UNCLASSIFIED

AD NUMBER

AD852956

NEW LIMITATION CHANGE

TO

Approved for public release, distribution unlimited

FROM

Distribution authorized to U.S. Gov't. agencies and their contractors; Administrative/Operational use; Mar 1969. Other requests shall be referred to Air Force Materials Laboratory, Wright-Patterson AFB, Ohio 45433.

AUTHORITY

AFML ltr, 7 dec 1972

THIS PAGE IS UNCLASSIFIED

AFML-TR-66-402, PART II

CROSSLINKING AND FILLER REINFORCEMENT OF PERFLUOROALKYLENE TRIAZINE ELASTOMERS

T. L. GRAHAM

TECHNICAL REPORT AFML-TR-66-402, PART II

MARCH 1969

This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of the Elastomers and Coatings Branch, (MANE), Nonmetallic Materials Division, Air Force Materials Laboratory, Wright-Patterson AFB, Ohio 45433.

AIR FORCE MATERIALS LABORATORY
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

64

NOTICE

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of the Elastomers and Coatings Branch (MANE), Nonmetallic Materials Division, Air Force Materials Laboratory, Wright-Patterson AFB, Ohio 45433.

The distribution of this report is limited because the U. S. Export Control Act is applicable.

Copies of this report should not be returned unless return is required by security considerations, contractual obligations, or notice on a specific document.

S00 - May 1969 - CO455 - 76-1689

AFML-TR-66-402, PART II

CROSSLINKING AND FILLER REINFORCEMENT OF PERFLUOROALKYLENE TRIAZINE ELASTOMERS

T. L. GRAHAM

This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of the Elastomers and Coatings Branch, (MANE), Non-metallic Materials Division, Air Force Materials Laboratory, Wright-Patterson AFB, Ohio 45433.

FOREWORD

This report was prepared by the Elastomers and Coatings Branch, Nonmetallic Materials Division, Air Force Materials Laboratory, Air Force Systems Command, with Mr. T. L. Graham as project engineer. The work was initiated under Project 7340, "Nonmetallic and Composite Materials," Task 734005, "Elastomeric and Compliant Materials."

This report covers work accomplished during the period September 1966 to February 1968.

The manuscript was released by the author November 1968 for publication.

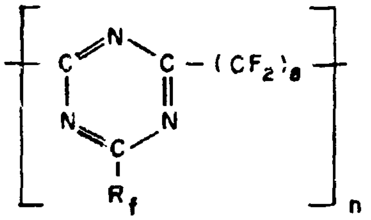
This technical report has been reviewed and is approved.

W P Johnson

W. P. JOHNSON, Chief
Elastomers and Coatings Branch
Nonmetallic Materials Division
Air Force Materials Laboratory

ABSTRACT

This report covers further progress made toward the development of a high-strength general-purpose vulcanizate based on perfluoroalkylene triazine polymer for potential use in the 500 to 800°F range. The triazine polymer involved in this research had the following generalized structure:



Of the several lots of experimental perfluorooctamethylene triazine polymer evaluated, a polymer with trifluoromethyl and n-cyanoperfluoropropylene groups in the pendant position yielded vulcanizates with the best overall properties. Tetraphenyl tin and surface-treated silica proved to be, respectively, the most satisfactory curing and reinforcing agents for this polymer system. The compounded triazine polymer does not become brittle when aged in air for extended periods even at temperatures as high as 700°F and in addition retains a substantial portion of its original tensile properties. The tetraphenyl-tin cured polymer was also found to possess excellent electrical insulating properties and exhibited good resistance to compression set at 500°F. Results of hot wire ignition tests have shown this type of polymer to be noncombustible in pure oxygen. Further, it does not appear to be moisture sensitive under ordinary conditions.

This abstract is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of the Elastomers and Coatings Branch (MANE), Nonmetallic Materials Division, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio 45433.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF ILLUSTRATIONS (CONTD)

FIGURE PAGE

LIST OF TABLES

LIST OF TABLES (CONTD)

SECTION I

INTRODUCTION

Perfluoroalkylene triazine polymers, among other experimental fluorinated polymers, are being developed for fulfilling Air Force materials needs in the area of high-temperature resistant elastomers. About three and one-half years ago an internal research program was initiated to obtain suitable modifiers for crosslinking and reinforcing these high-temperature stable triazine elastomeric polymers.

The purpose of this internal exploratory compounding work, in addition to providing data to guide future polymer synthesis programs, is to develop high strength general purpose elastomeric compositions (e.g., an extrusible compound for insulating wire, a moldable compound for fabricating O-ring seals, etc.) for use in advanced Air Force weapon systems at temperatures up to 800°F.

The initial samples of polymers available during the early stages of this exploratory compounding research program were highly gelled and difficult to process, but proved useful for evaluating candidate curing agents. Good states of cure of the triazine elastomer were developed with several of the selected metallic and nonmetallic candidate compounds. Although the results were encouraging from this viewpoint, the resultant vulcanizates had relatively poor mechanical properties and lacked in thermal stability. Since the completion of this earlier work, additional quantities of polymer have been prepared and the results of research with these advanced materials are covered in this report.

SECTION II

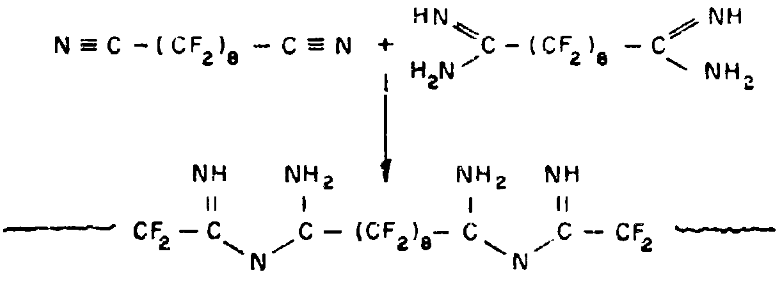
SYNTHESIS OF PERFLUOROALKYLENE TRIAZINE ELASTOMERS

A. GENERAL SYNTHESIS PROCEDURE

Several approaches (Reference 1) are under investigation for the synthesis of triazine elastomers. Of the approaches being investigated, one pursued by the Hooker Chemical Corporation under contract with the Air Force has produced the most suitable gums for this exploratory compounding development program. The process is based on the addition polymerization of perfluoroalkylene dinitriles with diamidines; this forms high molecular weight polyimidoylamidine intermediates. An excess of a perfluorinated acid anhydride or an excess of a mixture containing a perfluorinated acid anhydride and a perfluorinated cyanoacyl chloride are used to convert these types of polymeric intermediates into triazine elastomeric polymers. The products obtained by this approach are comprised of triazine rings separated by perfluorinated polymethylene groups, bearing all perfluoroalkyl pendant groups or perfluoroalkyl and n-cyanoperfluoroalkylene pendant groups.

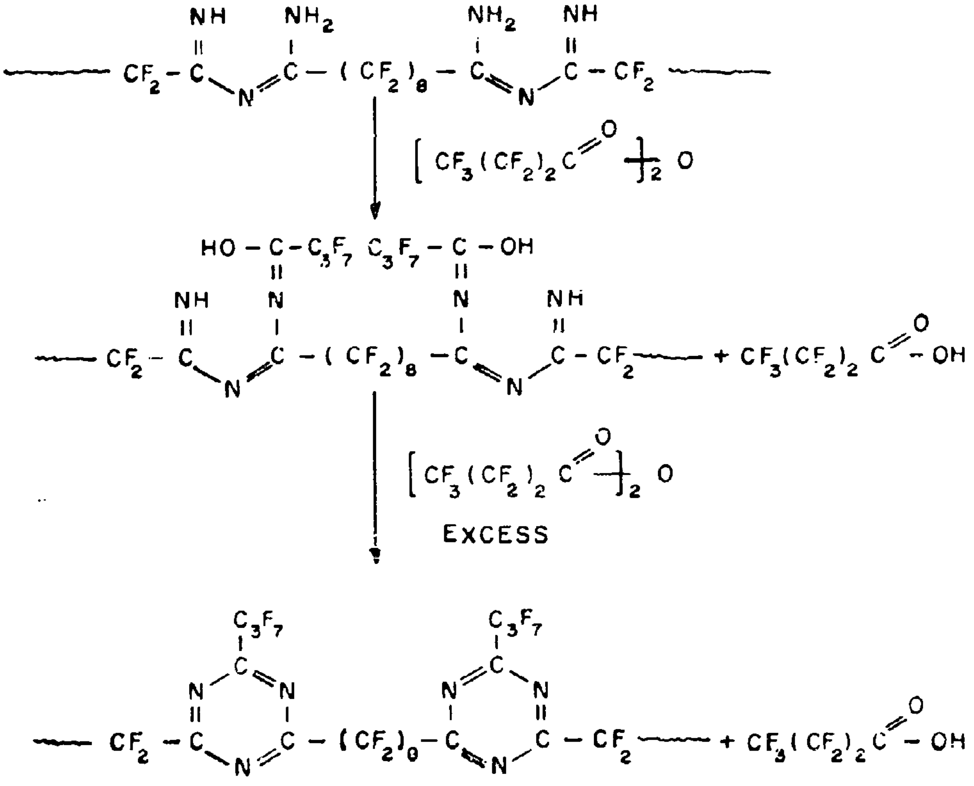
B. CHEMICAL COMPOSITIONS OF THE EXPERIMENTAL POLYMERS

The polymers of interest were derived from polyimidoylamidine intermediates obtained by copolymerizing perfluorosebaconitrile and perfluorosebacamidine, Equation I:

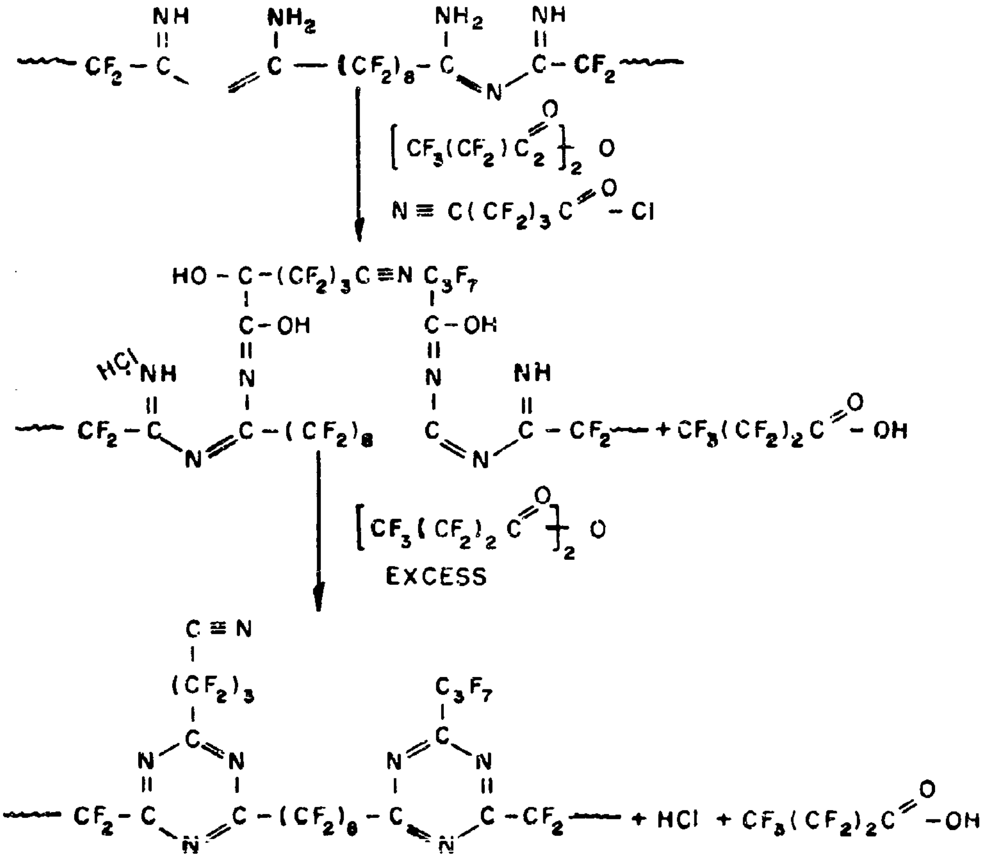


I

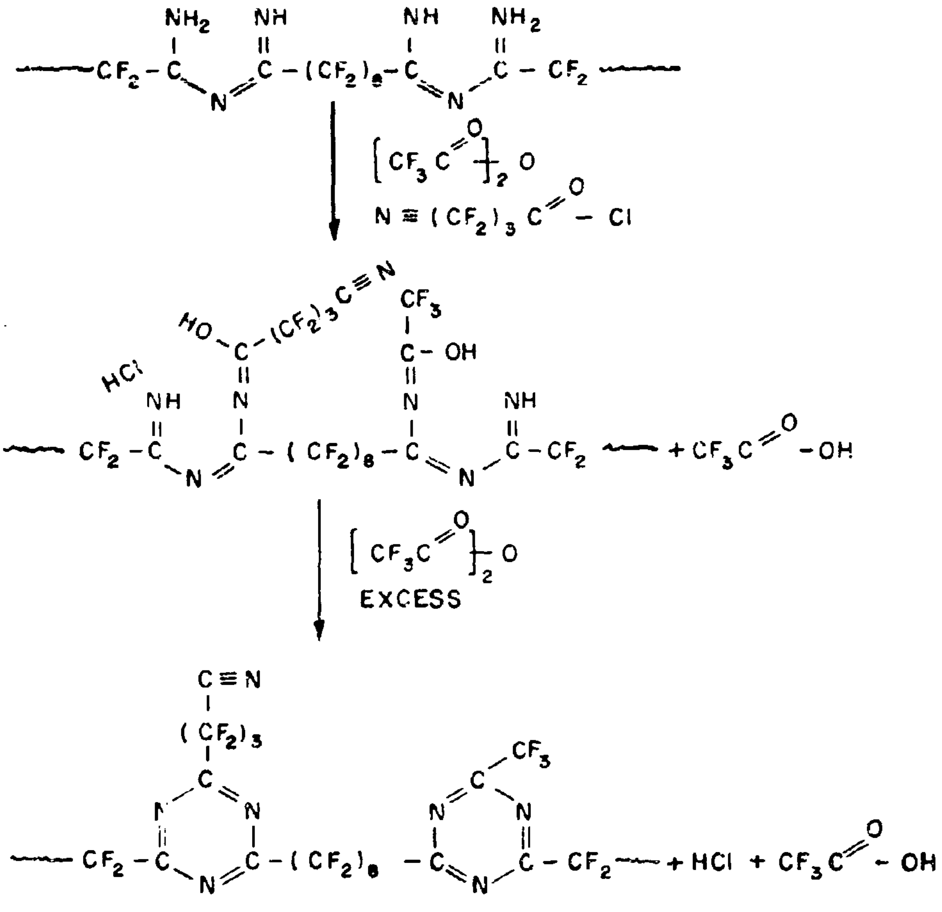
The types of polymers exploited, i.e., polymers bearing all perfluoropropyl pendant groups, polymers with n-cyanoperfluoropropylene and perfluoropropyl pendant groups, and polymers bearing n-cyanoperfluoropropylene and trifluoromethyl pendant groups were prepared by treating portions of the above intermediate (I) with, respectively: an excess of perfluorobutyric anhydride, Equation II; mixtures comprised of an excess of perfluorobutyric anhydride and n-cyanoperfluorobutyryl chloride, Equation III; and mixtures comprised of an excess of perfluoroacetic anhydride and n-cyanoperfluorobutyryl chloride, Equation IV.



II



III



IV

C. PHYSICAL CHARACTERISTICS OF THE EXPERIMENTAL POLYMERS

The molar ratios of the acylating-cyclodehydrating reactants used in preparing the gums versus the reduced viscosities and the percent of soluble polymer are summarized in Table I.

Although a polymer with increased numbers of functional pendant n-cyanoperfluoropropylene pendant groups is anticipated as the ratio of the n-cyanoperfluorobutyryl chloride to perfluorinated anhydride increases, the exact number of functional groups introduced in each case has not been established. Analytical results obtained by the contractor indicated that not more than 5 mole percent of the functional monomer is incorporated using mixtures containing 20% of n-cyanoperfluorobutyryl chloride.

As indicated by the results of viscosity measurements, there were variations in molecular weight. The variations in part, were due to differences in the processing techniques used in recovering the finished polymer. To ensure the removal of impurties, the gums (IV)* prepared employing reaction mixtures containing 7 and 12 mole percent of n-cyanoperfluorobutyryl chloride were reprecipitated from hexafluoroxylene using glyme. In the process, low molecular weight polymer was inadvertently extracted; consequently, the recovered products had much higher molecular weight than the other polymers (II) and (III), which were recovered by vaccum removal of the volatile by-products formed and solvent used.

The solubility of the experimental polymers was determined at room temperature using hexafluoroxylene as the solvent. A 1/100 polymer to solvent ratio was used. The percent soluble polymer was determined after approximately a two-week period.

TABLE I

PHYSICAL CHARACTERISTICS OF EXPERIMENTAL POLYMERS

Sample Identity	Ratio of Reactants	Reduced Viscosity(1)	Soluble Polymer, %(1)
Triazine 16B-1, (II)	0/100(2)	0.722	52.4
Triazine 17B-2A, (IV)	7/93(3)	1.3	98.6
Triazine 17B-1A, (IV)	12/88(3)	1.4	82.5
Triazine 16B-2, (III)	20/80(2)	-	68.1

(1) in hexafluoroxylene

(2) n-cyanoperfluorobutyryl chloride/perfluorobutyric anhydride

(3) n-cyanoperfluorobutyryl chloride/trifluoroacetic anhydride

---

*NOTE: The Roman numerals (II), (III), and (IV) refer to the reaction equations which show the fundamental differences in chemical composition of the various species of triazine gum involved in this research.

SECTION III

INTRINSIC OXIDATIVE THERMAL STABILITY OF EXPERIMENTAL TRIAZINE ELASTOMERS

The relative intrinsic thermal stability of the various lots of perfluorooctamethylene triazine gums were determined at 500°F in an oven having forced circulating air. As shown in Figure 1, the lot of gum (II) bearing all perfluoropropyl pendant groups proved to be more stable than those lots of gum (III and IV) prepared using an excess of mixtures containing n-cyanoperfluorobutyryl chloride and a perfluorinated anhydride. The difference in thermal stability, however, of the gum (IV) prepared using an excess of the 12/88 mole percent ratio of reactants (curve C) and gum (II) bearing all perfluoropropyl pendant groups (Curve A) was slight. Approximate total accumulative weight losses for these gums after aging 3000 hours at 500°F were 4.7 and 3.5%, respectively.

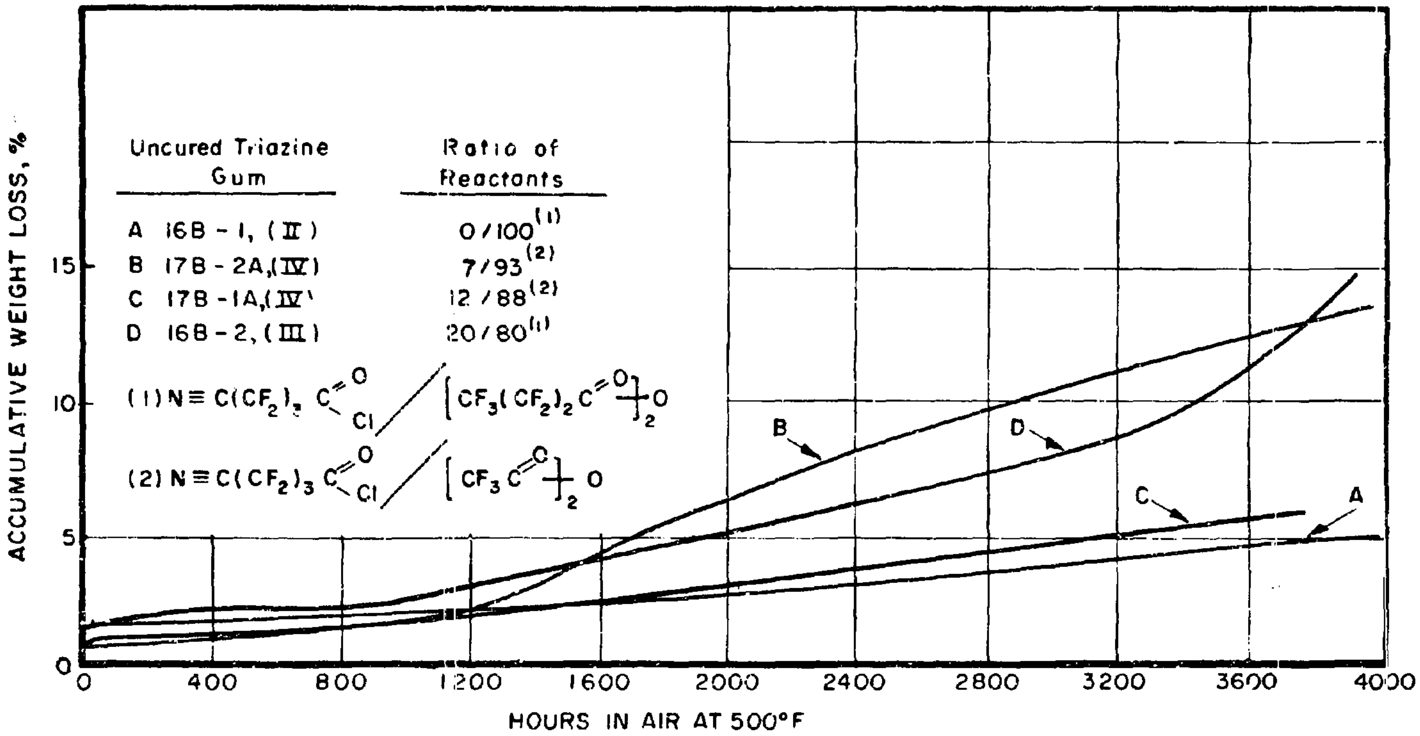


Figure 1. Intrinsic Oxidative Thermal Stability of Experimental Triazine Elastomers

SECTION IV

EFFECTS OF MILLING ON THE INTRINSIC STABILITY OF EXPERIMENTAL TRIAZINE GUMS

Research was conducted to determine the extent to which the intrinsic thermal stability and chemical compositions of the triazine elastomers are altered by milling on a cold mill under normal atmospheric conditions. This investigation was prompted by earlier observations which had shown that triazine gums, like many other elastomeric polymers, were rendered less viscous on milling.

Weight loss data obtained at 500°F on samples of gum milled for 5, 20, and 60 minutes are shown in Figures 2 and 3. These results indicate that gum (III) prepared using an excess of the 20/80 mole percent ratio of reactants to be more susceptible to breakdown than elastomer (II) which has all perfluoropropyl pendant groups. This undesirable change, as the results of weight loss at 500°F indicated, can be minimized by limiting mill processing time.

Analytical data indicate that triazine polymer is also subject to hydrolysis under shear. Infrared spectra obtained on samples of the above lots of polymer after milling periods of 20 and 60 minutes (Figures 5, 6, 8, and 9) revealed the presence of carbonyl, hydrogen-nitrogen, and linear carbon-nitrogen structures. Absorption peaks for these components were not found in the infrared spectra (Figures 4 and 7) obtained on the unmilled gum samples.

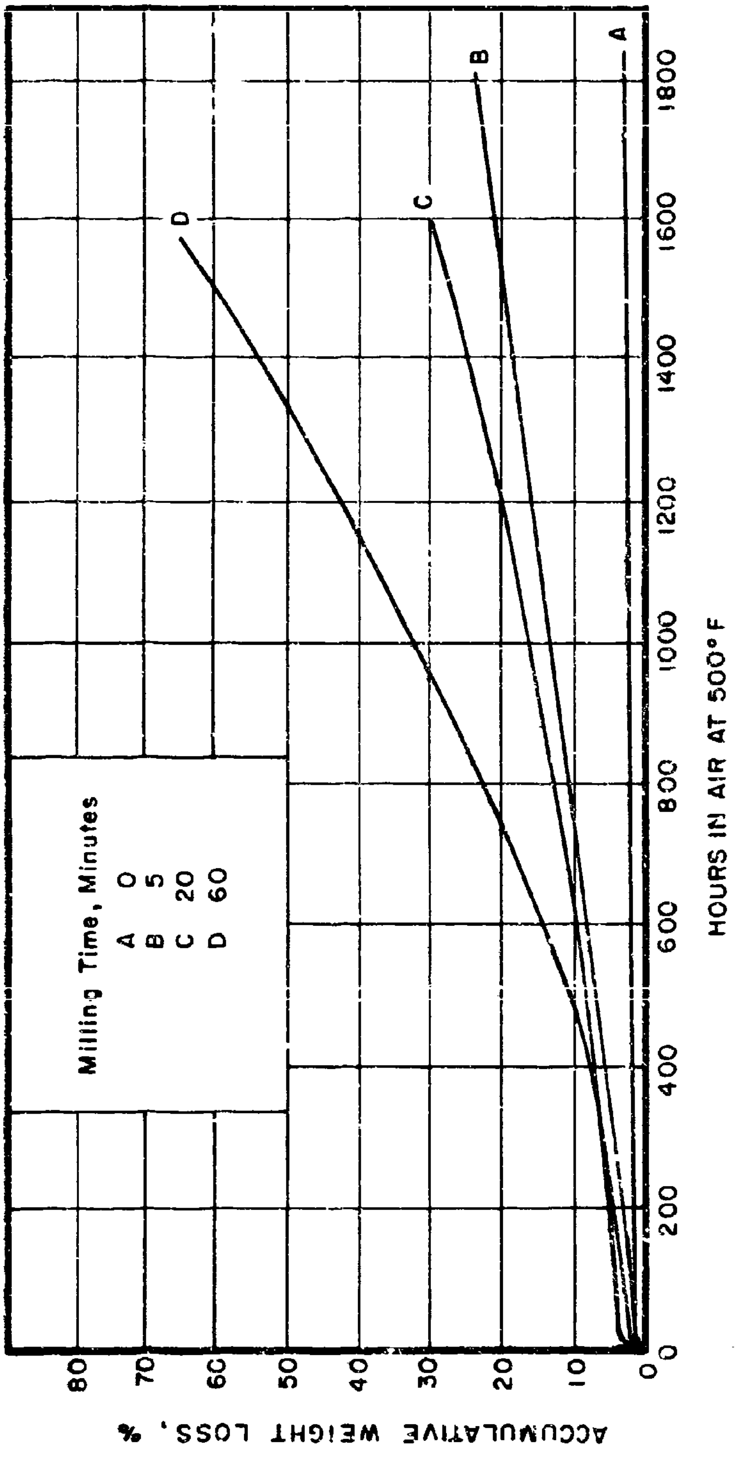


Figure 2. Effect of Milling on the Intrinsic Thermal Stability of Triazine Gum 16P-1, (II)

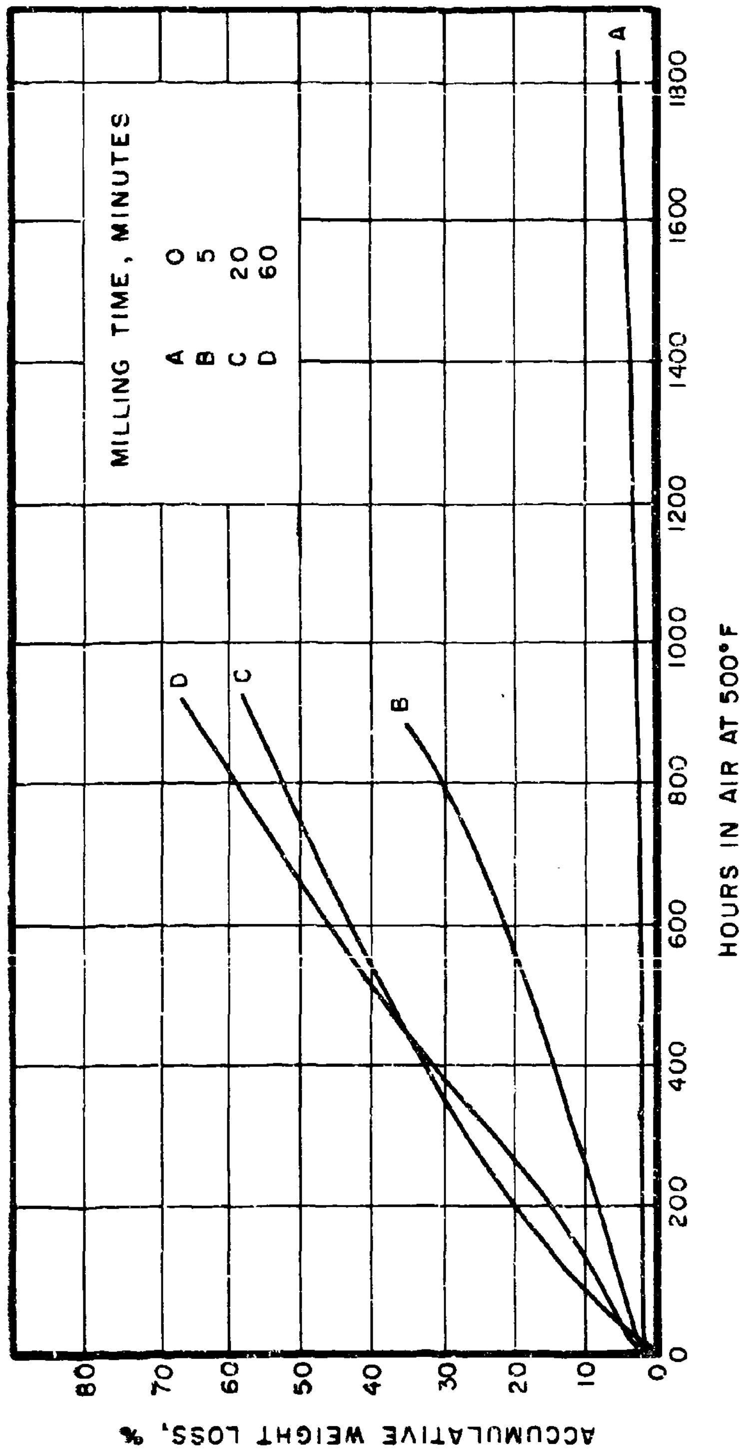


Figure 3. Effect of Milling on the Intrinsic Thermal Stability of Triazine Gum 16B-2, (III)

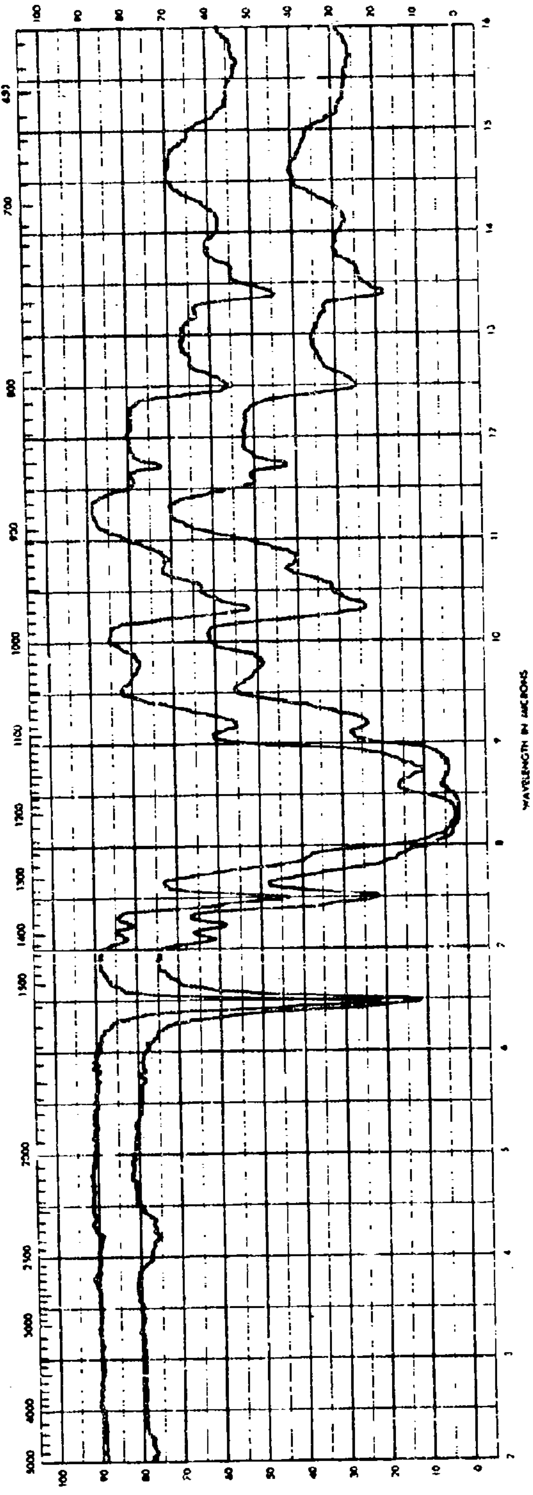


Figure 4. Infrared Absorption Spectrum Obtained on Triazine Gum 16B-1, (II), Prior to Milling

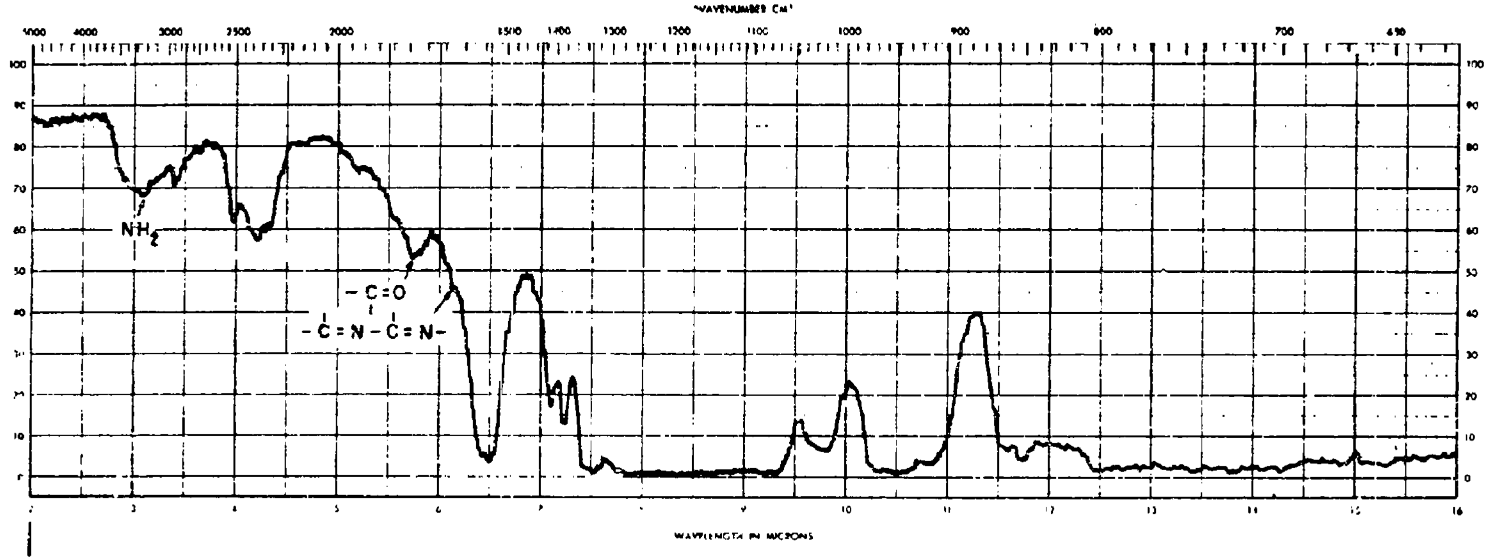


Figure 5. Infrared Absorption Spectrum Obtained on Triazine Gum 16B-1, (II), Milled for 20 Minutes

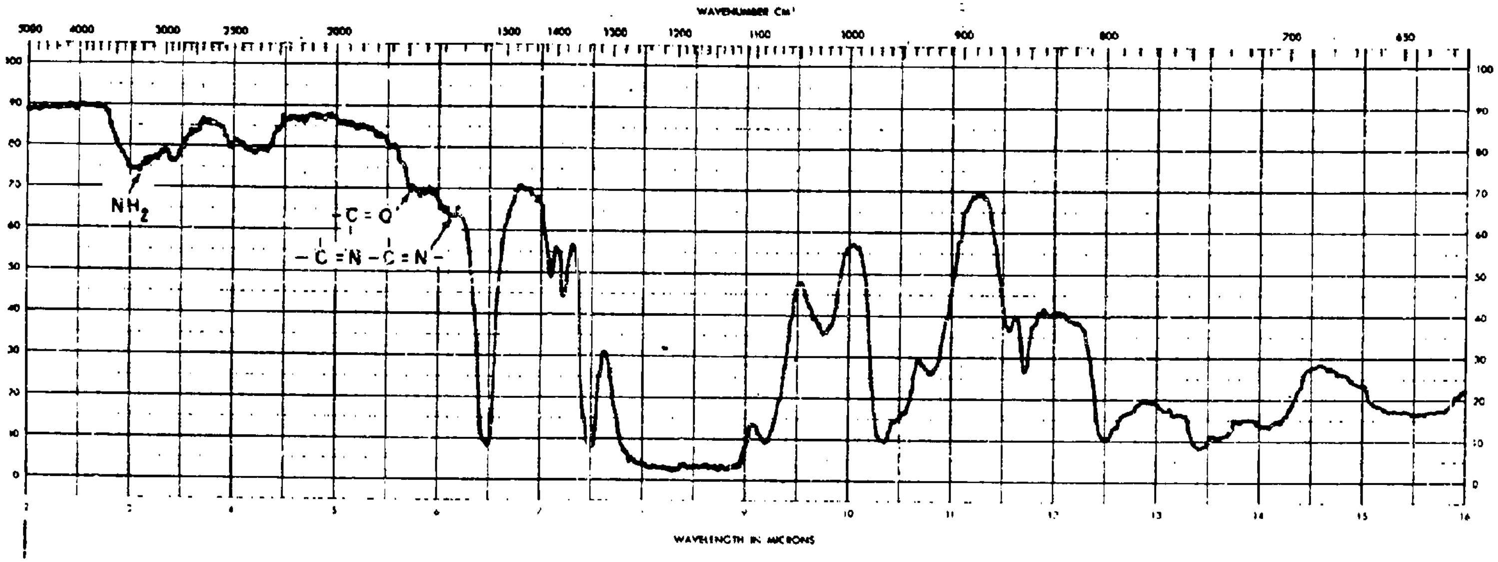


Figure 6. Infrared Absorption Spectrum Obtained on Triazine Gum 16B-1, (II), Milled for 60 Minutes

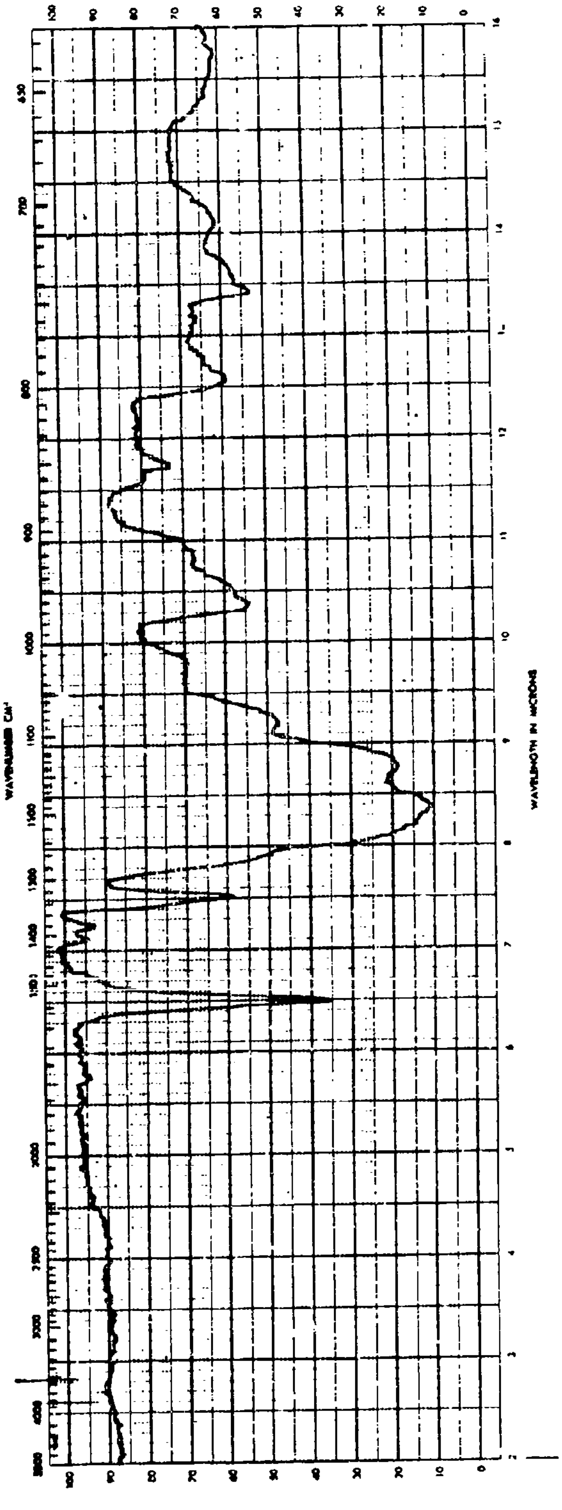


Figure 7. Infrared Absorption Spectrum Obtained on Triazine Gum 16E-2, (III), Prior to Milling

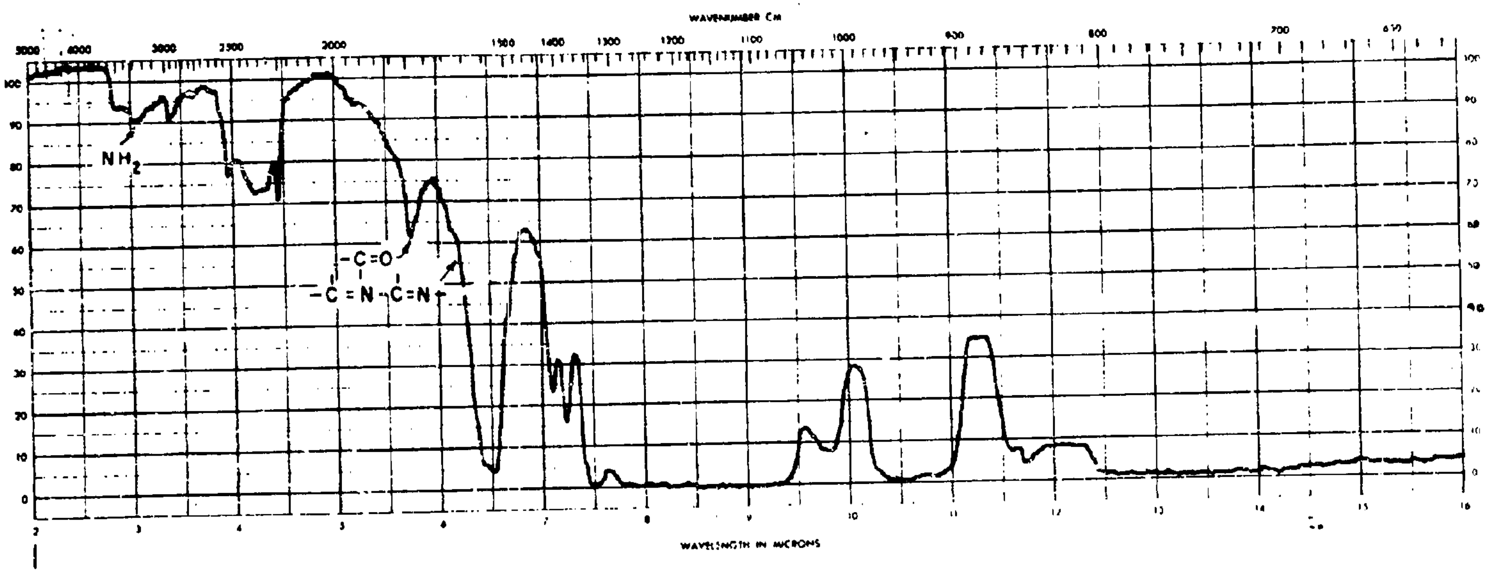


Figure 8. Infrared Absorption Spectrum Obtained on Triazine Gum 16B-2, (III), Milled for 20 Minutes

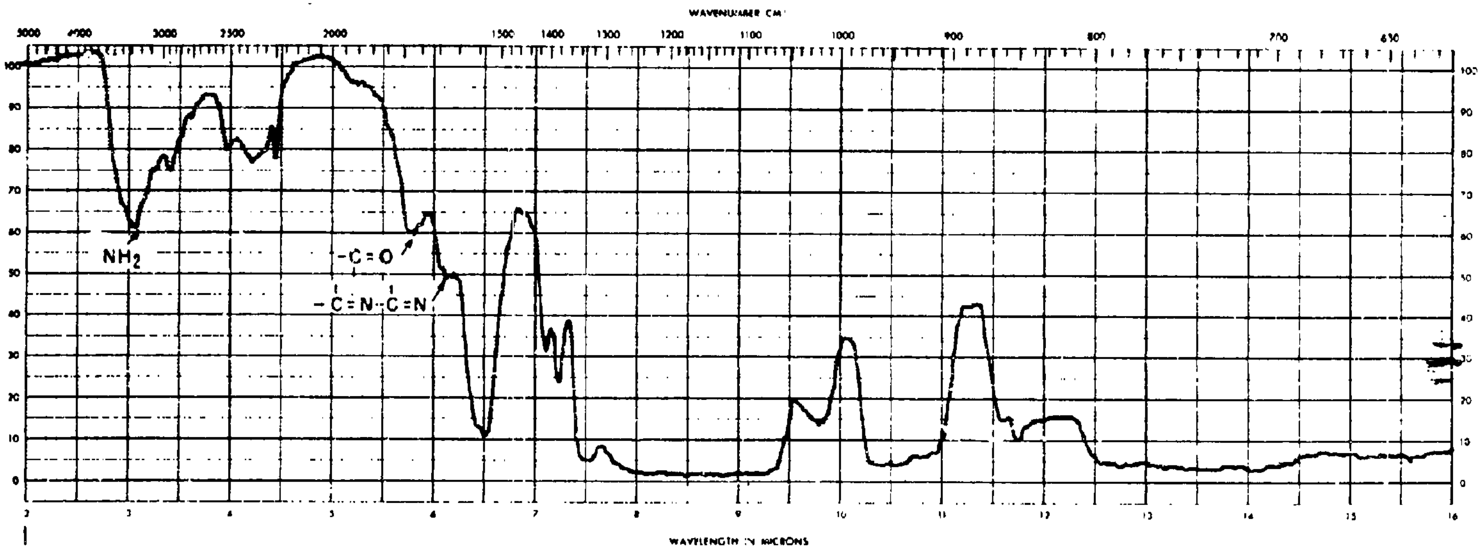


Figure 9. Infrared Absorption Spectrum Obtained on Triazine Gum 16B-2, (III), Milled for 60 Minutes

SECTION V

EXPLORATORY CHEMICAL CROSSLINKING INVESTIGATIONS

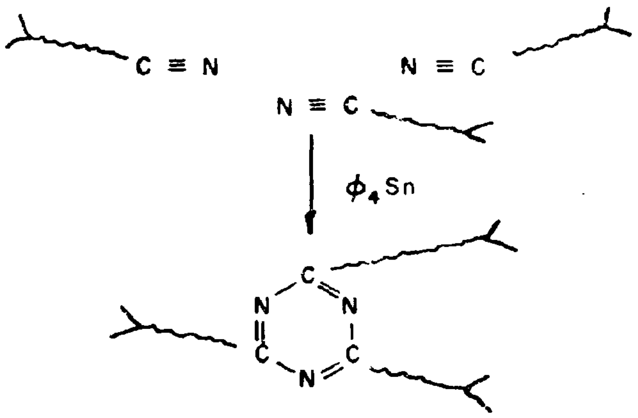
In further attempting to obtain an elastomeric triazine vulcanizate possessing exceptional stability at elevated temperatures, several of the compounds screened in the earlier lots of triazine gum (Reference 2) and other selected candidate curing agents were evaluated in conjunction with the improved lots of triazine polymer just described. Of the materials evaluated, structurally sound vulcanizates were obtained with the metallic and nonmetallic compounds listed below:

Metallic
Tetraphenyl Tin
Barium Oxide

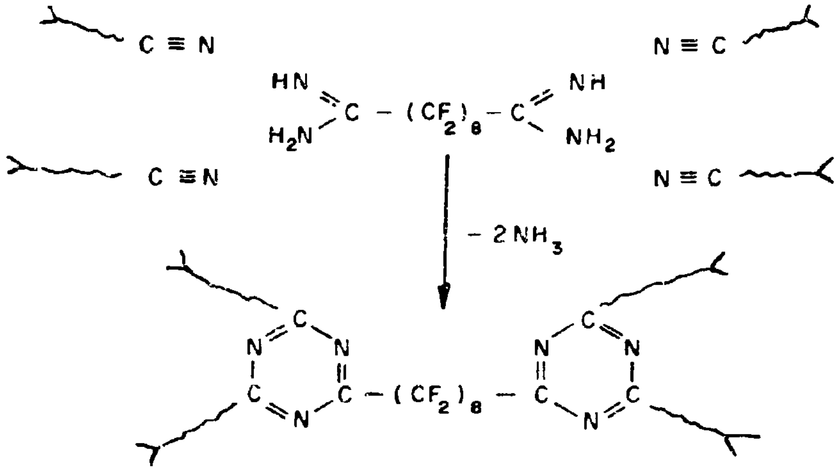
Nonmetallic
Perfluoroglutarimidine
Perfluorosebacamidine
Perfluoroglutarthioamide
N,N-bis(perfluorobutyrimidoyl)
perfluoroglutaramidine
Melamine

Tetraphenyl tin and perfluoroglutarimidine proved to be effective for curing both types of polymer. The remaining compounds were only effective for curing polymer-bearing nitrile pendant groups.

The mechanisms whereby cured products are obtained are not fully understood. As the above metallic compounds have been shown to be effective catalysts for trimerizing model perfluoroalkylnitrile compounds to triazines, it is feasible that triazine ring crosslinks are formed in curing reactions involving gums (III and IV) with nitrile pendant groups and metallic compounds as illustrated below:



Curing reactions involving the ammonia or the hydrogen sulfide adducts of dinitriles and gums (III and IV) containing nitrile pendant groups, it is believed, lead to crosslinked products consisting of triazine rings connected by perfluoroalkylene groups. Such linkages, schematically illustrated below for the ammonia derivative of perfluorosebaconitrile, would be formed by the addition and condensation of the diamidine with the nitrile pendant groups attached to the polymer chain, with ammonia being liberated in the process.



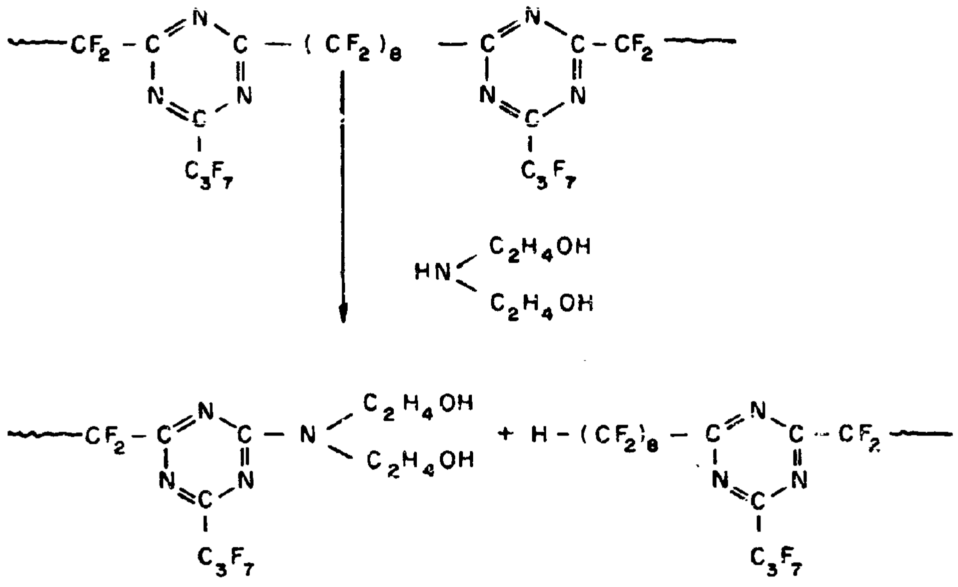
In the case of the H_2S dinitrile derivative, a similar reaction mechanism is postulated, H_2S being liberated in the process. With the 2:1 molar ratio monamidine to dinitrile adduct [N,N'bis (perfluorobutyrimidoyl) perfluoroglutaramidine] the mechanism of crosslinking is complicated. This adduct, it is suspected, quickly rearranges to a cyclic product which decomposes, liberating ammonia and perfluoroglutaronitrile or ammonia addition products of nitriles. These decomposition products are capable of interacting with the pendant cyanostructures to produce triazine-containing crosslinks. Curing reactions involving melamine and gum (III) bearing nitrile pendant groups as well as systems based on polymer (II) without functional groups are also complex. The attainment of cured products in these instances, it is thought, results from rearrangement of the basic polymer structure.

A standard reaction temperature of 320°F was used when molding and vulcanizing the samples required for evaluation. Compounds bearing metallic catalysts, in most cases, were cured for a period of 20 hours, although, in some instances, 16 hours may have been sufficient. Good states of cure were obtained with the nonmetallic vulcanizing agents within a period of two hours or less, as indicated.

Triazine gums 17B-2A (IV), and 17B-1A, (IV), yielded vulcanizates (Tables III and IV) with tensile properties superior to those of vulcanizates based on triazine gums 16B-1, (II), Table II, and 16B-2, (III), Table V. The high tensile strengths of the perfluoroglutarthioamide and tetraphenyl-tin-cured based on triazine gums 17B-1A and 17B-2A are attributed to the relatively high molecular weight of these particular lots of polymer.

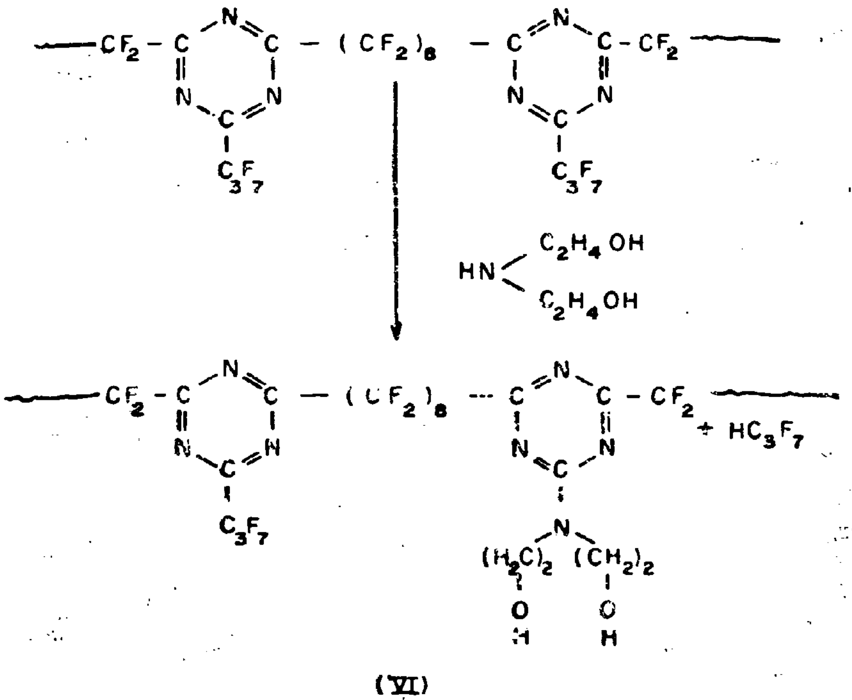
These vulcanizates proved to be less thermally stable than the uncured gums. As the results of 500°F aging show (Figures 10-13), the vulcanized gums lost substantially more weight than the corresponding uncured gums. In addition to the relatively high weight losses noted, vulcanizates obtained using melamine, perfluorosebacamidine, perfluoroglutarimidine, bis (perfluorobutyrimidoyl) perfluoroglutaramidine, and perfluoroglutarthioamide became spotted with pinholes. The vulcanizates obtained using tetraphenyl tin and barium oxide retained their structural integrity. Considering tensile properties and thermal stability, tetraphenyl tin in conjunction with triazine gum 17B-1A provided the most satisfactory vulcanizate.

In addition to the foregoing methods of obtaining cured triazine products, an approach involving the introduction of functional groups which would coordinate with a chromium ion to give a polymer with thermally stable crosslinks was also investigated. In investigating this approach, 1 part of diethanolamine was blended with 100 parts of triazine gum 2215-71-1, (II), bearing all perfluoropropyl pendant groups. The compounded gum was then heated in air at 120°C for 1 hour to induce a reaction. If the results of work, by Dr. Henry C. Brown and Mr. John Turnbull (Reference 3), involving the investigation of the reaction of amines with a model triazine compound apply, this treatment should have lead to the incorporation of aminodiethanol functional groups, predominately terminal groups, via the reaction (Equation V):



V

and possibly a small number of pendant groups through the replacement of perfluoropropyl groups as shown in Equation VI.



(VI)

TABLE II

TENSILE PROPERTIES OF VULCANIZATES BASED ON TRIAZINE GUM 16B-1, (II), CURED WITH SELECTED METALLIC AND NONMETALLIC CANDIDATE COMPOUNDS

Triazine Gum 16B-1, (II)	100	100
Tetraphenyl Tin	5	-
Perfluoroglutarimidine	-	5
Physical Properties at R.T.		
Press Cured at 320°F, hrs	20	2
Tensile Strength, psi	540	400
Elongation, %	700	440

TABLE III

TENSILE PROPERTIES OF VULCANIZATES BASED ON TRIAZINE GUM 17B-2A, (IV), CURED WITH SELECTED METALLIC AND NONMETALLIC CANDIDATE COMPOUNDS

Triazine Gum 17B-2A, (IV)	100	100
Tetraphenyl Tin	5	-
Perfluoroglutarthioamide	-	5
Physical Properties at R.T.		
Press Cured at 320°F, hrs	20	1
Tensile Strength, psi	940	1045
Elongation, %	500	550

TABLE IV

TENSILE PROPERTIES OF VULCANIZATES BASED ON TRIAZINE GUM 17B-1A, (IV), CURED WITH SELECTED METALLIC AND NONMETALLIC CANDIDATE COMPOUNDS

Triazine Gum 17B-1A, (IV)	100	100
Tetraphenyl Tin	5	-
Perfluoroglutarthioamide	-	5
Physical Properties at R.T.		
Press Cured at 320°F, hrs	20	1
Tensile Strength, psi	1260	1180
Elongation, %	415	565

TABLE V

TENSILE PROPERTIES OF VULCANIZATES BASED ON TRIAZINE GUM 16B-2, (III), CURED WITH SELECTED METALLIC AND NONMETALLIC COMPOUNDS

Triazine Gum 16B-2, (III)	100	100	100	100	100	100	100
Tetraphenyl Tin	5	-	-	-	-	-	-
Perfluoroglutarimidine	-	5	-	-	-	-	-
Perfluorosebacamidine	-	-	5	-	-	-	-
Melamine	-	-	-	2.5	-	-	-
Barium Oxide	-	-	-	-	5	-	-
Perfluoroglutarthioamide	-	-	-	-	-	5	-
N,N' bis (perfluorobutyrimidine) perfluoroglutaramidine	-	-	-	-	-	-	2.5
Physical Properties at R. T.							
Press Cured at 320°F, hrs	20	2	2	2	20	1	2
Tensile Strength, psi	415	465	385	325	345	540	355
Elongation, %	100	[illegible]	110	270	180	200	275

At any rate, structurally sound vulcanizates based on the diethanolamine modified gum were obtained using chromium trifluoroacetate, which previous work showed to be ineffective for curing the untreated polymer.

Physical properties of the diethanolamine modified triazine gum (Table VI) cured with 0.5 parts of chromium trifluoroacetate were somewhat better than those of the vulcanizate obtained using 1.0 part of this curing agent but were inferior to those of the tetraphenyl-tin vulcanizates based on triazine gums 17B-1A, (IV), and 17B-2A, (IV); see Tables III and IV. The chromium trifluoroacetate vulcanizates also proved to be less thermally stable than the tetraphenyl-tin triazine gum 17B-1A, (IV), vulcanizate (Figure 14). Accumulative eight losses for the modified gums cured with 0.5 and 1.0 parts of chromium trifluoroacetate after 1500 hours were respectively 29 and 25.5%. During the same period of aging the tetraphenyl-tin-cured triazine gum 17B-1A, (IV), vulcanizate had a weight loss of only 10.5%.

TABLE VI

TENSILE PROPERTIES OF VULCANIZATES BASED ON DIETHANOLAMINE MODIFIED TRIAZINE GUM 2215-71-1, (II), CURED WITH CHROMIUM TRIFLUOROACETATE

Triazine Gum 2215-71-1, (II)	100	100
Diethanolamine	1	1
Chromium Trifluoroacetate	0.5	1
Physical Properties at R. T.		
Press Cured 1 hr at 330°F		
Post Cured at 120°F, hrs	17	21
Tensile Strength, psi	420	350
Elongation, %	540	290

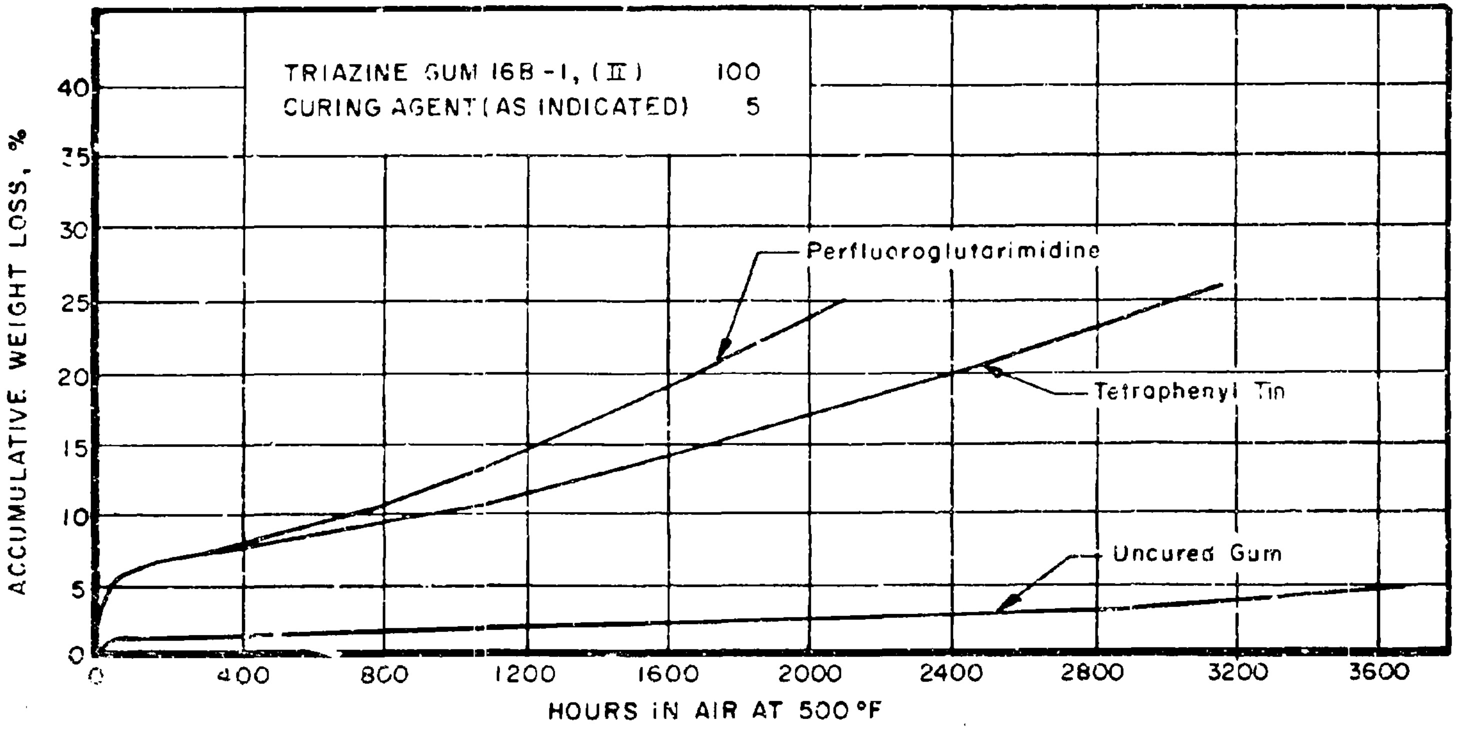


Figure 10. Thermal Stability of Gum Vulcanizates Based on Triazine Gum 16B-1, (II)

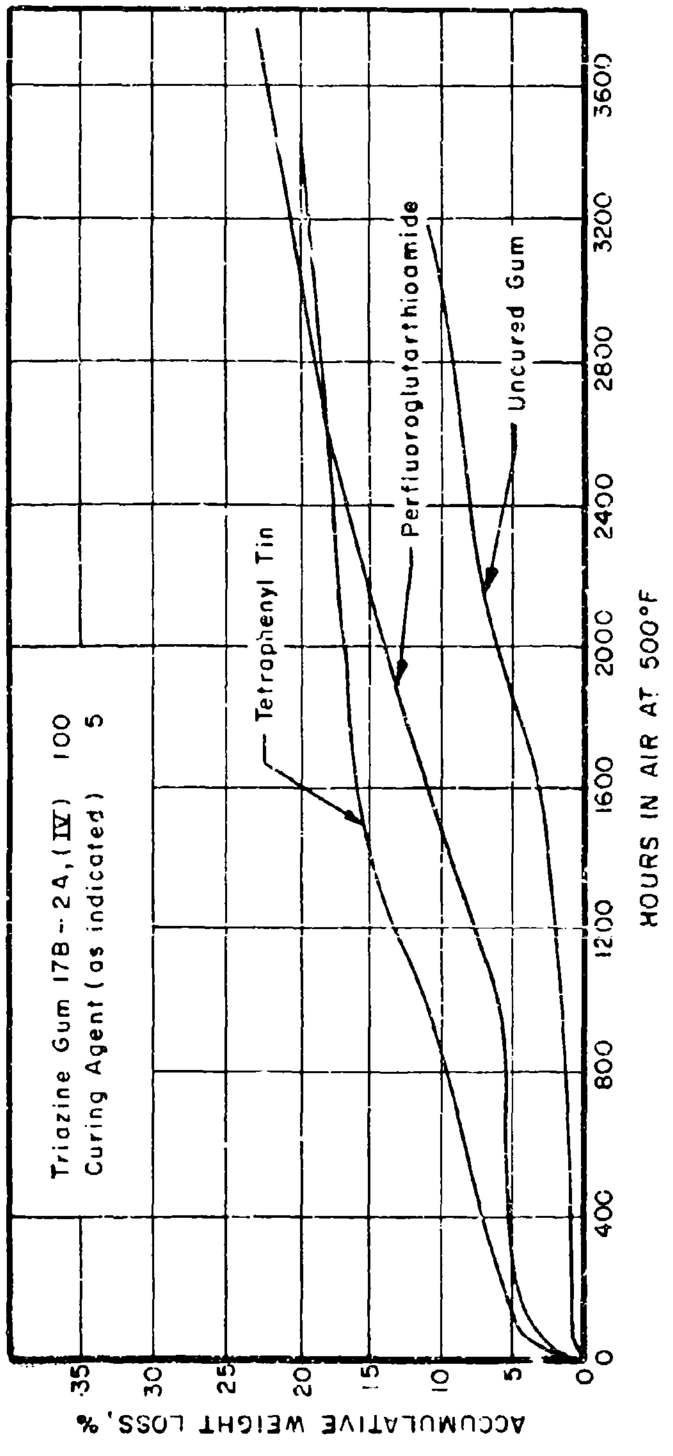


Figure 11. Thermal Stability of Gum Vulcanizates Based on Triazine Gum 17B-2A, (IV)

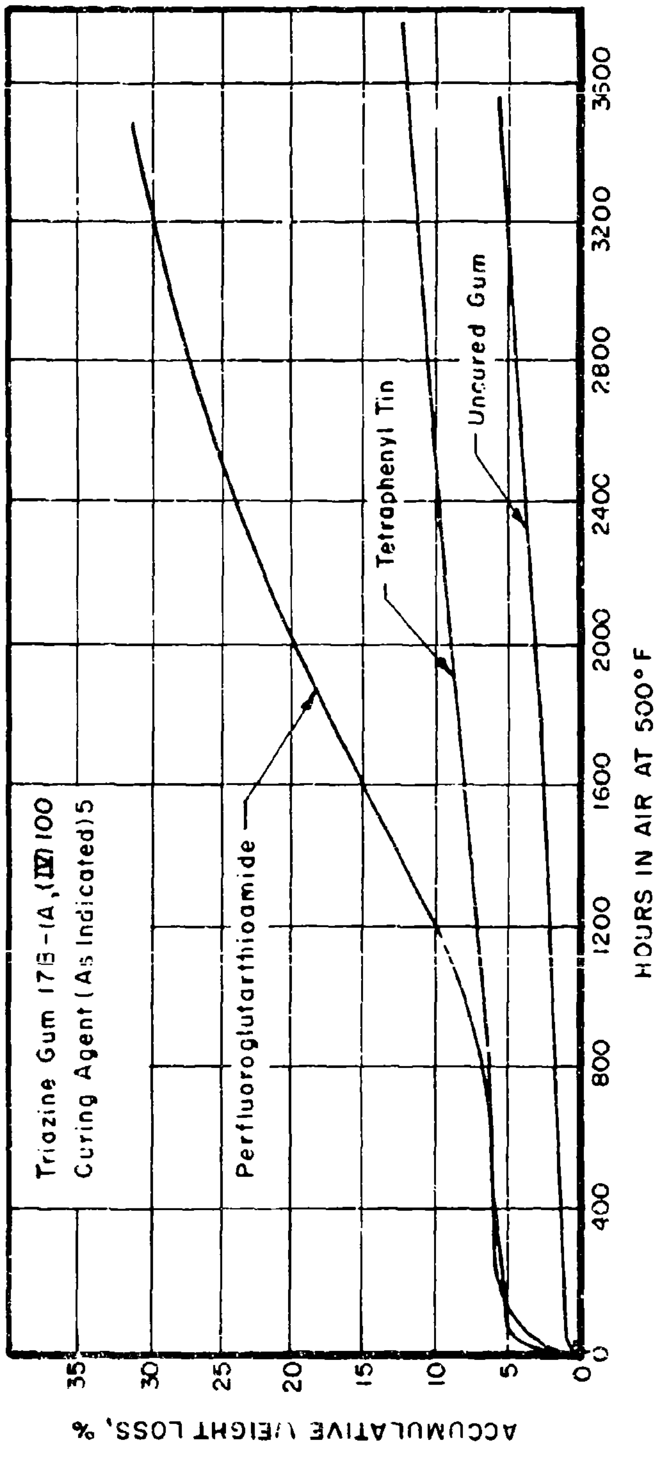


Figure 12. Thermal Stability of Gum Vulcanizates Based on Triazine Gum 17B-1A, (IV)

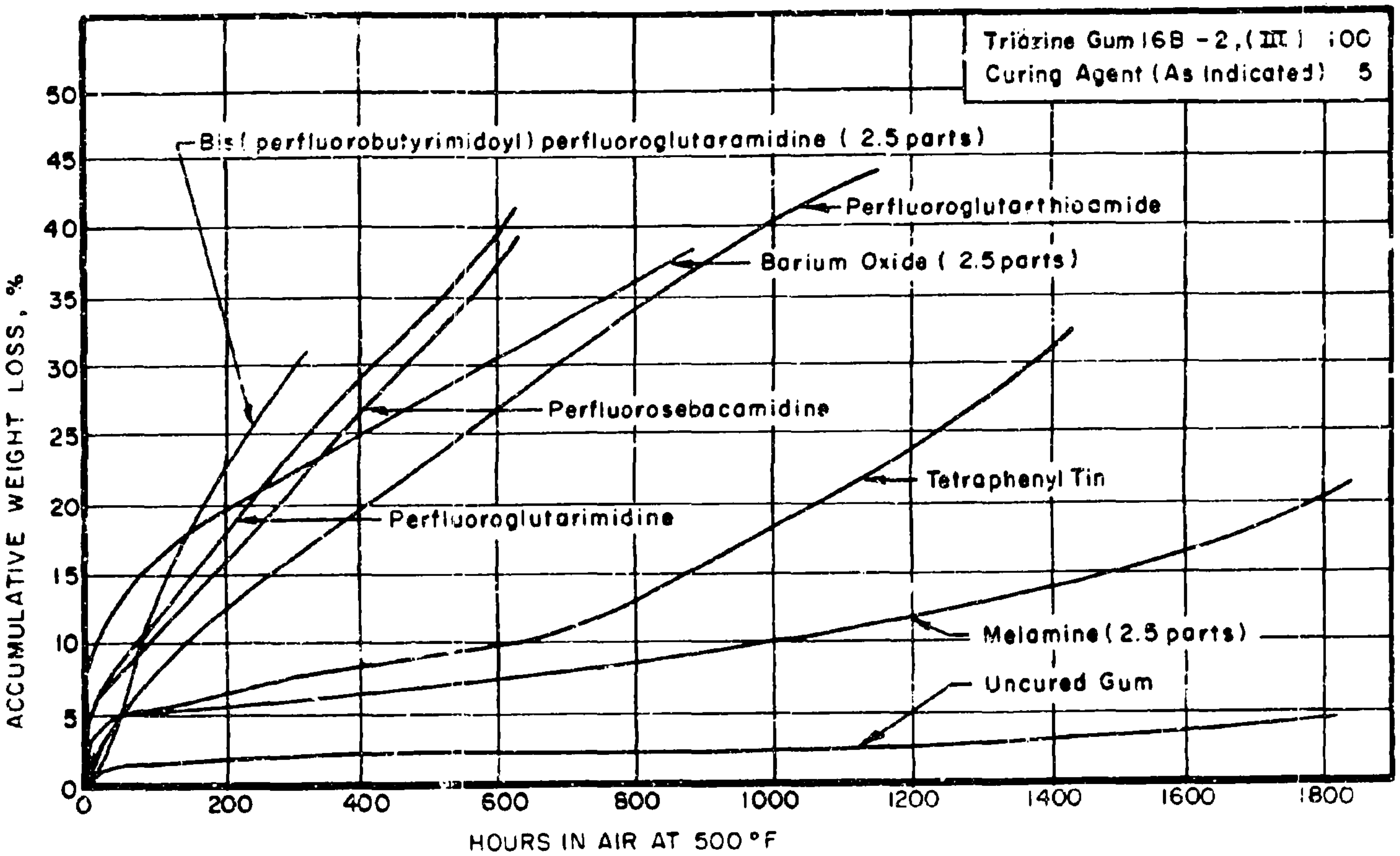


Figure 13. Thermal Stability of Gum Vulcanizates Based on Triazine Gum 16B-2, (III)

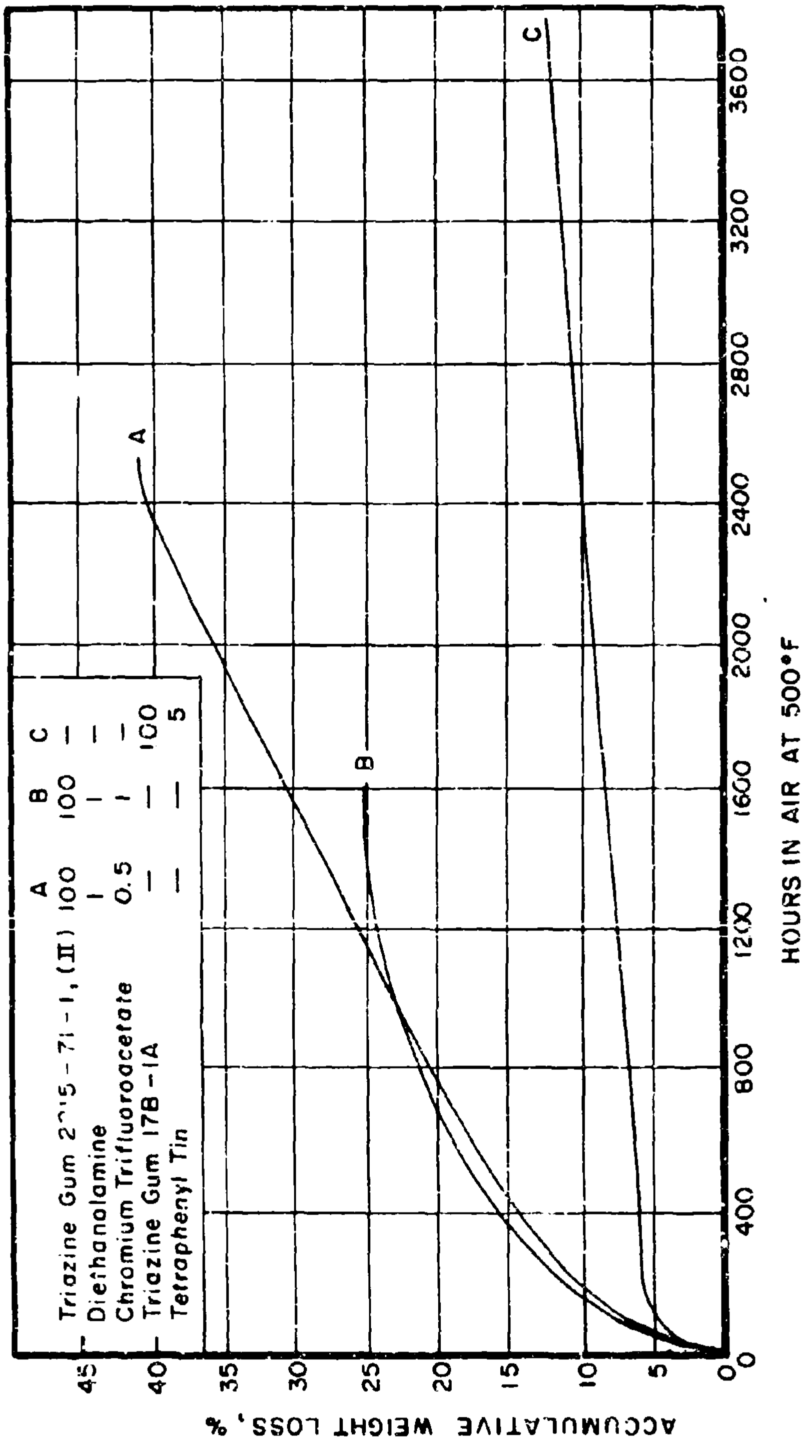


Figure 14. Thermal Stability of Chromium Trifluoroacetate Cured, Diethanolamine Treated Triazine Gum 2215-71-1 (II)

SECTION VI

EFFECTS OF HIGH TEMPERATURE AGING ON THE PHYSICAL PROPERTIES OF VULCANIZED TRIAZINE GUMS

To obtain more definitive information regarding the relative high temperature stability of tetraphenyl-tin-cured vulcanizates based on a polymer derived using an excess of perfluorobutyric anhydride, triazine gum 16B-1, (II) , and a polymer obtained using an excess of 12/88 mole percent ratio of reactants, triazine gum 17B-1A (IV) , room temperature physical properties of the above gum vulcanizates were determined after various periods of exposure at 500, 600, and 700°F.

These results concur with the weight loss data (Figures 10 and 12) previously obtained at an aging temperature of 500°F. The vulcanizate based on triazine gum 17B-1A, (IV), derived using an excess of the 12/88 mole percent ratio of reactants, proved to be more thermally resistant than the vulcanizate based on triazine gum 16B-1, (II), bearing all perfluoropropyl pendant groups. Even though the latter (Table VII) retained only 55% of its initial tensile strength when aged 24 days at 500°F and completely reverted when exposed for 72 hours at 600°F, the vulcanizate based on gum bearing n-cyanoperfluoropropyl pendant groups after aging periods of 24 days at 500°F, 72 hours at 600°F, and 8 hours at 700°F, respectively, retained approximately 65, 54, and 25% of its original tensile strength. In addition, this gum vulcanizate exhibited good resistance to compression set. A compression set value of 20% was obtained for specimens deflected 25% of their original height when aged 72 hours at 500°F.

TABLE VII

PHYSICAL PROPERTIES OF TETRAPHENYL-TIN-CURED TRIAZINE GUMS 16B-1, (II), AND 17B-1A, (IV), AFTER EXPOSURE TO ELEVATED TEMPERATURES

Triazine 16B-1, (II)	100	-
Triazine 17B-1A, (IV)	-	100
Tetraphenyl Tin	5	5
Physical Properties at R. T.		
Press Cured 20 hrs at 320°F		
Initial		
Tensile Strength, psi	680	1080
Elongation, %	780	415
Shore A Hardness, pts	37	53
Aged 48 hrs at 500°F		
Tensile Strength, psi	675	965
Elongation, %	825	410
Shore A Hardness, pts	53	54
Compression Set, 72 hrs at 500°F(1)	61.6	20
Aged 24 days at 500°F		
Tensile Strength, psi	375	700
Elongation, %	890	400
Shore A Hardness, pts	50	50
Aged 72 hrs at 600°F(2)		
Tensile Strength, psi	-	585
Elongation, %	Reverted	330
Shore A Hardness, pts	-	55
Aged 8 hrs at 700°F(2)		
Tensile Strength, psi	-	265
Elongation, %	-	305
Shore A Hardness, pts	-	76

(1) 25% deflection

(2) Results obtained on specimens heat treated 48 hrs at 500°F

SECTION VII

FILLER REINFORCEMENT INVESTIGATIONS

In continuation of the search for a suitable reinforcing agent, a number of additional experimental and conventional finely divided materials were investigated in the more recent lots of experimental triazine elastomers. Since the results of previous work (Reference 2) left doubts regarding the reinforcing effects of some of the materials screened in the earlier lots of highly insoluble triazine polymer, certain of these fillers were also included in this investigation.

Silica "H" S-17* (a silicon dioxide powder treated with a hydrophobic surface coating agent), carbon blacks (EPC, SRF, and Shawinigan), ASP 103 (a clay treated with a hydrophobic surface coating agent), and Protox 166 (zinc oxide) were among the nonfibrous materials evaluated which exhibited substantial reinforcing effects. With a 20-part loading of these fillers, tetraphenyl tin-cured gums (Tables VIII, IX, and X) were obtained having tensile strengths ranging from 1,555 to 2,490 psi and substantial elongations (295 to 650%). Micro fibrous products (Asbestine 3X, Chrysotile No. 38 III-2, Silicon Nitride Wool, and Fibrene C-400 also reinforced the tetraphenyl tin-cured gum, but to a lesser extent than the above cited nonfibrous materials. Perfluoroglutarthioamide-cured triazine compounds (Table XI) extended with carbon black also possessed good tensile properties. The other candidate materials evaluated were relatively ineffective.

All of the more effective reinforcing agents had an adverse effect on thermal stability (Figure 15, 16, 17, and 18). A tetraphenyl-tin vulcanized compound based on triazine gum 17B-1A, (IV), prepared using 12/88 mole percent ratio of reactants and reinforced with Silica "H" S-17, possessed the best balance in tensile properties and thermal stability. After 1900 hours at 500°F, this silica-reinforced vulcanized compound (Figure 16) had an accumulative weight loss of about 23%. Beyond the 1000-hour period, the rate of weight loss for this compounded gum was approximately 0.01% per hour which is about 5 times greater than the rate at which the cured unreinforced gum (Figure 12) loses weight.

---

* Additional information on the candidate reinforcing agents is given in the Appendix.

TABLE VIII

EFFECT OF CANDIDATE REINFORCING AGENTS ON THE TENSILE PROPERTIES OF TETRAPHENYL-TIN-CURED TRIAZINE GUM 17B-2A, (IV)

Triazine Gum 17B-2A, (IV)	100	100	100	100	100(1)	100
Tetraphenyl Tin	5	5	5	5	5	5
Shawinigan Black	-	20	-	-	-	-
Rilube No. 38	-	-	20	-	-	-
Aluminum Nitride Oxide	-	-	-	20	-	-
Fluorocarbon Resin	-	-	-	-	20	-
Magnesium Silicate	-	-	-	-	-	20
Physical Properties at R. T.						
Press Cured at 320°F, hrs	20	20	20	20	21	20
Tensile Strength, psi	940	2035	1090	985	1140	815
Elongation, %	500	365	515	580	580	460

(1) Compounded on a heated mill

TABLE IX

EFFECT OF CANDIDATE REINFORCING AGENTS ON THE TENSILE PROPERTIES OF TETRAPHENYL-TIN-CURED TRIAZINE GUM 17B-1A, (IV)

Triazine Gum 17B-1A, (IV)	100	100	100	100	100	100	100	100	100
Tetraphenyl Tin	5	5	5	5	5	5	5	5	5
Shawinigan Black	-	20	-	-	-	-	-	-	-
Silica "H" S-17	-	-	20	-	-	-	-	-	-
ASP 103	-	-	-	20	-	-	-	-	-
Protox 166	-	-	-	-	20	-	-	-	-
Stannic Oxide	-	-	-	-	-	20	-	-	-
Barosil	-	-	-	-	-	-	20	-	-
Boron Film (ground)	-	-	-	-	-	-	-	20	-
Silene EF(1)	-	-	-	-	-	-	-	-	20
Physical Properties at R. T.									
Press Cured 20 hrs									
at 320°F									
Tensile Strength, psi	1260	1955	1660	1840	1940	530	440	840	-
Elongation, %	415	300	650	400	500	290	260	340	-

(1) Did not cure

TABLE X

EFFECT OF CANDIDATE REINFORCING AGENTS ON THE TENSILE PROPERTIES OF TETRAPHENYL-TIN-CURED TRIAZINE GUM 16B-2, (III)

Triazine Gum 16B-2, (III)	100	100	100	100	100	100	100	100	100	100	100	100
Tetraphenyl Tin	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Asbestine 3X	-	20	-	-	-	-	-	-	-	-	-	-
Chrysotile No. 38 III-2	-	-	20	-	-	-	-	-	-	-	-	-
Fibrene C-400	-	-	-	20	-	-	-	-	-	-	-	-
EPC Black	-	-	-	-	20	-	-	-	-	-	-	-
Lithafrax 2121	-	-	-	-	-	20	-	-	-	-	-	-
Lithium Fluoride	-	-	-	-	-	-	20	-	-	-	-	-
Min-U-Sil (5U)	-	-	-	-	-	-	-	20	-	-	-	-
Silicon Carbide Whiskers	-	-	-	-	-	-	-	-	20	-	-	-
WFA Graphite Fiber	-	-	-	-	-	-	-	-	-	20	-	-
Silicone Nitride Wool	-	-	-	-	-	-	-	-	-	-	20	-
SAF Black	-	-	-	-	-	-	-	-	-	-	-	20
Physical Properties at R. T.												
Press Cured 20 hrs												
at 320°F												
Tensile Strength, psi	310	1015	1105	905	1555	515	610	680	645	550	1080	2030
Elongation, %	90	100	110	90	380	105	110	105	110	90	95	295

TABLE XI

EFFECT OF A CANDIDATE REINFORCING AGENT ON THE TENSILE PROPERTIES OF PERFLUOROGLUTARTHIOAMIDE-CURED TRIAZINE GUMS 17B-1A, (IV), AND 17B-2A, (IV)

Triazine Gum 17B-1A, (IV)	100	-
Triazine Gum 17B-2A, (IV)	-	100
Perfluoroglutarthioamide	5	5
Shawinigan Black	20	20
Physical Properties at R. T.		
Press Cured 1 hr at 320°F		
Tensile Strength, psi	2220	1645
Elongation, %	440	520

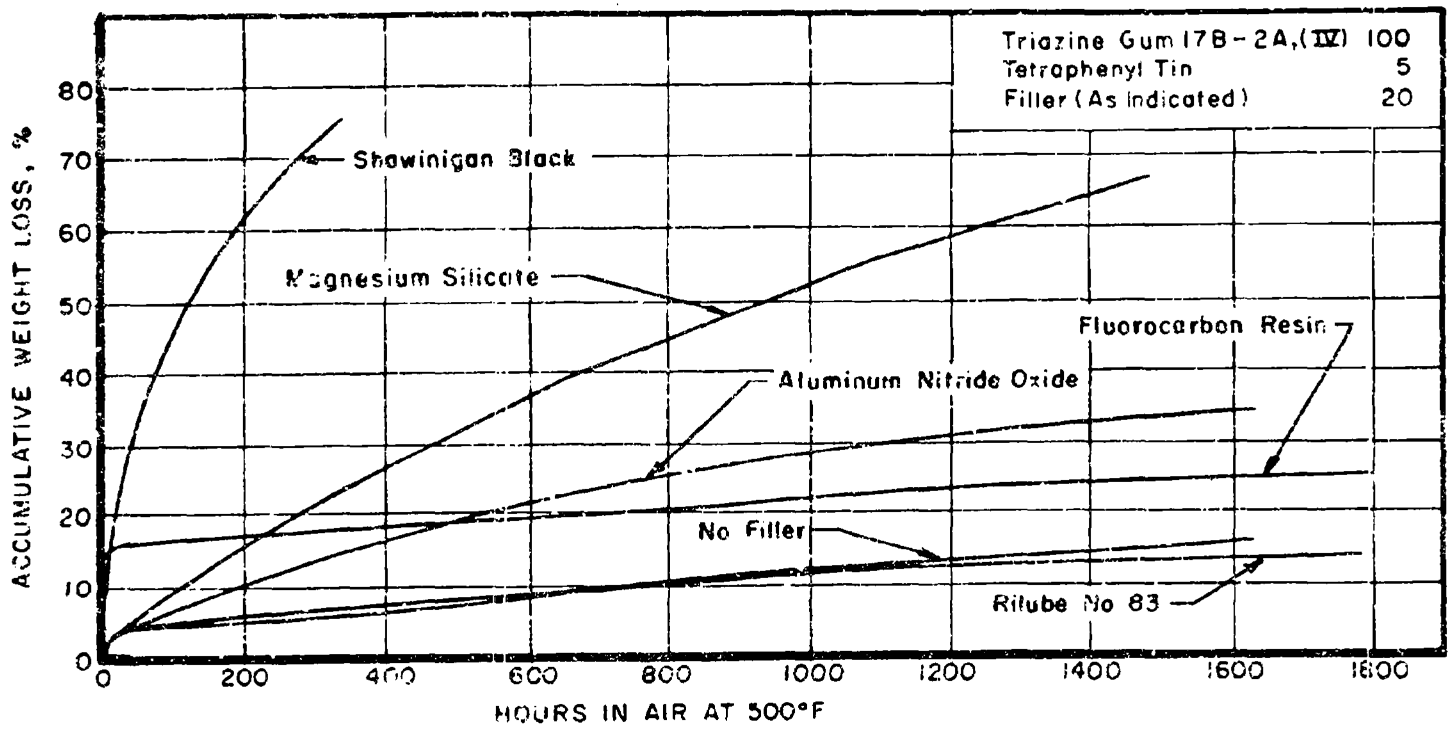


Figure 15. **Effect of Candidate Reinforcing Agents on the Thermal Stability of Tetraphenyl-Tin-Cured Triazine Gum 17B-2A, (IV)**

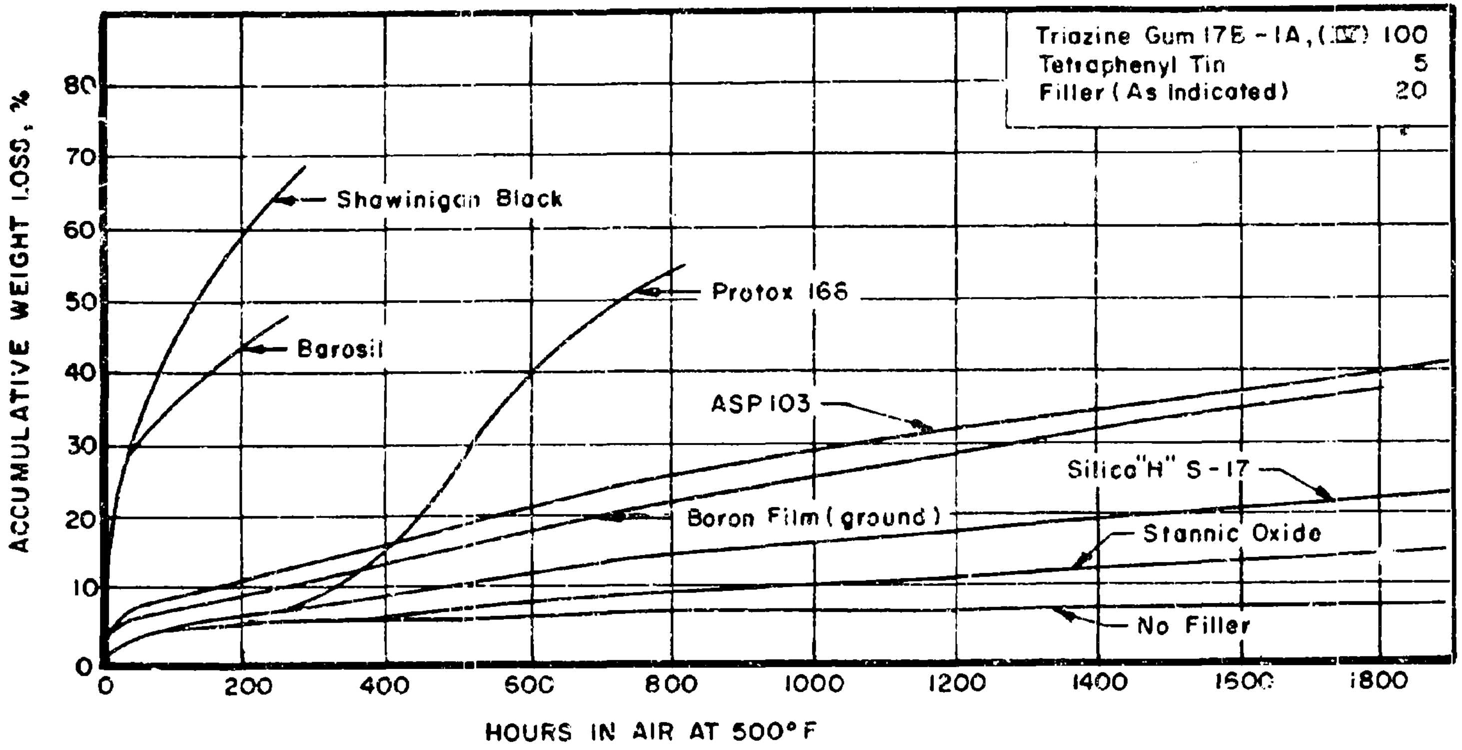


Figure 16. Effect of Candidate Reinforcing Agents on the Thermal Stability of Tetraphenyl-Tin-Cured Triazine Gum 17B-1A, (IV)

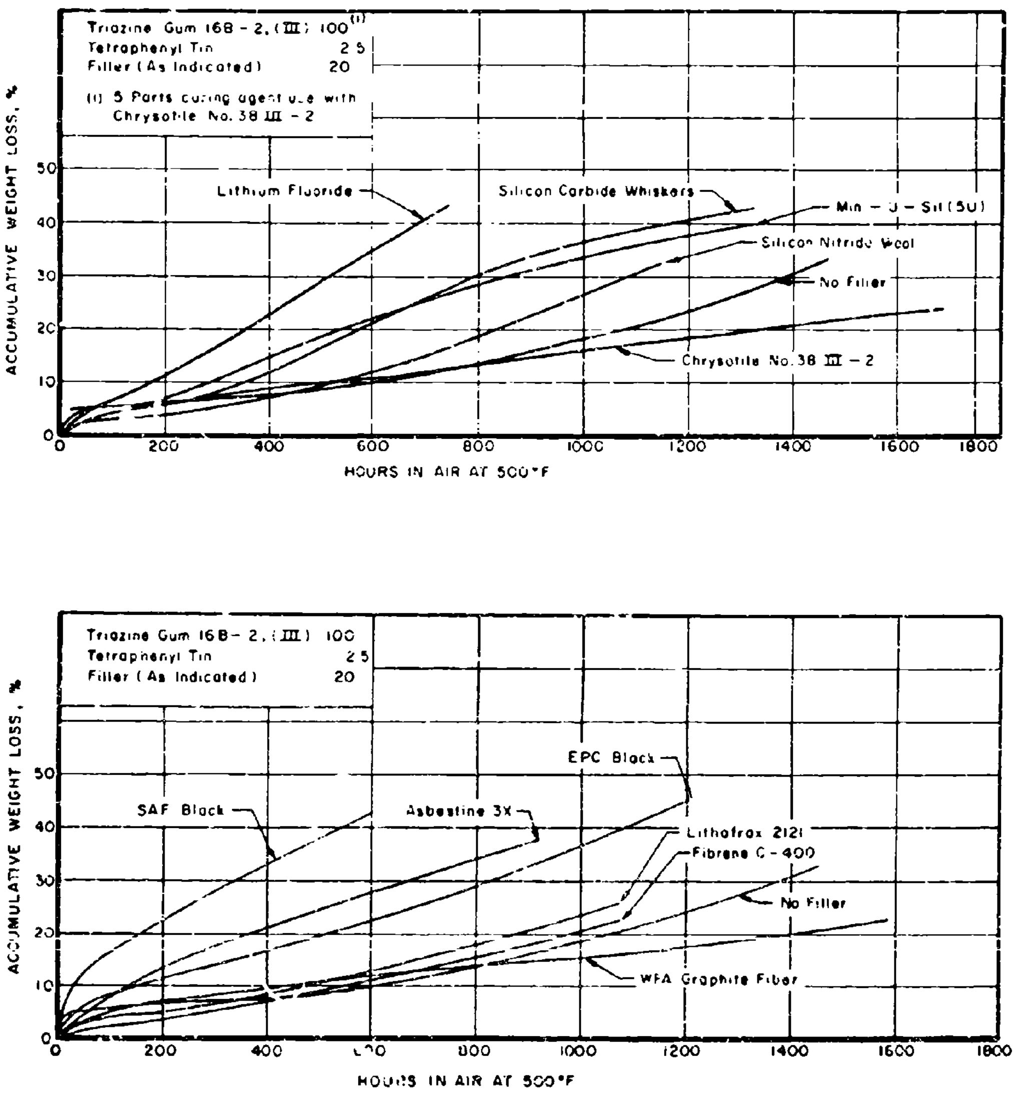


Figure 17. Effect of Candidate Reinforcing Agents on the Thermal Stability of Tetraphenyl-Tin-Cured Triazine Gum 16B-2, (III)

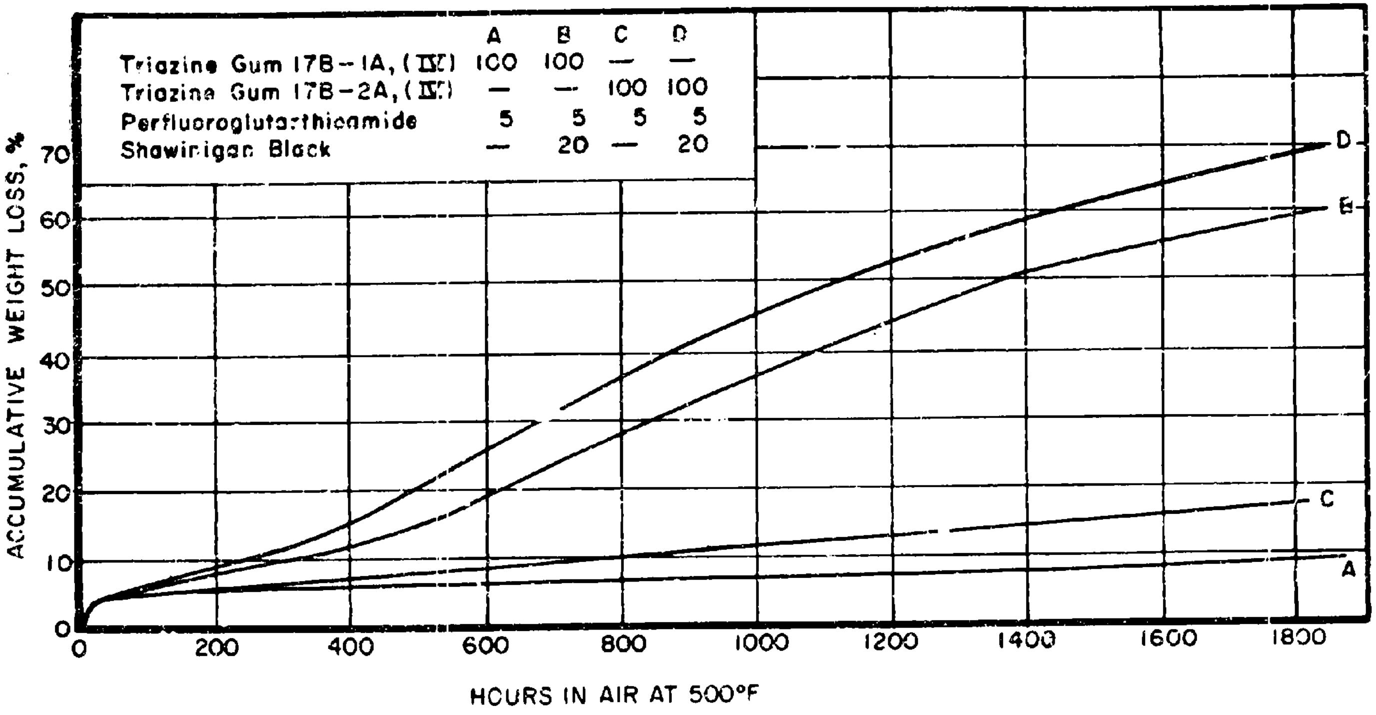


Figure 18. Effect of a Candidate Reinforcing Agent on the Thermal Stability of Perfluoroglutarthioamide-Cured Triazine Gums 17B-1A, (IV), and 17B-2A, (IV)

SECTION VIII

EFFECTS OF HIGH TEMPERATURES ON THE PHYSICAL PROPERTIES OF A SILICA "H" S-17 REINFORCED TETRAPHENYL TIN TRIAZINE 17B-1A, (IV) VULCANIZATE

Further research was conducted to determine the effects of high temperatures on the physical properties of the silica "H" S-17-reinforced, tetraphenyl-tin vulcanizates based on triazine gum 17B-1A, (IV).

The original tensile strength of this particular vulcanizate (Table XII) was much higher than that of a previous sample of this composition (Table IX). A substantial reduction in strength resulted on post curing. Tensile properties of this vulcanizate at 500 and 600°F were considered marginal. A review of the literature revealed that at 500°F the tensile properties of this triazine vulcanizate were found to be equivalent to those of Viton B vulcanizates aged 8 hours at 400°F and tested at 400°F.

The results obtained on specimens of the silica "H" S-17-reinforced vulcanizate aged at 600 and 700°F and comparable data taken from the literature on a compounded Viton B vulcanizate (Reference 4) are presented in Table XIII. As these results show, the silica-reinforced triazine vulcanizate after aging 72 hrs at 600°F retained a substantially greater portion of its original tensile properties than the Viton B vulcanizates.

Although the reported data based on specimens of these vulcanizates aged 8 hours at 700°F do not differ substantially, the silica-reinforced triazine vulcanizate, unlike Viton B and hydrocarbon elastomer vulcanizates, remained flexible.

TABLE XII

TENSILE PROPERTIES OF SILICA "H" S-17 REINFORCED, TETRAPHENYL-TIN-CURED TRIAZINE GUM 17B-1A, (IV), AT ELEVATED TEMPERATURES

Triazine Gum 17B-1A, (IV)	100
Silica "H" S-17	20
Tetraphenyl Tin	5
Physical Properties	
Original, tested at R. T.	
Tensile Strength, psi	2490
Elongation, %	630
Post Cured 48 hrs at 500°F, tested at R. T.	
Tensile Strength, psi	1525
Elongation, %	505
Post Cured 48 hrs at 500°F, tested at 500°F	
Tensile Strength, psi	465
Elongation, %	115
Post Cured 48 hrs at 500°F, tested at 600°F	
Tensile Strength, psi	80
Elongation, %	350

TABLE XIII

TENSILE PROPERTIES OF SILICA "H" S-17 REINFORCED, TETRAPHENYL-TIN-CURED TRIAZINE GUM 17B-1A, (IV), AND A VITON B COMPOUND AFTER EXPOSURE TO ELEVATED TEMPERATURES

Triazine Gum 17B-1A, (IV)	100	-
Silica "H" S-17	20	-
Tetraphenyl Tin	5	-
Viton B	-	100
Thermal MT	-	30
Maglite Y	-	15
Diak No. 4	-	2
Physical Properties at R. T.		
Original		
Tensile Strength, psi	2,490	2460
Elongation, %	630	275
Shore A Hardness, pts	73	75
Aged 72 hrs at 600°F (1)		
Tensile Strength, psi	1435	490(2)
Elongation, %	200	80
Shore A Hardness, pts	85	90
Aged 8 hrs at 700°F (1)		
Tensile Strength, psi	475	360(2)
Elongation, %	85	85
Shore A Hardness, pts	88	84

(1) The triazine vulcanizate was post cured 48 hrs at 500°F; the Viton B compound was post cured 24 hrs at 400°F prior to obtaining these results

(2) Brittle, broke when bent 180°

SECTION IX

ELECTRICAL CHARACTERISTICS

Recognizing that triazine elastomers could be potentially suitable for use as a high temperature electrical insulating material, the Air Force Materials Laboratory through arrangements made with Dow Corning Corporation obtained pertinent data to assess the performance of the triazine polymer in this applications area. In general, materials used for electrical insulation should have a low dielectric constant, a low dissipation factor, a high dielectric strength, a high volume resistivity, and good arc resistance characteristics. The electrical data obtained from Dow Corning Corporation on the triazine gum cured with tetraphenyl tin, Teflon, and a vulcanized compound based on Silastic 1603 are presented in Table XIV. The overall results showed the electrical insulation characteristics of tetraphenyl-tin-cured triazine gum to be intermediate to those of Teflon, which is known to be outstanding electrical insulating material, and a compound based on Silastic 1603, which is widely used as a high temperature wire insulator. Despite its tendencey to hydrolyze, immersion in distilled water for 24 hours at room temperature did not (as a comparison of the results indicate) have a significant effect on the good electrical insulating properties of the tetraphenyl-tin-cured triazine elastomer.

TABLE XIV

ELECTRICAL INSULATION CHARACTERISTICS OF TETRAPHENYLTIN-CURED TRIAZINE GUM, TEFLON AND SILASTIC 1603

Original Electrical Properties	Cured Triazine Gum	Teflon	Dow Corning Silastic 1603
Dielectric Constant, 60 to 10^6 Cycles	2.03 to 1.98	2.00 to 2.00	3.02 to 3.01
Dissipation Factor, 60 to 10^6 Cycles	0.0045 to 0.0028	0.0002 to 0.0002	0.0020 to . . . .
Dielectric Strength, Volts/mil	595	480	550
Volume Resistivity, ohm-cm	2.7×10^{13}	-	2.0×10^{15}
Arc Resistance, seconds	185(1)	-	125
After Immersion in Distilled Water, 24 hrs at R. T.			
Dielectric Constant, 60 to 10^6 Cycles	2.06 to 1.98	-	3.06 to 3.05
Dissipation Factor, 60 to 10^6 Cycles	0.0022 to 0.033	-	0.0050 to 0.0022
Dielectric Strength, volts/mil	565	-	500
Volume Resistivity, ohm-cm	6.8 to 10^{13}	1.0 to 10^{16}	1.0 to 10^{15}
Arc Resistance, seconds	180(1)	-	-

(1) Does not appear to carbon track, material sublimes under arc.

SECTION X

FLAMMABILITY INVESTIGATIONS IN PURE OXYGEN

In view of the manned-space programs' requirement for materials which will not burn in pure oxygen, a limited amount of effort was devoted to establishing the combustible nature of the triazine polymer. This investigation was confined to evaluating tetraphenyl-tin-cured triazine polymers. The hot-wire ignition method was used. Specimens (1 x 0.125 x 0.020) of the samples prepared were spirally wound with Ni-Cr ignition wire 0.006 in. diameter and 10-cm long. The assembly was mounted in the ignition chamber (which was evacuated and pressurized with oxygen to the desired pressure) and subjected to a hot wire ignition temperature in the vicinity of 1800°F using a 23-volt AC-power ignition source.

The results obtained (Table XV) on the specimens which had been aged for 20 hours at 500°F, showed tetraphenyl-tin vulcanizates based on polymers derived using an excess of perfluorobutyric anhydride (II) and an excess of the 7/93 mole percent ratio of reactants (IV) to be non burning in pure oxygen at 24.7 and 29.7 psia, respectively. Specimens of the latter vulcanizates, which had not been aged at 500°F and consequently contained hydrocarbon components were found to be non burning in pure O_2 at pressures up to 22 psia, but ignited and supported combustion at a pure oxygen pressure of 25 psia.

TABLE XV

COMBUSTIBLE CHARACTERISTICS OF TETRAPHENYL-TIN-CURED TRIAZINE GUMS IN PURE OXYGEN

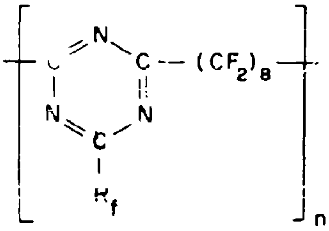
	Triazine Gum (as indicated)		100	
	Tetraphenyl Tin		5	
Press Cured 20 hrs at 320°F				
Triazine Gum	17B-2A, (IV)	17B-2A, (IV)	16B-1, (II)	Remarks
Aged at 500°F, hrs	0	204	204	
Pure O_2, psia	22	29.7	24.7	Did not ignite
Pure O_2, psia	25	34.7	29.7	Ignited and burned

SECTION XI

SUMMARY AND CONCLUSIONS

This internal research program was initiated to obtain suitable modifiers for crosslinking and reinforcing triazine polymers. Efforts were devoted to developing high-strength general-purpose vulcanizates which would be capable of withstanding temperatures in the 500 to 800°F range.

Polymers bearing all perfluoropropyl groups and either perfluoropropyl or trifluoromethyl groups in combination with n-cyanoperfluoropropylene groups in the pendant position were evaluated. The polymers were derived by acylating and cyclodehydrating polymer intermediate obtained by copolymerizing perfluorosebaconitrile and perfluorosebacamidine with (a) an excess of perfluorobutyric anhydride, (b) an excess of a mixture containing perfluorobutyric anhydride and n-cyanoperfluorobutyryl chloride, and (c) mixtures containing trifluoroacetic anhydride and n-cyanoperfluorobutyryl chloride. The general chemical structure of these polymers is illustrated below:



The exact number of n-cyanoperfluoropropylene pendant groups present in the various lots of gum prepared using mixtures obtaining n-cyanoperfluorobutyryl chloride has not been precisely established. Results of analytical work, however, indicated that less than 5 mole percent of n-cyanoperfluorobutyryl chloride is introduced when mixtures containing as much as 20 mole percent of this reactant are used.

Triazine gum bearing all perfluoropropyl pendant groups and a lot of polymer obtained using 12/88 mole % ratio of n-cyanoperfluorobutyryl choloride and trifluoroacetic anhydride proved to be more stable than polymer derived using 20/80 and 7/93 mole percent ratios of, respectively, n-cyanoperfluorobutyryl chloride/perfluorobutyric anhydride, and n-cyanoperfluorobutyryl chloride/perfluoroacetic anhydride. The approximate percents of accumulative weight loss for these triazine gums, after 3500 hours aging at 500°F, were respectively 3.5, 6, 12.5, and 11.

Mill processing techniques not only render the triazine polymers less thermally resistant, but appear to promote hydrolysis and structural changes within the polymer network. Triazine polymer milled for 20 minutes and aged at 500°F lost several times more weight than samples of the corresponding unmilled gums. Infrared data obtained on milled samples of gum showed absorption peaks at wavelengths denoting the presence of carbonyl, hydrogen-nitrogen, and linear carbon-nitrogen components which were not found in the infrared spectra obtained on the unmilled polymers.

Tetraphenyl tin, barium oxide, melamine, perfluoroglutarthioamide, perfluoroglutarimidine, perfluorosebacamidine and N,N' bis (perfluorobutyrimidoyl) perfluoroglutaramidine proved to be effective for curing polymer bearing n-cyanoperfluoropropylene pendant groups. Cured products, however, based on polymer bearing all perfluoropropyl pendant groups were only obtained using tetraphenyl tin and perfluoroglutarimidine.

Tensile properties of the vulcanizates prepared were dependent on molecular weight. The tetraphenyl tin and perfluoroglutarthioamide-cured gums based on the comparatively high molecular weight polymer samples derived from polymer intermediate using perfluoroacetic anhydride reaction mixtures containing 7 or 12 mole percent of n-cyanoperfluorobutyryl chloride had good tensile strengths for an unreinforced experimental elastomer. The tetraphenyl-tin-cured gum obtained using the reaction mixture containing 12 mole percent of the functional monomer had the best tensile properties and proved to be the most thermally stable.

All of the vulcanizates proved to be less stable than the uncured elastomeric polymers. The tetraphenyl-tin vulcanizate based on polymer obtained by treating polyimidoylamidine intermediate with an excess of the mixture containing 12/88 mole percent ratio of n-cyanoperfluorobutyryl chloride and perfluoroacetic anhydride lost the least amount of weight and retained a substantial portion of its original properties after various periods of aging at 500, 600, and 700°F.

The tetraphenyl-tin vulcanizate based on the lot of polymer bearing all perfluoropropyl pendant groups completely reverted at 600°F. Vulcanizates cured with the nonmetallic compounds lost their structural integrity (became spotted with pinholes) after relatively short periods at 500°F in air.

Other than the above cured triazine polymer systems, structurally sound vulcanizates based on polymer treated with diethanolamine was obtained using chromium trifluoroacetate as the crosslinking agent. The vulcanizates prepared exhibited relatively poor physical properties and lost weight when aged at 600°F at a comparatively high rate.

Among the candidate reinforcing agents evaluated, carbon blacks, a modified silica, a clay, and a zinc oxide were more effective than the other selected candidate reinforcing materials. Of the permutations and combinations of materials involved in this work, a silica-reinforced, tetraphenyl-tin-cured compound based on triazine gum derived using 12/88 mole percent ratio of n-cyanoperfluoropropylene and trifluoroacetic anhydride possessed the best balance of tensile properties and thermal stability. The tensile strength of this triazine compound of approximately 2500 psi was equivalent to that of a standard Viton B compound reinforced with a medium thermal carbon black. Results of 600 and 700°F aging showed it to be more thermally resistant than the Viton B compound. In contrast to Viton B, which becomes brittle at these temperatures, this triazine vulcanizate retains its elastomeric characteristics. Tensile properties of the experimental triazine compound at 500 and 600°F were marginal and its resistance to compression set was found to be poor.

On the basis of preliminary results the triazine polymer holds promise as an electrical insulating material. Comparative electrical data obtained showed the electrical insulating qualities of tetraphenyl-tin-cured triazine gum to be intermediate to those of Teflon, which is known to be outstanding, and a compound based on Silastic 1603, which is widely used as a high temperature wire insulator. Although known to be hydrolytically sensitive, the electrical properties of the triazine vulcanizates were not significantly affected by a 24-hour room-temperature soak in distilled water.

A rather unique characteristic of the triazine gum is that it does not readily ignite and support combustion in a pure oxygen environment. Results of hot wire ignition experiments showed a tetraphenyl-tin vulcanizate based on polymer derived by using the 7/93 mole percent ratio of n-cyanoperfluorobutyryl chloride and trifluoroacetic anhydride to be noncombustible in pure O_2 at pressures up to 22 psia. If precaution is taken to destroy the combustible tetraphenyl-tin catalyst by oven aging the vulcanizated product at 500°F, it was found that pure O_2 pressures in excess of 29.7 psia are required to cause ignition and combustion.

REFERENCES

(1) W. R. Griffin, "Triazine Elastomers," Rubber Chemistry and Technology, Volume 39, Number 39, Number 4, Part 2, September 1966

(2) T. L. Graham, Crosslinking and Filler Reinforcement of Perfluoroalkylene Triazine Elastomers, Air Force Materials Laboratory, Technical Report AFML-TR-66-402, August 1967

(3) E. Dorfman, W. C. Emerson, and R. J. Gruber, Perfluoroalkylene Triazine Elastomeric Polymers, Air Force Materials Laboratory, Technical Documentary Report No. ML-TDR-64-249, Part IV (see appended report by H. C. Brown and J. Turnbull)

(4) J. K. Sieron, New Reinforcement and Stabilization Systems for Extreme Environment Elastomers, Air Force Materials Laboratory, Technical Report AFML-TR-66-376, April 1967

APPENDIX I

DESCRIPTION OF CANDIDATE REINFORCING AGENTS

Shawinigan Black, Conductive furnace black, Shawinigan Chemicals, Ltd.

Silica "H" S-17, a surface treated silica, Dow Corning Corporation

Lithafrax 2121, fired, ground lithium aluminum silicate, The Carborundum Company

Protox 166, a propionic acid surface treated zinc oxide, The New Jersey Zinc Company

Fluorocarbon Resin LNB 2129-85-1, a powered tetrafluoroethylene resin, Pennsalt Chemicals Corporation

Barosil, a complex barium silicate, National Lead Company

Silene EF, calcium silicate, Harwick Standard Chemical Company

ASP 103, a cationic surfactant surface treated kaolin clay, Minerals and Chemicals Phillip Corporation

WFA Graphite Fiber, chopped graphite fiber, Union Carbide Corporation

Stannic Oxide, reagent grade, Fisher Scientific Company

Boron Film, ground boron film, National Research Corporation

Chrysotile No. 38 III-2, experimental chemically treated silica ribbon, Case Institute of Technology

Rilube No. 83, powdered tetrafluoroethylene resin, The Duriron Company

Aluminum Nitride Oxide, Type 6A fiber crystals, Thermokinetic Fibers, Inc.

Asbestine 3X, asbestos fiber, International Talc Company, Inc.

Fibrene C-400, magnesium silicate, Sierra Talc Company

EPC Black, easy processing channel black, J. M. Huber Corporation

Lithium Fluoride, experimental powder, commercially unavailable

Min-U-Sil (5U), a crystalline unfumed silica, The Carborundum Company

APPENDIX I (CONTD)

Silicon Carbide Whiskers, The Carborundum Company

Silicon Nitride Wool, experimental whiskers Type 7A, Thermokinetic Fibers, Inc.

SAF Black, super abrasion furnace black, J. M. Huber Corporation

Magnesium Silicate, experimental fibrous product, commercially unavailable

UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Air Force Materials Laboratory Wright-Patterson AFB, Ohio 45433	2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED 2b. GROUP

3. REPORT TITLE

CROSSLINKING & FILLER REINFORCEMENT OF PERFLUOROALKYLENE TRIAZINE ELASTOMERS

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

Final Report - September 1966 to February 1968

5. AUTHOR(S) (First name, middle initial, last name)

Graham, T. L.

6. REPORT DATE February 1969	7a. TOTAL NO. OF PAGES 64	7b. NO. OF REFS 4

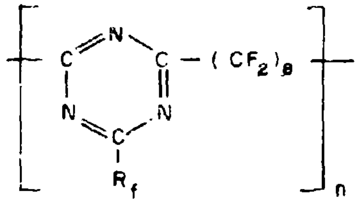
8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S) AFML-TR-66-402, Part II
b. PROJECT NO. 7340	
c. Task No. 734005	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)
d.	

10. DISTRIBUTION STATEMENT This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of Elastomers and Coatings Branch (MANE), Nonmetallic Materials Division, Air Force Materials Laboratory, W-PAFB, Ohio 45433.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY

13. ABSTRACT

This report covers further progress made toward the development of a high strength general-purpose vulcanizate based on perfluoroalkylene triazine polymer for potential use in the 500 to 600°F range. The triazine polymer involved in this research had the following generalized structure:



Of the several lots of experimental perfluorooctamethylene triazine polymer evaluated, a polymer with trifluoromethyl and n-cyanoperfluoropropylene groups in the pendant position yielded vulcanizates with the best overall properties. Tetraphenyl tin and surface-treated silica proved to be, respectively, the most satisfactory curing and reinforcing agents for this polymer system. The compounded triazine polymer does not become brittle when aged in air for extended periods even at temperatures as high as 700°F and in addition retains a substantial portion of its original tensile properties. The tetraphenyl-tin cured polymer was also found to possess excellent electrical insulating properties and exhibited good resistance to compression set at 500°F. Results of hot wire ignition tests have shown this type of polymer to be noncombustible in pure oxygen. Further, it does not appear to be moisture sensitive under ordinary conditions.

DD FORM 1 NOV 65 1473

UNCLASSIFIED

Security Classification

13. ABSTRACT (Continued)

This abstract is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of the Elastomers and Coatings Branch (MANE), Nonmetallic Materials Division, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio 45433.

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Triazine Elastomers						
Elastomers						
Triazine Polymer Crosslinking Agents						
Compounding Triazine Elastomers						