

FLUORINE-CONTAINING ELASTOMERS

J. C. MONTERMOSO*

QUARTERMASTER RESEARCH AND ENGINEERING COMMAND, NATICK, MASS.

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I. INTRODUCTION

Fluoroprene, the first fluorine-containing elastomer, was developed by E. I. du Pont de Nemours & Company and reported by Mochel¹ and others in 1948. However, intensive research to develop specialty rubbers from fluorocarbons was not started until the early 1950's. At the time, there was an urgent

* The present address of Dr. Montermoso is the R. E. Darling Company, Inc., Washington, D. C.

military need for fuel and chemical resistant rubbers for service under extremely low temperatures. Consequently, most of the fluorine-containing elastomers were the result of research conducted or sponsored by the Department of Defense. Army experiences in the Aleutians during World War II and in several task force operations² in the Arctic regions showed, among others, that fuel hoses became brittle and cracked. Gaskets failed to function. On ship-board, the Navy was experiencing similar difficulties with rubber items. The Air Force³, on the other hand, was being plagued with an epidemic of fuel leakage on many of its aircraft. The extraction of the plasticizers from the nitrile rubber compounds and the low temperature of the environment caused shrinkage of the seals and gaskets resulting in leakage of fuels. Obviously, a solution to these problems was to develop new fuel resistant rubbers which would be inherently flexible at extremely low temperatures.

II. CURRENT OBJECTIVE IN ELASTOMER RESEARCH

In the early 1950's the original objective⁴ was to develop fuel and chemical resistant elastomers which would be serviceable at a range of temperature from minus 65° to plus 160° F. The operational requirements for rubber have multiplied within a decade. Tremendous changes in the development of new weapons systems have created additional and more stringent rubber requirements. New rubbers which will resist the concentrated acids, propellants, and potent oxidizers used in modern weaponry are urgently needed. Thermally stable elastomers at extremely high temperatures (above 1000° F) will continue to be a target for elastomer development. The military services also need elastomers that are highly resistant to the deleterious effects of flame for use in items or components that may be exposed to short-impulse, high-intensity heat and radiation⁵ from nuclear blasts. Materials now available burst into flame when exposed to nuclear blasts. The individual soldier is still the most indispensable part of our modern Army. If we can provide him, for example, with a uniform which will not flame, although it may decompose when exposed to such hazards, then we will have made a big step in protecting him. Admittedly, the functional requirements of the three military services may only differ in degree, intensity or severity due to differences of operations. Nevertheless, the current overall objective of military rubber research, applicable to all the services, is to develop elastomers possessing the following characteristics: (a) fuel and chemical resistance, (b) low temperature flexibility, (c) stability at high temperatures, (d) flame retardance or nonflammability, (e) radiation resistance, and (f) ozone and weather resistance. There are rubbers currently available which possess singly any of these characteristics. The desired elastomers, however, must have a combination of several of these properties. Significant progress has been made, although a great deal of research work still remains to be accomplished. Various areas or approaches have been investigated. Research on fluorine-containing compounds during the past decade offers the most promise.

III. FUNCTION OF FLUORINE IN THE POLYMER MOLECULE

Elemental fluorine does not occur free in nature, but its compounds are widely distributed in such minerals as cryolite (Na_3AlF_6) and Fluorspar (CaF_2). It is the most reactive chemical element and combines directly and very vigorously with many substances. All attempts in its isolation failed until

Henri Moissan⁶, a 1906 Nobel Prize winner, obtained it by an ingenious method of electrolysis. The preparation of elemental fluorine by Moissan in 1886 is a significant event in the history of chemistry. Fluorine is prepared commercially by electrolysis of potassium hydrogen fluoride.

After World War II, the requirements for various materials, including elastomers, possessing the desired properties of chemical inertness, thermal stability and low temperature generated an intensive program on fluorine and fluorocarbon research. These properties which were found to be characteristic of organic fluorine compounds were responsible for the continuing emphasis in this field of investigation. Numerous fluorocarbon products have been produced and widely recognized during the last decade.

The fluorine atom imparts unusual characteristics when incorporated into the molecular structure of high polymers. Properties which can be directly attributed to the presence of the fluorine atom in the polymer molecule include heat and chemical resistance, flame retardance and electrical characteristics. Let us examine the possible causes for these phenomena.

There are many factors, such as forces between atoms and molecules, their sizes, and steric hindrance effects to which the properties of polymers are attributed. The forces acting in high polymers are of two kinds: (1) primary valence forces which are acting between atoms within the molecule and (2) secondary valence forces, frequently called Van der Waals forces which are acting between the molecules. The former forces are quite high; whereas, the latter are weak but very important.

Most of the physical properties of polymers are directly related to the intermolecular forces between the polymer molecules. These include viscosity, melting point, solubility and adhesion. Mechanical properties such as tensile strength and compression characteristics are basically related to the intermolecular forces, but can be altered by the method of synthesis which may affect, for example, the orderly arrangement or pattern of crystallinity of the polymer molecule. The secondary valence forces are the summation of a number of individual forces which are produced by residual fields left around the atoms. In general, the larger the polymer molecule, the more important these residual or intermolecular forces become.

In the fluorocarbons, the stability of the molecule greatly depends on the primary valence forces between carbon and fluorine. The bond energies⁸⁻¹¹ in kcal/per mole for radicals occurring in fluorocarbons are: 94 to 120 for C—F, 87 to 94 for C—H, 66 to 73 for C—Cl and 59 to 70 for C—C linkages. These figures show that fluorine forms a much stronger bond to carbon than those of either hydrogen, chlorine or carbon to carbon and hence imparts the highest order of stability. In highly fluorinated polymers such as Teflon, increased chemical inertness and thermal stability are attributed to a third factor, steric hindrance effects¹². The superior stability of the fluorocarbons is significant in contrast to that of the chlorocarbons. The "oversize" of the chlorine atom undoubtedly hinders the formation of long chain molecules in contrast to the "just right" size of fluorine. Brewster and McEwan¹³ state that attempts to prepare perchlorocarbons of the type $\text{C}_n\text{Cl}_{2n+2}$ where n is greater than 3 have failed. For example, chlorination of n -butane resulted in fragmentation of the molecule, yielding C_2Cl_4 and C_2Cl_6 , etc., instead of the desired decachlorobutane, C_4Cl_{10} . To date, there is no indication that polytetrachloroethylene ($-\text{CCl}_2-\text{CCl}_2-$) _{n} has been synthesized. Apparently, the chlorine atoms are so large that they produce a decided strain upon bonds and valence angles.

On the other hand, the smaller fluorine atoms fit snugly and uniformly around the carbon chain and form a protective shield which effectively prevents chemical attack on the weaker carbon to carbon linkages. The fluorocarbons have been described¹³ as having "hearts of diamond and skins of rhinoceros hide". The steric effect also applies, in a certain degree, to Kel—F polymers and to fluorinated nitroso elastomers which will be discussed subsequently.

Undoubtedly, there are other factors contributing to the various properties present in fluorine-containing polymers. The degree of bond saturation of the molecule has definite effects on the ability of the polymer to resist attacks from oxygen, ozone, acids, bases and other strong oxidizers. Flame resistance or nonflammability is a characteristic property of the halogens.

IV. THE RESEARCH ON FLUORINE-CONTAINING COMPOUNDS

The original objective of the military research which started about 1950 on fluorine-containing compounds was to develop chemical resistant elastomers which would be flexible and serviceable at Arctic and normal temperatures (-65° to 160° F). This was later extended in 1955 to include high temperature (500° F and up) elastomers. At the inception of the intensive research, two fluorocarbon polymers were outstanding: polytetrafluoroethylene (Teflon) and polychlorotrifluoroethylene (Kel-F, Genetron and Fluorothene). Both possess excellent chemical resistance and thermal stability. Although the first successful polymerization of polytetrafluoroethylene was discussed by Plunkett¹⁴ in 1941, its commercial production was described, including the polymer properties, by Renfrew and Lewis in 1946¹⁰. Brubaker¹⁵ and Joyce¹⁶ stated that tetrafluoroethylene can be polymerized readily under superatmospheric pressure and with suitable catalysts. Its average molecular weight ranges from 389,000 to 8,900,000 as discussed by Dolan¹⁷ and others. Polychlorotrifluoroethylene has been prepared by various methods and described in several patents^{18, 19}. The method of Dittman, Passino and Wrightson²⁰ is the commercial method employed by The M. W. Kellogg Company and subsequently by Minnesota Mining and Manufacturing Company. By this method the polymer is prepared in yields of up to 88% using distilled water as a diluent in concentration of 1 to 5 times the weight of the monomer. The pressure in these reactions is high enough to keep all reactants liquid and the reaction time is usually 5 to 35 hours. Rudner¹² summarized the properties of fluorocarbon resins as (1) capable of withstanding higher and lower temperatures than more complex resins, (2) chemically inert to both acids and alkali, (3) excellent moisture absorption characteristics, (4) better than average mechanical characteristics, and (5) excellent electrical properties. Teflon, in particular, is the only plastic material known where the "dielectric constant does not vary with temperature or frequency".

A decade ago, the possibility of developing fluorine-containing elastomers with the inherent properties of Teflon and Kel—F was exclusively a matter of faith with the optimistic few. Even the small but select group of fluorine experts had doubts as to the feasibility of synthesizing elastomers containing large quantities of fluorine in the molecule. Until the recent synthesis of a nitroso rubber, no vulcanizable elastomer existed that did not contain hydrogen atoms in the molecule. The substitution of fluorine for hydrogen in the olefins and dienes tended to produce plastic or resinous materials. For example, polyperfluorobutadiene is a plastic; polybutadiene, on the other hand, is an elas-

tomers. It is also known that polyvinylidene fluoride is a resin and polychlorotrifluoroethylene is a plastic; however, copolymers of the monomers of these two plastic materials produced good elastomers (Kel—F Elastomers 3700 and 5500) which are now commercially available.

With the above setting as background, the Quartermaster Corps, U. S. Army, initiated in 1950 a research project with The M. W. Kellogg Company who was at the time producing and marketing Kel—F plastic and various waxes and oils obtained from chlorotrifluoroethylene derivatives. This QMC project, directed toward developing chemical-resistant low-temperature rubbers from fluorinated compounds, was continued by Minnesota Mining and Manufacturing Company in 1957 when it purchased the Chemical Division of The M. W. Kellogg Company. Almost simultaneously with The M. W. Kellogg Company contract, two projects on the synthesis of fluorine-containing monomers were initiated by the Quartermaster Corps; one with the University of Florida, which is still in effect, and the other with Ohio State University. The monomers synthesized by the universities were delivered to Minnesota Mining and Manufacturing Company for polymerization. The resulting elastomers were then sent to the Quartermaster Corps Laboratories for evaluation, screening, vulcanization and compounding studies. The above team was expanded in 1958 to include the University of Colorado for the purpose of synthesizing novel fluorine-containing monomers. Several outstanding elastomers have been developed by this team from industry, universities and government laboratories. To date, about 150 monomers have been covered by this investigation. More than 500 fluorocarbon-based copolymer systems have been explored of which approximately 175 systems resulted in elastomeric materials.

At about the same time, the Air Force initiated a research contract with Minnesota Mining and Manufacturing Company on fluorocarbons with emphasis on fluoroacrylates. The choice seemed appropriate since Minnesota Mining and Manufacturing Company had already in operation an electrochemical fluorination method known as the Simons process. The Air Force contract with Minnesota Mining and Manufacturing Company was terminated in 1957. The Air Force also sponsored monomer synthesis projects with several universities including Purdue, Duke, Florida and Pennsylvania State. Later on, the Air Force initiated contracts with Hooker Electrochemical Company and Peninsular Chem-Research, Inc. Several elastomers produced under Air Force sponsored research will be discussed. It might be apropos to mention that concurrent with the work of the Army and Air Force, basic research on fluorine was extensively being investigated by the Office of Naval Research, U. S. Navy²¹. It would be amiss not to recognize the efforts and contributions of segments of industry, such as E. I. du Pont de Nemours and Company, Dow Corning Corporation and others who were undertaking the investigation on their own, without government or military services support. The results of their efforts, which are offered and always available to military applications, will be evident later in this discussion.

It would be practically impossible to present in this brief review all the fluorine-containing elastomers, which in the majority of cases, have been made in gram quantities only. Consequently, only the outstanding ones will be discussed in detail; those elastomers which have been produced commercially or at least in pound quantities and whose chemical and physical properties have been conclusively determined in the vulcanizate.

V. PROPERTIES OF FLUORINE-CONTAINING ELASTOMERS

A. FLUORINATED POLYBUTADIENES

The substitution of fluorine for hydrogen in hydrocarbons containing 1 to 5 carbons, with particular emphasis on dienes and olefins and their derivatives, was a logical start from which to prepare fluorine-containing elastomers. Lovelace, Postelnek and Rausch²² made a comprehensive summary of aliphatic fluorocarbon synthesis.

1. *Polyfluoroprene*.—Polyfluoroprene is the first fluorinated elastomer which has been investigated quite extensively. It is the homopolymer of 2-fluorobutadiene-1,3 which was developed by E. I. du Pont de Nemours Company. The synthesis of fluoroprene, reported in a number of patents²³⁻²⁹ was accomplished by the gas phase addition of anhydrous hydrogen fluoride to monovinylacetylene in the presence of nitrogen. The monovinylacetylene is made by the dimerization of acetylene, according to Nieuwland³⁰. The patent literature contains information on its polymerization³¹⁻³⁵ which is generally by the persulfate-mercaptan water emulsion method. Modifications of this method have been made. Several investigators summarized the properties and synthesis of the polymer^{1, 36}. Valuable polymerization data were supplied by Orr and Williams³⁷ who also showed that the molecular structure of polyfluoroprene is a random combination of 1,2 addition, 3,4 addition and *trans*-1,4 head to tail linkage. This is distinctly different from polychloroprene (neoprene) which is almost 100% *trans*-1,4 head to tail chain structure.

TABLE I
PROPERTIES OF POLYFLUOROPRENE TREAD STOCK COMPOUND

Polyfluoroprene	100	Tensile strength, psi	2900
MPC black	40	Elongation %	400
Phenyl-1-naphthylamine	2	Modulus (300%), psi	1650
Stearic acid	1	Hardness, Shore A	72
Zinc oxide	10	Rebound, Schopper, %	44
XLC magnesia	10	Tear resistance, lb/inch	210
Sulfur	2		
Cure: 60 minutes @ 153° C			

In most of its physical and chemical properties, reported by Mochel and others³⁸, polyfluoroprene occupies a position between polychloroprene and randomized polybutadiene synthesized by redox emulsion method. Like polybutadiene, it requires filler reinforcement to develop high tensile strength. The oil resistance, tested in kerosene, is similar to that of polychloroprene (neoprene) but its resistance to sunlight and ozone is not as outstanding. The low temperature flexibility compares favorably with neoprene behavior. While neoprene self-extinguishes a flame, polyfluoroprene propagates a flame when ignited but it burns at a much slower rate than polybutadiene or natural rubber. It is superior, however, to neoprene in electrical properties, approaching natural rubber in resistivity and power factor. The density of polyfluoroprene is 1.13 compared with neoprene of 1.23, natural rubber of 0.93, and nitrile rubber of 1.00³⁹. In polymerization behavior, fluoroprene polymerizes approximately 25 times faster than butadiene under comparable conditions but slower than chloroprene. Fluoroprene copolymerizes readily, like butadiene, in wide proportions with most dienes and olefins. Chloroprene, on the other hand, does not copolymerize readily with many monomers.

TABLE II
COMPARISON WITH OTHER ELASTOMERS

	Polyfluoro- prene	Neoprene FR	Natural rubber	Nitrile 75/25	SBR
Volume swell, %	75	95	200	24	200
TR10, ° C	-48	-39	-44	—	-49

Polyfluoroprene is easily vulcanized in gum or filler-reinforced stocks. A typical tread stock formulation in parts by weight and the properties of the vulcanizate are shown in Table I.

At 70° C (158° F), tensile strength of the above stock was 1850 psi and ultimate elongation was 400 per cent. After oven aging for 24 hours at 121° C, the vulcanizate retained 56% (1620 psi) of its original tensile strength and 45% of the elongation.

Polyfluoroprene was compared with other elastomers for oil resistance and low temperature flexibility. The samples were immersed in kerosene for 48 hours at 100° C and the volume swell determined. There is a direct relationship⁴⁰ between degree of swelling and loss of tensile strength and other properties. To determine low temperature flexibility, the rubber samples were stretched and held in clamps and then subjected to an atmosphere of minus 70° C. The clamps were then released, and the temperature gradually raised. The temperature at which the sample retracted 10% (TR10)⁴¹ of the original stretch was determined. The results are shown in Table II.

After immersion in boiling water for 48 hours, polyfluoroprene vulcanizates generally exhibit 5 to 6% volume increase.

2. *Fluoroprene copolymers*.—Fluoroprene copolymerizes readily with most dienes and olefins. Orr and Williams³⁷ investigated its copolymerization characteristics with styrene, 2-methylstyrene, methyl methacrylate, isoprene and acrylonitrile at 50° C using the butadiene copolymerization formula developed by Gilbert and Williams⁴². Mochel¹ and others did a great deal of research on the copolymerization of fluoroprene at various comonomer ratios and determined the properties of the vulcanizates.

a. *Dimethyl(vinylethynyl)carbinol-fluoroprene*.—Vulcanizates of copolymers with dimethyl(vinylethynyl)carbinol showed improvement in tensile strength and more significantly in mill processing. As the proportion of the carbinol increased, there was an increase in oil resistance accompanied by a decrease in low temperature flexibility, as determined from the vulcanizate, Table III.

b. *Styrene-fluoroprene*.—The styrene copolymers of fluoroprene are less oil resistant than the corresponding dimethyl(vinylethynyl)carbinol copolymers and do not process as easily. The tensile strength is superior to polyfluoroprene, but compares unfavorably in oil resistance and low temperature flexibility, Table IV.

TABLE III
PROPERTIES OF DIMETHYL (VINYLETHINYL) CARBINOL-FLUOROPRENE COPOLYMERS

Comonomer ratios	100/0	95/5	90/10	80/20	75/25
Tensile strength, psi	2900	3410	3530	3610	2950
Elongation, %	400	475	520	480	380
Volume increase*, %	75	74.5	69.5	61.0	48.6
TR10, ° C	-48	-46.9	-40.2	-33.5	-27.0

* 48 hours immersion in kerosene at 100° C.

TABLE IV

PROPERTIES OF STYRENE-FLUOROPRENE COPOLYMERS

Comonomer ratios	100/0	95/5	90/10	85/15	75/25
Tensile strength, psi	2900	3580	3320	4090	3320
Elongation, %	400	500	425	520	500
Volume increase*, %	75	102	100	97.3	92.8
TR10, °C	-48	-46	-42	-38	-29

* 48 hours immersion in kerosene at 100° C.

c. *Acrylonitrile-fluoroprene*.—Greatly improved oil resistance and tensile strength are obtained from the copolymers of fluoroprene and acrylonitrile at the sacrifice of low temperature flexibility, Table V. The copolymers with high acrylonitrile content tend to be dry and difficult to process without the use of softeners and plasticizers.

Terpolymers of fluoroprene-acrylonitrile-butadiene have also been synthesized. Some of these showed high oil resistance and some superior low temperature flexibility depending upon the monomer ratios of the terpolymer.

TABLE V

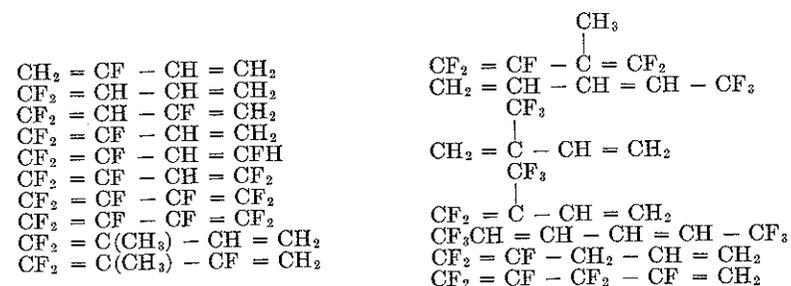
PROPERTIES OF ACRYLONITRILE-FLUOROPRENE COPOLYMERS

Comonomer ratios	100/0	95/5	90/10	85/15	75/25
Tensile strength, psi	2900	3070	3480	4090	4460
Elongation, %	400	390	380	520	400
Volume increase*, %	75.0	58.5	31.1	23.9	15.0
TR10, °C	-48.0	-46.0	-37.1	-32.6	-23.0

* 48 hours immersion in kerosene at 100° C.

In over-all properties, the terpolymers showed little or no improvement over the copolymers or homopolymers. Starkweather³⁶ and others also copolymerized fluoroprene with butadiene.

d. *Chlorotrifluoroethylene-fluoroprene*.—Hoyt⁴⁸ investigated the copolymerization of fluoroprene with chlorotrifluoroethylene. The polymerization reaction was carried out in the presence of a free-radical forming initiator. This was done by using water-soluble peroxy-type initiators, as potassium persulfate, in a water-suspension type recipe or halogen-substituted organic peroxides, as trichloroacetyl peroxide, in bulk type system.

TABLE VI
FLUORINATED DIENE MONOMERS

The meager data on this copolymer system was obtained from molded unvulcanized samples. For a copolymer containing 93 mole per cent of fluoroprene and 7 mole per cent of chlorotrifluoroethylene, the low temperature characteristics are shown by the Gehman values: T_2 -minus 5° C, T_5 -minus 12° C, T_{10} -minus 16.5° C and T_{100} -minus 27° C. (Gehman values measure the stiffness of the elastomer at various temperatures. For example, T_2 indicates the temperature at which the elastomer becomes twice as stiff as it is at room temperature (25° C); T_5 means five times as stiff, etc.). Its volume increase, after 48 hours immersion in a mixed solvent of 40% toluene (ASTM

TABLE VII

COMPARISON OF PROPERTIES OF POLYTRIFLUOROBUTADIENE (PTFB) WITH THOSE OF NEOPRENE AND NITRILE RUBBERS

	Formulations—parts by weight		
	PTFB	Neoprene	Nitrile
Polytrifluorobutadiene	100.0		
Neoprene		100.0	
Nitrile (Hycar 1001)			100.0
Stearic acid	0.5	0.5	0.5
Zinc oxide	5.0	5.0	5.0
Carbon black (Philblack-O)	30.0	40.0	40.0
Plasticizer (TP90B)	10.0	10.0	10.0
Dicumyl peroxide	4.0		
XLC		2.0	
Tetramethyl thiuram monosulfide		1.0	
Benzothiazyl disulfide			1.5
Sulfur		1.0	1.5
Optimum cure: min/° F	30/307	30/307	30/307

Original Properties of Vulcanizate

Tensile strength, psi	2600	2400	2800
Elongation, %	380	340	390
Modulus, 300% elongation	1700	2100	1700
Hardness, Shore A	52	61	58

After 48 Hours Immersion in ASTM Type III Fuel*

Volume increase, %	16	65	19
Tensile strength, psi	1700	750	1550
Tensile loss, % of original	34.6	68.8	44.7

Low Temperature Flexibility Tests

Gehman relative stiffness: T_2 ° C	-27	-32	-17
T_5	-36	-37	-20
T_{10}	-38	-39	-22
T_{100}	-43	-45	-26
Temperature retraction: TR10° C	-36	-44.3	-27.7
TR30	-14	-34.9	-23.1
TR50	+2.4	-20.5	-20.2
TR70	+12.0	-2.0	-16.4

Compression Set at Various Temperatures, 30 Minutes after Release of Compression

After 70 hrs @ 212° F in air oven, %	15.6	69.0	72.3
After 24 hrs @ -30° F, %	86.0	62.8	97.5
After 7 days @ -30° F, %	91.0	62.0	99.0

* 70:30 mixture of isooctane and toluene.

Type II Fuel) and 60% by volume of isooctane was 69.1%. Copolymerization of fluoroprene with tetrafluoroethylene also resulted in rubbery products.

The overall properties of the homopolymer and copolymers of fluoroprene did not show significant advantages over neoprene and nitrile rubbers.

3. *Polytrifluorobutadiene*.—This elastomer is really not a homopolymer, but a 40:60 copolymer of 1,1,2 and 1,1,3 trifluorobutadienes. The fluorinated dienes which received considerable attention under the Army Quartermaster Corps Rubber Research Program are shown in Table VI⁴⁴.

Fluoroprene, the first on the list, was relatively easy to synthesize from the reaction of hydrogen fluoride and monovinyl acetylene. The difluoro and trifluoro derivatives of butadiene and isoprene were much more difficult to make and in many cases, entirely new methods of synthesis had to be developed. The 1,1,2 and 1,1,3-trifluorobutadiene monomers were synthesized by Prof. Tarrant⁴⁵ and his staff at the University of Florida. The polymerization was carried out by Dr. Copenhaver⁴⁶ and his group at the M. W. Kellogg Company and subsequently at Minnesota Mining and Manufacturing Company. Almost all these monomers homopolymerized and copolymerized readily to produce rubbery materials. Perfluorobutadiene, however, reacted with difficulty and its homopolymer was a powdery product. The perfluoroisoprene, using the regular emulsion recipe, did not homopolymerize.

The homopolymers of 1,2,3 and 1,1,3-trifluorobutadienes were made but the copolymer had overall properties superior to either of the homopolymers. Although the copolymer did not reach commercial production, approximately 40 pounds of the elastomer had been produced for extensive vulcanization and compounding research. The physical and chemical properties⁴⁸ of the copolymer presented here, (Table VII) are unpublished data from the laboratories of the Quartermaster Research and Engineering Command.

The data show that the polytrifluorobutadiene is as oil resistant as nitrile rubber and definitely superior to neoprene. In low temperature characteristics, it is equal to neoprene and superior to nitrile rubber in relative stiffness; however, it is inferior to both rubbers in the ability to retract at low temperatures. In compression set properties, polytrifluorobutadiene is superior to neoprene and nitrile rubber at high temperatures; however, at subzero temperatures, it is slightly better than nitrile rubber, but inferior to neoprene. Its overall properties did not show significant advantages over neoprene or nitrile rubber to warrant its commercial production, which is estimated to be several times as costly.

B. VINYLIDENE FLUORIDE COPOLYMERS

Of the many fluorinated olefins investigated, the following have shown the most promise: vinylidene fluoride, $\text{CH}_2=\text{CF}_2$; chlorotrifluoroethylene, $\text{CFCl}=\text{CF}_2$; perfluoropropylene, $\text{CF}_3-\text{CF}=\text{CF}_2$; and tetrafluoroethylene, $\text{CF}_2=\text{CF}_2$.

Vinylidene fluoride copolymerized readily with other monomers resulting in rubbery materials. The fluorine present as CF_2 provided chemical resistance and the CH_2 contributed to the chain flexibility and freedom of segmental rotation. Vinylidene fluoride is described by Swarts⁴⁹ as "a colorless, odorless gas—not oxidized in air and not polymerized by sunlight." McBee, Hill and Bachman⁵⁰ obtained vinylidene fluoride by dechlorination of 1,1-difluoro-1,2-dichloroethane by zinc in acetamide solution. Other methods of monomer synthesis have been reported^{51, 52}. Both the monomer and the homopolymer

are available commercially from Allied Chemical and Dye Corporation and Pennsalt Chemical Corporation. Like other fluorinated plastic materials, polyvinylidene fluoride is resistant to most corrosive chemicals and solvents and possesses a high degree of thermal stability.

1. *Chlorotrifluoroethylene-vinylidene fluoride copolymers*.—The first elastomer developed under the QMC Rubber Program and commercially produced by the M. W. Kellogg Company and currently by Minnesota Mining and Manufacturing Company was a 50:50 (mole ratio) copolymer of chlorotrifluoroethylene and vinylidene fluoride. This was designated as X-300 and later was given a trade name of Kel—F Elastomer 5500. In an effort to improve the low temperature flexibility and the tensile strength, another elastomer containing 30 mole % of chlorotrifluoroethylene and 70 mole % of vinylidene fluoride was developed, and was designated as Kel—F Elastomer 3700. Robb, Honn and Wolf⁵³ determined the properties of the unvulcanized gums, shown in Table VIII.

Griffis and Montermoso⁵⁴ reported that the Kel—F Elastomers could be vulcanized by peroxides, diisocyanates, or amines, preferably hexamethylene diamine carbamate. No vulcanization was effected by sulfur-containing com-

TABLE VIII
GUM PROPERTIES OF KEL-F ELASTOMERS

Properties	Type 5500	Type 3700
Specific gravity	1.85	1.85
Per cent fluorine by weight	Approx. 54	Approx. 56
Color	off-white	off-white
Hardness, Shore A	45	45
Embrittlement temperature, °C	-51	-64
Tensile strength, psi	350-600	350-600
Low temperature, Gehman °C, T ₂	+7	-7
T ₅	+3	-11
T ₁₀	+1	-14
Processibility on the mill at 120° F	good	poor
Processibility on the mill at 170° F	good	good

pounds. These elastomers also responded to vulcanization by gamma radiation. Jackson and Hale⁵⁵ found that a dose of 10 megareps crosslinked a black-loaded stock of Kel—F Elastomer 5500 to produce a tensile strength of 1530 psi. Numerous diisocyanates, peroxides and amines have been investigated. The diisocyanates, particularly toluene-2,4-diisocyanate and methylene-bis(4-phenylisocyanate), were effective in vulcanizing the Kel—F Elastomers. However, the vulcanizates were less acid-resistant than the peroxide vulcanizates. Although the peroxide cures, in general, produced higher tensile strength than those of the amine cures, their vulcanizates were less heat and chemical resistant. The amines produced good overall results if properly handled. The amines were difficult to incorporate into the stock during mixing on the mill. It was practically impossible to incorporate 1 or 2 parts (per 100 parts of rubber) of triethylene tetramine, for example, without serious scorching. To date, the generally used curing system of Kel—F Elastomers is the inner salt of hexamethylene diamine carbamate (HMDA—C) which has the structure $\text{NH}_3^+(\text{CH}_2)_6\text{NHCO}_2^-$. It processes satisfactorily on the mill and imparts good physical properties to the vulcanizate. Silicone oxide is the best reinforcing filler for Kel—F Elastomers. Table IX shows a typical basic formulation.

TABLE IX
BASIC FORMULATION FOR KEL-F ELASTOMERS

Kel-F Elastomer	100
SiO ₂ (Hi-Sil)	10
Zinc oxide	5
Dibasic lead phosphite (Dyphos)	10
HMDA	3
Press cure: 30 min @ 320° F	
Post oven cure: 16 hrs @ 350° F	

The Kel—F Elastomers have tensile strengths of 2500 and 3000 psi and an elongation of approximately 400% based on the above formulation. The physical properties of Kel—F Elastomers 5500 and 3700 are practically the same except that the latter is slightly superior⁵⁶ in low temperature flexibility and in resistance to hydrocarbon fuels as shown in Table X.

Conroy⁵⁷ and others showed that the Kel—F Elastomers possessed good chemical resistance and were superior in thermal stability to any oil and fuel resistant rubbers commercially available at the time. Headrick⁵⁸ found that properly compounded stocks of Kel—F Elastomers showed outstanding resistance to hydraulic fluids at temperatures up to 400°F. Smith⁵⁹ and others also reported that properly compounded stock of Kel—F Elastomers retained good physical properties after 500 hours at 400° F in JP-5 fuel (approx. 15% aromatics). At about this time, the Air Force's need for high temperature elastomers, due to the development of high speed aircrafts and high temperature hydraulic fluids, was accentuated. These findings and reports by other investigators led to a request from the Air Force to the Quartermaster Corps to include in the QMC objective the development and evaluation of thermally stable elastomers. The scope of the QMC research projects with the M. W. Kellogg Company and the University of Florida was therefore expanded to include development of fluorinated elastomers stable at 500° F and higher⁶⁰. A considerable number of compounding studies⁶¹⁻⁶³ directed toward varied applications, such as O-rings, hose, seals, gaskets and tanks, revealed not only the desirable qualities but also some deficiencies of Kel—F Elastomers. For high temperature seals and gaskets, the Kel—F Elastomers found limited service due to poor resistance to compression set. They could not be used for service at subzero temperatures.

2. *Perfluoropropylene-vinylidene fluoride copolymers.*—Copolymers of perfluoropropylene and vinylidene fluoride have produced elastomers with outstanding stability and chemical resistance. The researches responsible for the development of these copolymers were carried out independently by the M. W. Kellogg Company under QMC sponsorship and by E. I. du Pont de Nemours Company without any government financial support. The Kellogg elastomer is a 30:70 copolymer of perfluoropropylene and vinylidene fluoride. In the experimental stage of development, it was designated as Fluorocarbon Elastomer 214. Currently, it has a trade name of Fluorel, produced by Minnesota Mining

TABLE X

Tests	Elastomer 5500	Elastomer 3700
Low temperature, Gehman T ₅ , ° C	+32	+7
Volume increase*, %	30	14

* Immersed in 70:30 isooctane-toluene for 7 days at 25° C.

and Manufacturing Company. Fluorel is an improved version of Fluorocarbon Elastomer 214. The du Pont polymer is known as Viton A and Viton A-HV is a modification of Viton A. Both Fluorel and Viton are prepared by water emulsion polymerization using potassium persulfate initiation. However, for emulsifying agent du Pont uses ammonium perfluorooctanoate⁶⁴ and Minnesota Mining and Manufacturing Company uses perfluorooctanoic acid. There may also be minor differences in conditions of polymerization such as temperature.

TABLE XI
COMPARISON OF ELASTOMERS 214 AND 3700
(HMDA-Carbamate Cure)

Original physical properties	Type 214	Type 3700
Tensile strength, psi	1710	2640
Elongation, %	265	395
Hardness, Shore A	65	65
Low temperature properties		
Gehman torsional, T ₅ , ° C	-5	-9
T ₅	-9	-14
T ₁₀	-11	-16
T ₁₀₀	-16	-23
Temp. retraction, TR10, ° C	-16	-16
TR30	-13	-6
TR50	-11	+1
TR70	-8	+7
Volume increase in test fluids after 48 hrs @ 25° C, %		
In 70:30 isooctane-toluene	0	4
In Turbo Oil 15 (diester oil)	0	49
Tensile strength after 5 hrs in air, psi		
at 400° F	1660	2480
500° F	1480	1150
550° F	1310	950
600° F	1120	—
Tensile strength after 70 hrs in air, psi		
at 400° F	1700	1320
500° F	1000	480
550° F	440	—
600° F	—	—
Tensile strength after 5 hrs in Turbo Oil, psi		
at 400° F	1670	540
500° F	1400	80
Tensile strength after 70 hrs in Turbo Oil, psi		
at 400° F	1770	160
500° F	630	—
Tensile strength after 5 hrs in MLO 8200*, psi		
at 400° F	1690	2490
500° F	1510	1160
550° F	1110	600
600° F	870	—
Tensile strength after 70 hrs in MLO 8200*, psi		
at 400° F	1630	1660
500° F	440	—
550° F	—	—

* Silicate ester oil.

We know that polyvinylidene fluoride exists as a plastic and that perfluoropropylene does not homopolymerize^{65, 66}; therefore, no matter how high a ratio of perfluoropropylene is present in the initial feed, the composition of the resulting polymer will not exceed 50 mole per cent of perfluoropropylene.

Fluorel and Viton elastomers can be vulcanized by peroxides and amines. In general, they possess similar properties.

a. Fluorel.—The development of Fluorel was started as early as 1953. However, its properties were not reported until 1955⁶⁷⁻⁶⁹. Fluorel vulcanizates cured with benzoyl peroxide exhibited higher tensile strength than those of the HMDA-Carbamate; however, the latter possess better balance of physical properties, including heat resistance and compression set. Wilson, Griffis, and Monterroso^{70, 71} compared Fluorocarbon Elastomer 214 and Kel-F Elastomer 3700 in thermal stability and in resistance to various solvents and liquids. Based on the basic formulation of Table IX with minor modifications, the result of the comparison is shown in Table XI.

Fluorocarbon Elastomer 214 showed superiority in its resistance to diester oil and to hydrocarbon fuels. Its stability at high temperatures both in air and in hydraulic liquids, particularly in diester oil, is a marked improvement over the Kel-F Elastomers. This is supported by the results on volume increase

TABLE XII
RAW GUM PROPERTIES OF FLUOREL

Specific gravity	1.85
Fluorine content, wt %	>60
Color	off-white
Mooney viscosity, ML-4/212° F	135
Embrittlement temperature, ° F	-50
Gehman torsional, T ₂ , ° F	+15
T ₅	+5
T ₁₀	+2
Storage stability	excellent
Solubility	esters and ketones

at 25° C after 48 hours immersion. The Gehman stiffness test indicates a slight superiority in low temperature flexibility for Kel-F Elastomer 3700. The temperature retraction test, on the other hand, shows a slight superiority for Fluorocarbon Elastomer 214. Neither are suitable for use below 10° C. Bovey⁷² presented some data on the vulcanizates cured with benzoyl peroxide. In general, the results were comparatively similar to those of the HMDA-carbamate vulcanizates.

Several modifications and improvements have been made on Fluorocarbon Elastomer 214. Subsequently, it was also designated as Kel-F Elastomer 2140. Admittedly, this is a misnomer, since the elastomer does not contain chlorotrifluoroethylene or Kel-F monomer. Currently, the improved elastomer with maximum heat resistant properties is known as Fluorel. Stivers, Honn and Robb⁷³ made a comprehensive evaluation of Fluorel. The raw gum properties of Fluorel are shown in Table XII.

Several Fluorel compounds, designed to meet the performance requirements of Specification MIL-R-25897-A-Rubber, have been developed by Stivers, Peterson and Meier⁷⁴. Medium thermal carbon black, Thermax, was used for easy and smooth processing; magnesium oxide, (Maglite K,) for maximum heat resistance; and a combination of HMDA-carbamate and copper inhibitor

TABLE XIII
HEAT RESISTANT FLUOREL COMPOUNDS

Fluorel Elastomer	100	100
Carbon black (Thermax)	15	15
MgO (Maglite K)	20	20
HMDA-carbamate	1	1.4
Copper Inhibitor No. 65	—	0.2
Press cure: 30 min/300° F; post oven cure: 24 hrs/400° F		
Original Properties		
Tensile strength, psi	2400	2340
Elongation, %	310	225
Hardness, Shore A	68	71
After Aging, Tensile Strength Retention, %		
Air aged 16 hrs/600° F	56	73
72 hrs/400° F in MIL-0-8200	85	91
72 hrs/400° F in Anderol L-774	81	87
72 hrs/77° F in Ref Fuel B	80	92
Compression Set (ASTM Method B), %		
70 hrs/250° F	18	9
70 hrs/350° F	30	30
70 hrs/400° F	42	47
22 hrs/450° F	52	61

No. 65 (active ingredient disalicylal propylenediamine) for improved aging properties. Table XIII shows two typical formulations, with and without Copper Inhibitor No. 65, and some properties of Fluorel compounds.

b. Viton A and Viton A-HV.—E. I. du Pont de Nemours Company announced in 1956 the development of Viton A. Dixon, Rexford, and Rugg⁷⁵ reported its unusual thermal stability and resistance to fuels, lubricants and hydraulic fluids at ordinary and elevated temperatures. Other investigators^{76, 77} have confirmed these findings. Viton A, like Fluorel, can be vulcanized by peroxides, amines and high energy radiation. Vulcanizates from HMDA-Carbamate have the best combination of chemical and physical properties. Compounding studies⁷⁸⁻⁸², covering reinforcement and vulcanization, have improved the properties of Viton A vulcanizates. Griffin^{83, 84} has developed a technique for room temperature vulcanization for Viton A compounds. Smith⁸⁵ studied the chemistry of vulcanization of Viton A. He also reported⁸⁶ that dithiol-cured Viton A has high tensile strength, low compression set and good aging characteristics.

In addition to changes in compounding, the properties can be improved by polymer modifications. Gallagher, Eubank and Moran⁸⁷ discussed the prop-

TABLE XIV
RAW GUM PROPERTIES OF VITON POLYMERS

	A	A-HV
Specific gravity	1.8	1.8
Mooney viscosity, ML-4/212° F	75	170
Molecular weight (Mn)	100,000	200,000
Appearance	white, translucent	
Storage stability	excellent	
Solubility	good in ketones	

TABLE XV
PROPERTIES OF VITON VULCANIZATES

Polymer	100	
MT carbon black	25	
Magnesium oxide	15	
HMDA-Carbamate	1.5	
Press Cure: 30 min @ 300° F; oven step-up cure: 1 hr. steps @ 212, 300 and 350° F followed by 24 hrs @ 400° F		
Original properties	A	A-HV
Tensile strength @ 75° F, psi	2250	2725
Elongation @ 75° F, %	180	190
Hardness, Shore @ 75° F	71	71
Tensile strength @ 300° F, psi	550	720
Elongation @ 300° F, %	90	90

erties of Viton A-HV which is the improved version of Viton A. Viton A-HV has higher molecular weight, increased tensile strength and is less susceptible to blistering of the vulcanizate when used in high temperature applications. The properties of the unvulcanized uncompounded rubber are shown in Table XIV.

Note that Viton A-HV has a molecular weight twice that of Viton A. Table XV shows the typical formulation for Viton elastomers and the properties of the two types. The aging properties of Viton A-HV are given in Table XVI.

Viton A-HV, like Viton A, has excellent solvent resistance. The values in parenthesis after the various fluids in Table XVI represent the volume increases in per cent after 7 days at the specified temperatures.

Gallagher, Eubank and Moran⁸⁷ also investigated the problem of blistering in high-temperature, high-pressure hydraulic hose made of Viton A elastomer. It seemed that one of the fundamental causes of blistering was the relatively high solubility of gases in Viton A coupled with extremely low diffusion rates. Under high pressure the low diffusion rate permits compression of any gas present in the rubber stock. The compressed gas can presumably collect in tiny voids in the rubber and blister when the pressure exceeds the tensile strength and/or tear strength. The solubility and diffusion rates of various gases through a vulcanized Viton A gum stock were determined. The solubilities decreased in the order $\text{CO}_2 > \text{N}_2 > \text{He}$ and the rate of diffusion increased in the order $\text{CO}_2 < \text{N}_2 < \text{He}$. Maximum blistering, therefore, should occur with CO_2 . Blister-free stocks have been developed from Viton A-HV by the use of a particular type of MgO, "Maglite D", and a special additive, N,N'-bis-o-

TABLE XVI

AGING PROPERTIES OF VITON A-HV

Original tensile strength retained, %	
After 28 days in oven at 450° F	80
After 6 hours in oven at 600° F	67
After 7 days immersion in various fluids	
Petroleum aircraft fuel at 75° F	100 (0.4)
ASTM #3 oil at 300° F	95 (4.3)
Turbo Oil 15 at 400° F	60 (19.6)
Benzene at 75° F	73 (19.6)
Conc. NaOH 47% at 75° F	75 (2.1)

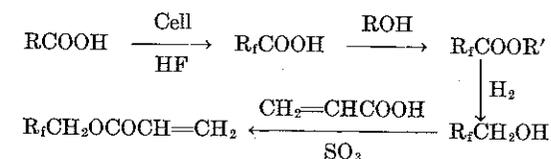
hydroxybenzylidene)-1,2-propylenediamine. The exact role of the additive was not completely understood. The blistering test was done in an autoclave using Turbo Oil No. 15 at 400° F and with nitrogen pressure of 1000 to 1400 psi for one hour.

Undoubtedly the elastomers obtained from copolymerization of perfluoropropylene and vinylidene fluoride, both Fluorel and Viton, will find many military and civilian applications due to the excellent combination of their high thermal stability and unusual solvent resistance.

Other copolymer systems, with vinylidene fluoride have been tried. For example, tetrafluoroethylene, $\text{CF}_2=\text{CF}_2$, has been successfully copolymerized⁸⁸ with vinylidene fluoride, resulting in a flexible plastic material at ordinary room temperature. It became rubbery at approximately 250° F. It was thermally stable up to 650° F; however, on standing overnight at 700° F, the polymer decomposed leaving no residue.

C. FLUOROACRYLATE POLYMERS

Emphasis of the fluorocarbon elastomer research at Minnesota Mining and Manufacturing Company, under the Air Force sponsorship, was on fluorinated olefins and dienes, vinyl esters of fluorocarbon acids, acrylate esters of fluorinated alcohols, perfluoroacrylonitrile, and perfluoroamines. The Fluoro-Rubber Research at 3M from 1949 to 1957 was reviewed by Abere⁸⁹. The esters of acrylic acid with 1,1-dihydroperfluoroalcohols were found to be the most promising class of monomers from which rubbery polymers and copolymers were prepared. Synthesis of the 1,1-dihydroperfluoroalkyl acrylate monomers is schematically shown:



The first step shown above is the electrofluorination of a carboxylic acid by Simons⁹⁰ process. The symbol R_f denotes any fluorinated alkyl group. The most practical and preferred polymerization method for the acrylates was by water-emulsion persulfate system. Coagulation of the latex was by freezing

TABLE XVII

PROPERTIES OF FLUOROACRYLATE ELASTOMERS

Fluoroelastomer	100		
Carbon black (Philblack O)	35		
Triethylene tetramine	1.25		
Sulfur	1.0		
Cure: 30 min at 310° F			
	1F4	2F4	NBR
Tensile strength, psi	1200	1000	4000
Elongation, %	360	400	470
Gehman, T_{10} , ° C	-7	-30	-13
Volume increase, %			
70:30 isooctane-toluene	17	15	33
Benzene	26	19	160

perature retraction, TR, properties of the elastomer. The TR values showed that the elastomer, if held at low temperatures in a stretched condition, would lose its elasticity or "rubbery" properties due to crystallization. Bartholomew³ and others also reported the crystallization of the fluoropolyester at moderately low temperatures. Additional tests at the QMC laboratory showed that samples of the vulcanizate held for 3 days at minus 30° F were approximately 25 times stiffer than those held for 10 minutes at the same temperature. The TR test also indicated once elasticity is lost due to stretched exposure at low temperatures, that elasticity was not regained until the vulcanizate was heated to approximately 40° F.

The fluorinated polyester elastomer possesses good fuel and solvent resistance at elevated temperatures. Postelnek⁹⁷ stated that when carbon black alone was used as filler, good oil aging was observed and the use of calcium carbonate resulted in good air aging. Griffin⁸⁸ obtained 31% volume increase and 65% tensile strength retention after immersion of the vulcanizate in 70:30 isooctane-toluene for 70 hours; and 4% volume increase and 85% tensile strength retention after immersion in JP-5 under the same conditions of time and temperature. The volume increase, after 24 hours in boiling water was only 1% and a loss of only 14% of the original tensile strength. The combination of solvent resistance and low temperature flexibility was better than that of the commonly used NBR rubbers. The superiority was due mainly to good solvent resistance. The low temperature limit of its serviceability was in approximately the same temperature range as for the nitrile rubbers. One serious disadvantage of the fluoropolyester elastomer, however, was the high degree of crystallization at low temperatures resulting in high compression set and loss of rubberiness.

A modified polyester, the hexafluoropentylene adipate-isophthlate was reported by Wilson⁹⁸ to be superior in solvent and chemical resistance to the original polyfluoroester elastomer, but inferior in low temperature characteristics.

E. FLUORINATED SILICONE ELASTOMER

The early researches of Van Helmont, Berzelius, Crafts, Wohler, Friedel and particularly Kipping on organo-silicones are well known. Dumas⁹⁹ as early as 1840, predicted that the carbon atom in the hydrocarbons could be replaced by other elements such as those under Group IV of the Periodic Table. Silicone belongs to this group. The development of silicone rubbers is closely identified with works of Rochow¹⁰⁰, Post¹⁰¹ and the industrial companies of Dow Corning Corporation, General Electric Company and Union Carbide Corporation.

Silicone rubbers have the distinct reputation for retention of physical properties over the widest range of temperatures (minus 100° F to plus 600° F). It is, therefore, a logical step to incorporate the necessary chemical resistance into the silicones with the hope that their original low and high temperature characteristics could be retained. Two of the methods attempted were the development of silicone polysulfide¹⁰² and fluorinated silicone¹⁰³ rubbers. The latter was more successful.

The early work of McBee and Pierce¹⁰⁴, in cooperation with the Air Force, led the way for the synthesis of fluoroalkyl silicone monomers. Subsequently, Tarrant, Dyckes and Wise¹⁰⁵ synthesized, among others, the trifluoropropyl methylchlorosilane monomer which would be readily converted into the cyclic trimer and tetramer. The Dow Corning Corporation, under a cooperative

TABLE XXI

PROPERTIES OF FLUOROSILICONE RUBBER, LS-53

Tensile strength, psi		1000
Elongation, %		200
Hardness, Shore A		60
Low temperature characteristics:		
Gehman torsional, ° C	T ₂	-51.3
	T ₅	-56.3
	T ₁₀	-60.4
Temp.-retraction, ° C		
	TR10	-66.7
	TR30	-60.3
	TR50	-54.3
	TR70	-48.5
Compression set, %		
After 4 days at	-40° F	-65° F
10 sec reading	52.4	95.2
30 min reading	23.6	88.9

program with the Air Force, was successful in polymerizing the fluoroalkyl silane. The homopolymer of trifluoropropyl methylchlorosilane, known as Silastic LS-53, is currently produced commercially by Dow Corning Corporation. The backbone of the molecular chain of the polymer is still a siloxane unit and the fluorine atoms are in the pendant position. Polmanteer and Hunter¹⁰⁶ recently discussed the relationship of polymer composition and low temperature characteristics of polysiloxane elastomers. Haszeldine, Newlands and Plumb¹⁰⁷ are currently investigating the chemistry of fluoroalkyl polysiloxanes, with particular emphasis on the effect of the position of the fluorine atoms within the molecule.

Silastic LS-53 possesses a good combination of low temperature flexibility, chemical resistance and stability at high temperatures. Its tensile strength is inferior to those of nitrile rubber, SBR and neoprene, although it compares favorably with other silicone rubbers. The original physical properties of LS-53¹⁰⁸ and its behavior at subzero temperatures are shown in Table XXI. Table XXII, taken from data by Dellaria¹⁰⁹, shows the resistance of LS-53 to fuels, solvents and hydraulic fluids at various temperatures. Talcott, Brown and Holbrook¹¹⁰ obtained similar results.

TABLE XXII

VOLUME INCREASE OF FLUOROSILICONE RUBBER AFTER IMMERSION IN LIQUIDS

Liquids	Immersion time & temp.	Volume increase, %
70:30 isooctane-toluene	3 days @ 158° F	18
JP-4	14 days @ 250° F	18
JP-5	7 days @ 75° F	4
Silicate ester*	3 days @ 350° F	6
Hydraulic fluid**	3 days @ 350° F	9
Skydrol 500	3 days @ 212° F	28
Kylene	7 days @ 75° F	19
Carbon tetrachloride	7 days @ 75° F	21

* Oronite 8200.

** Oronite 8515.

The low temperature flexibility of LS-53 is not as good as the ordinary silicone rubbers; however, it is better than any chemical and fuel resistant elastomers currently available. The fuel resistance is superior to nitrile and neoprene rubbers, but inferior to Fluorel or Viton A. Another outstanding property of LS-53 is heat stability. It was found that after 52 weeks of heat aging at 392° F, the rubber still retained approximately 35% of its original tensile strength. Servais and Polmanteer¹¹¹ reported that aging LS-53 for 16 weeks at 400° F reduced the tensile strength and elongation only 40% and the durometer hardness only a few points.

Dow Corning Corporation has placed on the market a modified fluorosilicone rubber known as Silastic LS-63. It was designed for easier handling and processing in extruders, calenders and rubber mills. It blends readily with other types of silicone rubbers and can be colored to any desired shade.

F. FLUOROPOLYAMIDINE

Although this experimental polymer has not been produced in any appreciable amount nor has it undergone regular vulcanization, it is mentioned here briefly due to its unusual stability at high temperatures. Brown¹¹² at the University of Florida, under a research project supported jointly by the Wright Air Development Division and the Office of Naval Research, first obtained the polymer by the pyrolytic condensation of a perfluoromonoamidine and perfluorodiamidine with the formation of a triazine nucleus. The product varied from the soft elastomeric solids to brittle resins. The elastomeric material has interesting properties. It was heated in air at 570° F for prolonged period of time with no apparent change; however, after 30 minutes exposure to 937° F (475° C), it lost 50% of its weight, although it still retained the rubbery properties¹¹³.

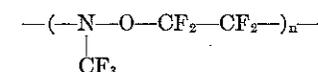
The primary deficiency of the elastomer, according to Gibbs¹¹⁴ and Bartholomew³, was the highly crosslinked nature of the gum, thereby rendering it unsuitable for most applications. Polymerization by melt and solution reactions using ionic and free-radical initiators¹¹⁵ also resulted in crosslinked products. Research is continuing to eliminate or minimize this deficiency. Brown^{116, 117} reported the progress of his investigations on difunctional monomers, including the reaction of the fluorinated dinitriles with the amidines, to produce linear polyfluoroamidines.

G. FLUORINATED NITROSO ELASTOMERS

Several rubber reviews¹¹⁸ which were published under different categories, such as "high temperature elastomeric compounds"¹¹⁹ and "rubbers for special service conditions"¹⁷² have included the various types of fluorine-containing elastomers. However, the nitroso-type rubbers due to their recent development, were not described in these reviews. The nitroso rubbers, therefore, will be discussed more fully to cover monomer synthesis, polymerization, vulcanization and properties. The elastomer program of the QMC during the past few years has placed major emphasis on fluorinated nitroso derivatives. A family of nitroso elastomers is being developed through the cooperative team effort of universities, industry and government laboratories. This is a continuation of the research on fluorine initiated by the QMC in 1950.

1. *Trifluoronitrosomethane-tetrafluoroethylene copolymer.*—The first elastomer developed was an equimolar copolymer of trifluoronitrosomethane (CF₃NO) and tetrafluoroethylene (C₂F₄). Since this copolymer has been studied more

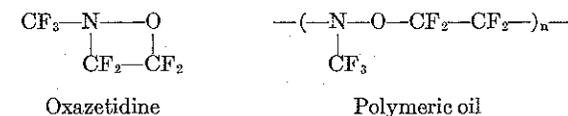
than the others, from monomer synthesis and polymerization to vulcanization (though far from complete), most of the description and discussion will be focused on this nitroso rubber. The molecular structure of the repeating unit of the polymer is represented by



a. *Monomer synthesis.*—Trifluoronitrosomethane, CF₃NO, is a deep blue gas with a boiling point of minus 84° C. It was first prepared by Ruff and Giese¹¹⁹ by the fluorination of silver cyanide in the presence of silver nitrate. It was claimed that the oxygen probably came from the impurities of the reactions. Barr and Haszeldine¹²⁰ synthesized it by the reaction of trifluoroiodomethane (CF₃I) and nitric oxide (NO) in the presence of ultraviolet light and with mercury as catalyst. Some experiments have been made by Tarrant¹²¹ and others in which it was found that strong sunlight gave better conversion and shorter reaction time than by irradiation with an ultraviolet lamp. The progress of this reaction can be followed readily, since the mixture of CF₃I and NO is brown in color and when the mixture turns blue, the reaction can be considered complete. Crawford, Rice and Monterroso^{122, 113} reported the use of trifluorobromomethane (CF₃Br) in lieu of CF₃I. CF₃BR is comparatively inexpensive and is readily available commercially.

The other comonomer, tetrafluoroethylene (C₂F₄) is commercially available. The du Pont Company is the major producer; its homopolymer is known as Teflon. As early as 1890 several papers¹²⁴⁻¹²⁶ were published describing attempts to prepare C₂F₄ by the reactions of fluorine with carbon or with chloromethanes and also of silver fluoride with tetrachloroethylene. The basic chemical reactions in the commercial synthesis of C₂F₄ are (1) reaction of fluorspar (CaF₂) and sulfuric acid to produce HF, (2) reaction of HF with chloroform to give chlorodifluoromethane, CHClF₂, and (3) pyrolysis of CHClF₂ to gaseous C₂F₄. The homopolymerization of C₂F₄ to Teflon has been discussed earlier.

b. *Polymerization.*—The elastomer is a 1:1 mole copolymer of CF₃NO and C₂F₄. Barr and Haszeldine¹²⁰ found that CF₃NO reacted slowly with C₂F₄ in the dark at room temperature giving rise to 30 to 65% of a colorless gas, b.p. -6.8° C of empirical formula C₃F₇NO, and they identified it as oxazetidine, a cyclic adduct. Another product amounted 35 to 70% of an almost colorless viscous oil, described as polymeric and of the same empirical formula. The molecular structures of these products are as shown



The ratio of the gaseous product to the polymeric oil could be controlled by reaction temperature; the higher temperatures favored the gas formation. An ionic mechanism was proposed for the reaction. Later, these same workers¹²⁷ suggested the alternative possibility of a gas-phase, radical-type mechanism for the formation of polymer, oxazetidine, or both. Crawford¹²² and others, on the other hand, presented experimental data which appear both to preclude an

ionic polymerization and heavily support a free radical mechanism. Preliminary kinetic data¹²³ was later presented. Recently, Crawford, Rice and Landrum¹²⁸ discussed the polymerization mechanism for formation of fluorinated nitroso elastomers and summarized the evidence supporting the free radical type of reaction.

In 1957, Minnesota Mining and Manufacturing Company and the Quartermaster Corps were already engaged in incorporating heteroatoms in the backbone of the polymer molecules as a means of improving the low temperature flexibility of fluorine-containing elastomers. Among the many approaches, the nitroso derivative was explored, theorizing that the reported oil (m.w.—7000)

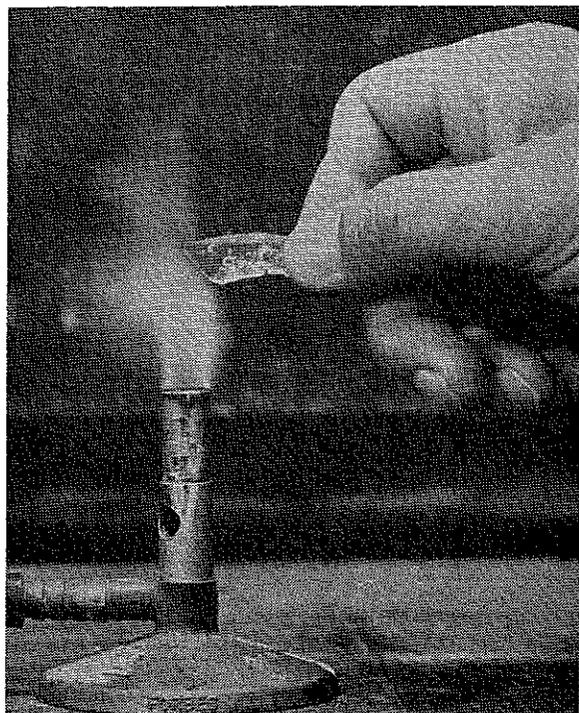


Fig. 1.—Showing nonflammability characteristic of $\text{CF}_3\text{NO}-\text{C}_2\text{F}_4$ elastomer. (From QMC Rubber Research reports.)

by Barr and Haszeldine¹²⁰ would be elastomeric at molecular weights of 100,000 or above. Crawford and Montermoso¹²⁹ reported in 1958 that an elastomeric copolymer of CF_3NO and C_2F_4 was obtained by bulk polymerization with the exclusion of air, moisture, or light.

It was found that the elastomer may be made in any of three methods: bulk, solvent and water emulsion polymerizations. The water emulsion method is the most desirable due to simpler control of reactions and to practical economy for potential large volume production; however, bulk polymerization has been found to produce the elastomer with higher molecular weight. The inherent viscosities of the materials obtained by this method which was carried out at minus 20°C , ranged from 0.6 to 0.85, indicating a significant increase over the

values obtained previously (0.15 to 0.3) by the water emulsion method. The solvent polymerization did not produce polymer with as high molecular weights as did the bulk method.

The laboratory procedure for the bulk polymerization as described by Crawford¹²² and others was essentially as follows: the monomers CF_3NO and C_2F_4 in equimolar amounts were condensed in pyrex ampoules, sealed and allowed to warm to the desired polymerization temperature. The progress of the reaction was indicated by the disappearance of the characteristic blue color of CF_3NO in the reaction mixture. The unreacted monomers were then removed by flashing under vacuum. The polymer was removed by dissolving it in trichlorotrifluoroethane (Freon 113) and the per cent yields, conversions and properties determined. Efforts are in progress on finding better, cheaper and

FLUORINE-CONTAINING RUBBERS
LOW TEMPERATURE SERVICE PROGRESS

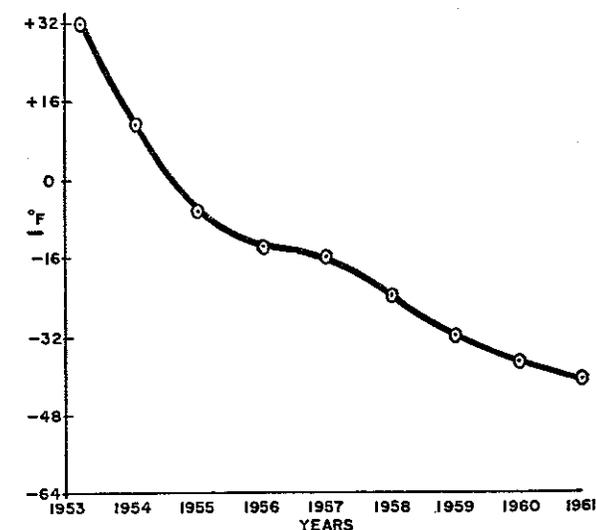


Fig. 2.—Showing progress in the development of chemical-resistant fluorine containing elastomers for use under sub-zero temperatures. (From QMC Rubber Research reports.)

more practical methods. Recently, a modified water suspension polymerization offers potential promise. A great deal of investigations needs to be done to improve polymerization methods and techniques.

c. Vulcanization and properties.—The properties of the unvulcanized copolymer of CF_3NO and C_2F_4 have been described in several papers¹³⁰⁻¹³². The unvulcanized gum is a clear transparent rubber which has been found to be completely nonflammable. When a piece of the gum was directly exposed to a flame of a bunsen burner, for example, some gas was evolved which tended to put out the flame, see Figure 1. This is probably the first rubber known that would not flame. Polychloroprene (neoprene), although possessing self-extinguishing properties, burns when exposed to direct flame. The molecular weight, determined by light scattering technique is over one million. Its glass

transition temperature is minus 51° C. The volume increase after immersion for 24 hours at 25° C in 70:30 isooctane-toluene mixture is only 3%. It is totally insoluble in acetone, methylethyl ketone, tetrahydrofuran and other solvents except to those containing fluorine such as the Freons. It was also found to possess unusual resistance to chlorine trifluoride. The weight loss after 20 hours in an oven at 200° C (392° F) is negligible. Thus, the elastomer has a good combination of inherent properties not present in any other rubber.

The most effective vulcanizing system, to date, for the $\text{CF}_3\text{NO}-\text{C}_2\text{F}_4$ copolymer is a combination of triethylene tetramine (TETA) and hexamethylene diamine carbamate (HMDA-C). The gum vulcanizate of the nitroso rubber, however, has a tensile strength of less than 300 pounds per square inch. A variety of reinforcing fillers were investigated to improve the tensile strength. The carbon black fillers caused sponging with the amine cures, regardless of the

FLUORINE-CONTAINING RUBBERS HIGH TEMPERATURE SERVICE PROGRESS

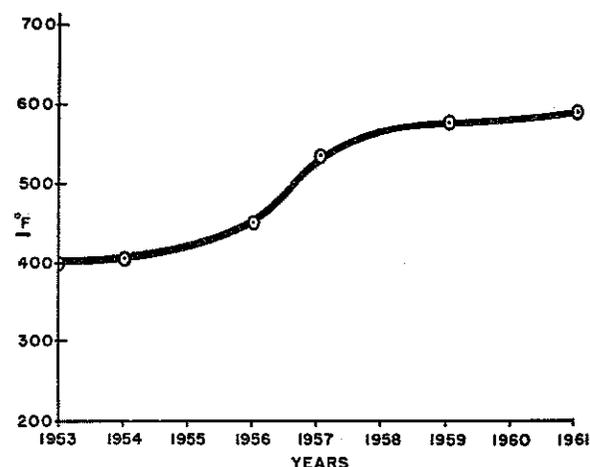


Fig. 3.—Showing progress made in the development of chemical-resistant fluorine-containing elastomers for use under extremely high temperatures. (From QMC Rubber Research reports.)

type and acidity (pH) of the blacks and of the temperature of vulcanization. Fine particle silicon oxides, such as the Hi-Sils, were the most effective reinforcing fillers. The physical properties were found to depend on the molecular weight of the polymers. Table XXIII shows the compound formulation and physical properties at 25° C.

The chemical resistance and low temperature characteristics of the nitroso elastomer were determined and compared with those of two commercially available rubbers, Fluorel and Hycar 1001 (NBR). These are shown in Tables XXIV and XXV.

Table XXIV indicated the superior chemical and solvent resistance of the nitroso elastomer. Even after immersion in red fuming nitric acid, RFNA, for 48 hours, it swelled only 28% compared to 70% for Fluorel, a copolymer of perfluoropropylene and vinylidene fluoride. It was also found that the effect

TABLE XXIII
FORMULATION AND PHYSICAL PROPERTIES AT 25° C

$\text{CF}_3\text{NO}-\text{C}_2\text{F}_4$ copolymer	100			
SiO_2 (HiSil 303)	15			
TETA	1.25			
HMDA-C	2.50			
Press cure: 60 min at 250° C				
Post oven cure: 18 hrs at 212° C				
M.W. $\times 10^6$.4	.6	.81	1.14
Tensile strength, psi	300	470	700	1100
Elongation, %	540	520	600	420
Hardness, Shore A	65	55	55	66

of red fuming nitric acid on the nitroso rubber has reached equilibrium after 24 hours. In another set of measurements, the volume increase after 24 hours immersion in RFNA was 25.2% and after 7 days, 25.5%.

The nitroso rubber, with Gehman T_g of minus 41° C and TR30 of minus 40° C would be serviceable at those temperatures. It can be seen from Table XXV that the nitroso rubber has an advantage of at least 25° C over the Fluorel and nitrile rubbers in low temperature flexibility.

In addition, the nitroso rubber has been found to be ozone and sunlight resistant. It was exposed in an ozonator for 24 hours at 150° F with an ozone concentration of 17,500 parts per 100 million in air without cracking. No

TABLE XXIV
CHEMICAL RESISTANCE
Volume increase, %, after 48 hours immersion at 25° C

Solvent	Nitroso	Fluorel	Nitrile
70:30 Isooctane-toluene	2	3	24
Acetone	2	188	147
Acetic anhydride	3	161	108
Benzaldehyde	1	75	259
Benzyl alcohol	1	1	179
Carbon tetrachloride	5	4	50
Ethylether	2	59	21
Formaldehyde	3	3	3
Methylethyl ketone	2	199	175
Red fuming nitric acid	28	70	decompose

TABLE XXV
LOW TEMPERATURE FLEXIBILITY
Gehman Relative Torsional Modulus, ° C

	Nitroso	Fluorel	Nitrile
T_2	-31	-10	-7
T_5	-41	-13	-13
T_{10}	-44	-14	-14
T_{100}	-47	-21	-18
Temperature Retraction, ° C			
TR70	-29	-9	-9
TR50	-36	-13	-12
TR30	-40	-16	-14
TR10	-46	-19	-18

visible cracks were observed after roof exposure for 2 months at 20% elongation. Although not as thermally stable as Viton A or Fluorel, its stability is better than most commercial rubbers. The weight loss of the raw gum was negligible after 20 hours in an oven at 200° C (392° F).

2. *Other nitroso copolymers.*—A large family of nitroso copolymers is being prepared. This can be achieved both by varying the structure of the nitroso monomer or by varying the comonomer. Two nitroso monomers of particular interest from the standpoint of their availability and properties of the copolymers formed are: 1-nitroso-2-nitrotetrafluoroethane (ONCF₂CF₂NO₂) and 1-nitroso-2-chlorotetrafluoroethane (ONCF₂CF₂Cl). Both copolymerize readily with C₂F₄. The properties of the copolymers are similar to those of the CF₃NO—C₂F₄ copolymer. Detailed investigations, however, are very preliminary and further discussion would be premature. The molecular structure of the copolymers may be represented:

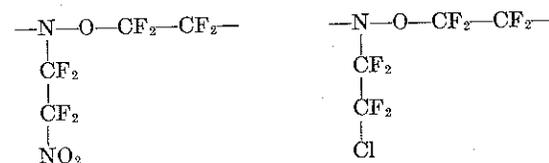


Table XXVI indicates the copolymer systems other than CF₃NO—C₂F₄ and the results obtained thus far.

TABLE XXVI
COPOLYMER SYSTEMS OTHER THAN CF₃NO—C₂F₄

Comonomer	Time, hrs	Temp. ° C	Conversion	Polymer
Copolymers of C ₂ F ₄				
C ₂ F ₅ NO	24	-16	Quant.	rubbery
C ₂ F ₇ NO	24	-20	Quant.	rubbery
C ₃ F ₇ NO	24	-20	50%	rubbery
HC ₂ F ₄ NO	24	-50 to -20	90%	rubbery
Copolymers of CF ₃ NO				
CF ₂ CFH	6	-20	85%	elastomeric
CF ₂ CFCl	24	-15	Quant.	elastomeric
CF ₂ CFCF ₂	11 weeks	-20	20%	elastomeric
CF ₂ CH ₂	3 weeks	-15 to -20	37%	grease
CFHCH ₂	48	-16 to -20	0	—
CH ₂ CH ₂	3 weeks	-16 to -20	0	—
CF ₂ CCl ₂	24	-20	Quant.	tough elastic
CFCICF—O—CH ₃	12	-15	Quant.	plastic
Styrene	24	-14	—	oil
Butyl methacrylate	24	-14	80%	oil
Copolymers of ONCF ₂ CF ₂ NO				
CF ₂ CF ₂	24	-25	90%	elastomeric
CF ₂ CFCl	24	-25	92%	brittle plastic
CF ₂ CFH	24	-25	80%	stiff gum
CF ₂ CH ₂ OCHCH ₂	24	-25	98	brown oil
Copolymers of ONCF ₂ Cl				
CF ₂ CF ₂	8 days	-65 to -35	82%	elastomeric
CF ₂ CFCl	20	-20	—	short elastic
CF ₂ CH ₂	20	-20	—	plastic

The current work on nitroso derivatives has opened up a broad and promising field for investigations. The new monomers used in the copolymerizations have been described by Crawford¹³³, Park¹³⁴, Tarrant¹³⁵, Stefani¹³⁶ and others in various publications and technical papers.

VI. DISCUSSION

At the early stage of the Arctic Rubber Program, which started in 1948, the author was asked what kind of ideal rubber was the QMC looking for. Without hesitation he said that QMC would settle for a rubber possessing the strength of natural rubber, the low temperature flexibility of silicone and the chemical resistance of Thiokol. We have not obtained this rubber yet but we are certainly getting close to it. What makes the current objective more difficult to meet is the addition of new requirements resulting from the development of modern weapons. However, it is not actually expected that any single rubber will solve all the problems.

In the search for elastomers possessing a combination or combinations of desirable qualities, it is felt that the area of fluorine-containing compounds was a wise choice to investigate. Significant progress has been made since 1950. Literally, thousands of new rubbers have been prepared, in gram quantities. After screening, only a small fraction of about 1% were selected for more detailed evaluation. Even then, there was no assurance that they will be commercially produced.

Not all the elastomers presented and discussed in this review reached commercial production. Polyfluoroprene occupied a position, as far as properties are concerned, between neoprene and polybutadiene. In addition, to produce polyfluoroprene would cost more than neoprene or polybutadiene. Hence, its production was discontinued. The trifluorobutadiene rubber was equal to neoprene in low temperature flexibility, but better in chemical resistance. Compared to nitrile rubber, the polytrifluorobutadiene was equal in chemical resistance, but better in low temperature flexibility. Here was a rubber that was better than both neoprene and nitrile rubber but did not reach the open market for economic reasons. The cost of producing this rubber would be prohibitive and noncompetitive with either neoprene or nitrile rubber. Besides, there were some rubbers commercially available that possessed better low temperature flexibility and others with superior chemical resistance. Polyfluoroester was not produced in larger quantities for similar considerations. The Vitons and Fluorel, Kel—F Elastomers and fluorinated silicone are commercially available. The fluoroacrylate elastomer, 1F4, is being produced commercially but its use has been limited since the development of vinylidene fluoride copolymers. The fluorinated nitroso rubbers are still in the experimental or laboratory stage, although larger production is being contemplated.

From the data presented, the fluorinated silicone, LS-53, has the best low temperature flexibility, followed by the nitroso rubber. In chemical resistance, the nitroso rubber comes first, followed by Viton or Fluorel, and the Kel—F Elastomers. The most comprehensive comparative study of high temperature stability of various rubbers, was made by Bergstrom¹³⁷. The nitroso rubber was not available for this study. He determined the temperature at which the vulcanizate retained 75% of the original tensile strength after aging for 8 hours. The tensile strength was measured at room temperature. The results obtained were in this order: Viton A@530° F; Kel—F Elastomer 3700@450° F; LS-53@430° F; and Poly FBA@370° F. When the tensile strength was

determined at high temperatures, these rubbers retained 50% of their original tensile strength at 170 to 190° F. In flame retardance or nonflammability, the nitroso rubber is outstanding, followed by Viton A or Fluorel, Kel-F Elastomers, LS-53 and 1F4. The nitroso rubber is the only elastomer known that would not flame. A deficiency of LS-53, 1F4 and the still experimental nitroso rubber is their low tensile strengths which are less than 1500 psi. Viton A, Fluorel and the Kel-F Elastomers have tensile strength over 2000 psi. All these fluorinated rubbers are expected to be resistant to ozone, weather and radiation since they are all saturated and contain fluorine in their molecule.

The steady progress made in the development of chemical-resistant fluorine-containing elastomers for use under extremely low and extremely high temperatures is graphically shown in Figures 2 and 3 respectively.

With the rapid continuous advances in travel, particularly in the fields of rockets, jets, missiles and nuclear submarines as well as in civilian transportation, the functional demands on elastomers will continue to increase. It is believed that the fluorine-containing elastomers, including those which may be developed in the future, will play an important role in meeting these requirements.

VII. ACKNOWLEDGMENT

A scientific review of this kind cannot be made without the considerable assistance of those associated with the particular field. The author would like to express his appreciation to the researchers and authors of technical papers surveyed in this review for their valuable contributions. Particular acknowledgement is made to his close associates, Drs. J. Copenhaver, B. F. Landrum and G. H. Crawford of Minnesota Mining and Manufacturing Company; Drs. P. Tarrant and J. D. Park of Florida and Colorado Universities respectively; Mr. C. B. Griffis, Mr. A. Wilson and Dr. G. R. Thomas of the QMC Laboratories. Appreciation is also expressed to Dr. G. E. P. Smith, Jr. and Dr. B. L. Johnson of Firestone Chemical and Physical Research Laboratories and to Dr. D. Craig of the B. F. Goodrich Research Center for reviewing the manuscript and for their valuable suggestions.

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