

PHASE V - FABRICATION

The objective of this phase is to conduct studies toward developing specific compounds of nitroso rubber that can be used in moldings, extrusions and proofed goods, and to produce gaskets, reinforced hose, and coated fabric. It is anticipated that this phase of work will not be initiated in favor of an increased effort to obtain suitable terpolymers.

TABLE VI
EFFECT OF MILLING AND CURE CONDITIONS ON
CF₃NO/C₂F₄ COPOLYMER⁽¹⁾ VULCANIZATE PROPERTIES

Formulation ⁽²⁾	<u>174B</u>	<u>188B2</u>	<u>183E</u>
Mill temperature (°F)	220	< 120	< 120
Milling time (min)	25	25	25
Cure temperature (°F)	Press - 250 Oven - 212	Press - 185 Oven - 212	Press - 250 Oven - 212
Cure time (hr)	Press - 1 Oven - 18	Press - 1 Oven - 18	Press - 1 Oven - 18
Tensile strength (psi)	210	280	140
Elongation (%)	400	350	100
Modulus (psi at 200%)	150	210	---
Comments	Nonporous	Nonporous	Porous

(1) Batch XP-5676

(2) Nitroso rubber - 100
Hi-Sil 303 - 15
Diak No. 1 - 2.5
TETA - 1.25

TABLE VII
 VARIATIONS IN CURE FORMULATION
 CF₃NO/C₂F₄ COPOLYMER

Formulation No.	<u>212</u>	<u>341A</u>	<u>338B</u>	<u>345A</u>
Ingredients (phr)				
Copolymer	100	100	100	100
Hi-Sil 303	15	15	---	15
Diak No. 1	2.5	---	---	2.5
Triethylene tetramine	1.25	2.5	2.5	1.25
Calcium oxide	---	---	---	2.0
Tensile strength (psi)	140	260	465	170
Elongation (%)	100	450	1500	200
Modulus (psi at 200%)	---	165	50	170
Comments	Porous	Nonporous	Nonporous	Nonporous

 (1) Ingredients milled at 100-120°F for 20 min.
 (2) Cure time: 1 hr at 250°F in press.
 18 hr at 212°F in oven.

III. SUMMARY

1. Production of 138 pounds of CF_3NO was successfully effected. The $\text{CF}_3\text{CO}_2\text{NO}$ utilized in these runs was also prepared in the production facility.
2. $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ copolymer production to date is 100.5 pounds.
3. Attempts to prepare carboxy-substituted fluoroaromatic nitroso compounds have not yet been successful.
4. Modified bulk $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ copolymerizations on a laboratory scale have resulted in the preparation of products with molecular weights up to 3,500,000.
5. Additional laboratory $\text{C}_6\text{F}_5\text{NO}/\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ terpolymerizations were completed.
6. Attempts to cure the first production lots of $\text{CF}_3\text{NO}/\text{C}_2\text{F}_4$ copolymer have not been entirely successful in that vulcanizates of low strength were obtained.
7. Attempts to improve vulcanizate properties by modifications of curing conditions or formulations have not been successful.

IV. REFERENCES

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