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**POLYMERS DERIVED FROM
DIHYDROPERFLUOROBUTYL ACRYLATE**

FRED W. KNOBLOCH

HORACE C. HAMLIN

MAJ, USAF

MATERIALS LABORATORY

SEPTEMBER 1955

WRIGHT AIR DEVELOPMENT CENTER

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PROJECT No. 7340

WRIGHT AIR DEVELOPMENT CENTER
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

FOREWORD

This investigation was conducted by the Organic Materials Branch under Project No. 7340, "Rubber, Plastic and Composite Materials", Task No. 73404, "Synthesis and Evaluation of New Polymers", formerly RDO No. 617-11, "Synthesis and Evaluation of New Polymers".

The project was under the supervision of Dr. R. N. Evans; Mr. F. W. Knobloch acted as project engineer and conducted all polymerization aspects of the investigation; Maj H. C. Hamlin compounded all polymers and compiled physical data on the compounded materials. Acknowledgment is also given to Lts R. M. Luck, S. A. Aspey, and E. J. Kupchik for their previous contributions.

This report covers work conducted from October 1952 to January 1954.

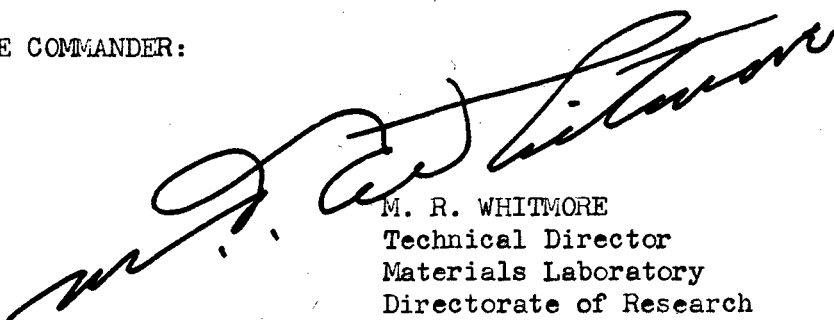
ABSTRACT

Exploratory copolymerizations of 1,1-dihydroperfluorobutyl acrylate with various other monomers selected from such general classes as 1,3 dienes, unsaturated acids, acrylamides, haloacrylates, vinyl alkyl ethers, vinyl silanes and allyl esters of unsaturated acids are described. Preliminary compounding recipes and evaluation data are presented for those systems which appeared to be of definite interest in connection with the development of specialty elastomers for Air Force applications. Attempts to prepare a copolymer possessing a balance of properties superior to that which exists in poly 1,1-dihydroperfluorobutyl acrylate were unsuccessful. However, considerable information was obtained regarding the behavior of 1,1-dihydroperfluorobutyl acrylate in copolymerization reactions and the search for potentially valuable polymers based on this important new monomer was extended to include preliminary investigation of many copolymer compositions not previously studied.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:



M. R. WHITMORE
Technical Director
Materials Laboratory
Directorate of Research

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I. INTRODUCTION

Elastomers for specialized applications are constantly being sought by the Air Force. Few synthetic rubbers are capable of withstanding temperatures in the neighborhood of 350°F for prolonged periods of time. None of these performs satisfactorily in advanced design applications which impose such additional conditions as immersion in diester base engine oils or other specialized fluids during exposure to elevated temperatures.

To date efforts toward the development of satisfactory rubbers for specialized Air Force applications have been concerned largely with the incorporation of polar groups into the base polymer structure. These polar groups reduce the swelling action and deteriorating effects of essentially non-polar fuels, oils and related fluids. Unfortunately, however, the introduction of polar groups also tends to increase the crystallinity of the polymer, which, in effect, decreases its elastomeric properties. In other words, polymers with high polarities are likely to have satisfactory solvent resistance for specialized applications but unsatisfactory mechanical properties. This report reviews a number of attempts to prepare a specific base polymer possessing a better balance of essential properties than is available in presently known elastomers.

The Minnesota Mining and Manufacturing Company, under Contract AF 33(038)515, has given this problem considerable study. The development of the fluorinated acrylates by this company, particularly 1,1-dihydroperfluorobutyl acrylate (commonly known as FBA), offers realistic possibilities for the preparation of valuable new rubbers for specialized applications.

The investigations described herein were undertaken to expand upon contractual effort to obtain a copolymer combination, involving FBA, which would be superior to poly FBA itself. Much of this effort was directed toward copolymerizing FBA with monomers which would react further during vulcanization. It was thought that in this manner more effective cures would be possible than had previously been obtained.

Lack of a completely satisfactory curing system has long been a major obstacle in the development of an FBA rubber compound of exceptional value to the Air Force; both amine and oxide cures, for instance, initially produced rubber compounds which were unsatisfactory, principally with respect to heat aging. Mechanical properties, including heat aging characteristics, have been much improved by the development of specific amine cures (see Appendix I), but still greater improvements are necessary if the stringent performance requirements of specialized Air Force applications are to be satisfied.

Detailed physical measurements such as molecular weight determinations, solution viscosities, and the like, were not considered of prime importance in this phase of the work. The general method of attack was to use theoretical and other considerations to determine what new copolymer systems should be investigated. Representative copolymers were then prepared and examined for properties of interest, using poly FBA as a standard; copolymer compositions have not been indicated because of analytical difficulties largely due to the presence of fluorine.

Since the accomplishment of this work, many of the referenced copolymer systems have been more extensively studied by the Minnesota Mining and Manufacturing Company; quantitative analytical information on typical copolymer compositions has also become available in some instances.

II. GENERAL EXPERIMENTAL METHODS AND TECHNIQUES

A. Polymerization Procedures

The limited supply and prohibitive cost of many of the monomers used in this investigation made it desirable to conduct copolymerizations with relatively small quantities of monomer. It was also necessary, however, to prepare the polymers on a scale large enough to permit preliminary compounding studies on a small rubber mill. As a compromise it was made standard practice to prepare experimental polymers with only five grams of monomer at a time.

The polymerizations were performed largely in emulsion systems, although bulk and solution polymerizations were occasionally run.

The polymerization apparatus employed was an end-over-end tumble type, consisting essentially of a rotating drum fixed on an axle; the drum contained provision for attaching small 15 ml. screw-cap polymerization vials. The entire drum assembly with attached vials was immersed in a thermostated water bath.

The polymerizations were generally run at either 77°F or 122°F. The following was extensively employed as a standard emulsion recipe:

Total Monomer	5.0	gms.
K ₂ S ₂ O ₈	0.015	gms.
Dodecyl Mercaptan	0.15	gms.
Duponol-ME*	0.45	gms.
Water	9.0	gms.

The air remaining in the polymerization vials after loading was swept out with nitrogen before the vials were closed and attached to the drum. Tumbling at constant temperature was continued for 16 hours or until the emulsions showed evidence of polymerization (percent conversions of polymers prepared in this manner were generally very high). Copolymers were usually prepared in three standard compositions; this facilitated comparison between systems as well as establishing trends within particular systems. These standard compositions as expressed in molar ratios were: FBA 50%/comonomer 50%; FBA 75%/comonomer 25%; and FBA 90%/comonomer 10%. Other ratios were prepared whenever more extensive investigation of a particular system was desired. More than 125 individual experiments were run in evaluating the copolymer systems reported upon.

* E. I. duPont deNemours and Company, Inc.

After preparation, all polymers were subjected to purification and washing; this was accomplished by one of several simple procedures. Steam distillation of the latex, followed by coagulation, and thorough washing with water was one such method employed. An alternate procedure was merely to coagulate the latex and wash thoroughly with water. In all cases, the latex was coagulated by addition to a methanol- $\text{Al}_2(\text{SO}_4)_3$ solution prepared by combining four volumes of methanol with one volume of saturated aqueous $\text{Al}_2(\text{SO}_4)_3$ (in some instances it was also necessary to cool the latex to bring about coagulation). The coagulated polymers were shredded or divided into small pieces to facilitate drying in a small vacuum oven (three hours at 140°F). Some of these polymers were then selected for further study which included film casting, thermal stability tests and compounding studies (many of the polymeric materials obtained were obviously unsuitable as elastomers, in fact had no recognizable virtues).

Table 1 lists the monomers which were copolymerized with FBA and otherwise investigated as indicated above.

TABLE 1. LIST OF MONOMERS INVESTIGATED

Diallyl oxalate	2-vinyl pyridine
Butadiene	n-Butyl vinyl ether
N- <u>tert.</u> -butylacrylamide	N-1,1 dihydrotrifluoroethylacrylamide
N,N' methylenebisacrylamide	Triallyl cyanurate
Maleic acid	Trihexyl aconitate
Thiosorbitol	Allyl alcohol
Methacrylic acid	Chloroprene
Acrylic acid	Ethyl <u>alpha</u> bromoacrylate
Acrylamide	N-1,1 dihydroperfluorobutylacrylamide
Methacrylamide	Diallylmaleate
Vinyl triethoxy silane	Thioglycolic acid
Hexamethylene dithiol	Allylglycidyl ether
Divinyl sulfide	

(All liquid monomers were freshly distilled just prior to use.)

B. Copolymer Evaluation

Polymers were examined visually to determine relative elasticity, elongation, toughness, homogeneity, and tack. Products which were non-elastomeric were not further evaluated at this time except for limited thermal stability tests. The latter involved film casting of selected polymers and determination of weight loss upon oven heating at 350°F. Suitable films were cast by introducing weighed samples of polymers and an appropriate solvent (a solvent mixture composed of equal parts by volume of methyl perfluorobutyrate, methyl ethyl ketone and acetone was often found exceptionally effective) into screw-cap vials. After tumbling for a week at 122°F the resulting solutions were filtered, placed in small aluminum foil dishes and the solvent slowly evaporated to constant weight. The polymer films were then baked at 350°F and weight changes noted periodically. Table 4 lists results considered to be of interest to this report.

Elastomeric polymerization products which appeared to be of interest were further evaluated through compounding and vulcanization studies. Promising rubber compounds realized from these studies were subjected to heat aging tests in air and in synthetic diester-base engine oils (MIL-L-7808A); the results of these tests are presented with other evaluation data under the sections of this report which describe the specific copolymer systems involved.

III. POLYMERIZATION AND COMPOUNDING STUDIES

A. Polymerization of FBA in the Presence of Thiols

The general modifier-promotor effect of thiols on vinyl polymerization is well known (1). Polymerization of FBA in the presence of varying amounts of the following thiols was investigated to determine applicability and specific effects:

<u>Modifier</u>	<u>Mole Percentage</u>
Hexamethylene dithiol	1.0%; 5%
Thiosorbitol	0.5%; 5%
Thioglycolic acid	1.0%; 5%

Low molecular weight polymers were obtained in all instances; polymers prepared with 5 mole percent of thiol, for instance, were thick, tacky liquids which could be poured.

The modified FBA polymer obtained with one mole percent thioglycolic acid was compounded as indicated by Table 2.

TABLE 2. COMPOUNDING RECIPES FOR THIOL-MODIFIED POLY FBA

	<u>A</u>	<u>B</u>	<u>C</u>
Polymer	100	100	100
HAF Black	15	10	10
TETA*	2	-	1
Stearic Acid	-	-	-
ZDEDTC**	-	1	-
MgO	-	1.5	-
SRF Black	-	10	10

* Triethylenetetramine

** Zinc diethyldithiocarbamate

After molding for 90 minutes at 310°F, the products ranged from stiff, weak, or crumbly materials, to flexible and fairly strong rubbers. Cure C produced the best elastomer. Some of these samples showed moderate flexibility after 25 days heat aging at 350°F, but the rubbers were generally inferior to poly FBA.

B. Acrylamide Copolymers of FBA

The possibility that copolymers of FBA and various acrylamides might function as rubbers of greater thermal stability and tensile strength than could be realized with poly FBA led to investigation of the systems listed in Table 3; all polymers were prepared by means of the standard emulsion recipe with a reaction time of 16 hours at 122°F:

TABLE 3. COPOLYMERS OF FBA AND VARIOUS ACRYLAMIDES

<u>Monomers</u>	<u>Mole Percent Charge</u>	<u>Polymers</u>
FBA/Am *	50 : 50	Hard, brittle solid
FBA/Am	75 : 25	Tough, nonhomogeneous elastomer
FBA/Am	90 : 10	Strong, snappy elastomer
FBA/FEAm	50 : 50	Lost during polymerization
FBA/FEAm	75 : 25	Strong, waxy elastomer
FBA/FEAm	90 : 10	Tacky elastomer
FBA/FBAm	50 : 50	Lost during polymerization
FBA/FBAm	75 : 25	Tough, waxy elastomer
FBA/FBAm	90 : 10	Somewhat tacky elastomer
FBA/BAm	75 : 25	Waxy elastomer
FBA/BAm	90 : 10	Snappy elastomer
FBA/MAm	50 : 50	Powdery, nonhomogeneous polymer
FBA/MAm	75 : 25	Mixture of homopolymers
FBA/MAm	90 : 10	Very tacky elastomer
FBA/MBAm	50 : 50	Rubbery crumb
FBA/MBAm	75 : 25	Rubbery crumb
FBA/MBAm	90 : 10	Tough, somewhat rubbery crumb
FBA/MBAm	95 : 5	Elastomer, tougher than poly FBA
FBA/MBAm	98 : 2	Elastomer, bluish cast

* See Abbreviations, Appendix II

Variations of the copolymerization ratio of amide to FBA had very marked effects on the physical properties of the polymers obtained. Increasing the mole ratio of any acrylamide produced less elastomeric materials which were tougher and more crystalline in nature than poly FBA. The increase in crystallinity is presumably due in part to the hydrogen bonding of the amine hydrogen.

The FBA/acrylamide copolymers tended to form as homogeneous gel-like latexes while the FBA/N-tert.-butylacrylamide copolymers were obtained as stable latexes; the latter copolymers were less crystalline

than the former. The 90/10 copolymer compositions in both systems were much tougher rubbers than poly FBA.

The FBA/FEAm and FBA/FBAm copolymers formed stable liquid latexes. The rubbers produced were both snappier and tougher than poly FBA. The properties of the copolymers produced with FEAm were very similar to those produced using FBAm.

The FBA/methacrylamide copolymers prepared from monomer charges of more than 10 mole percent of methacrylamide were not homogeneous and the latex contained considerable precoagulum.

The FBA/MBAm systems in general produced poor latexes, and gels resulted with as little as five mole percent of the MBAm constituent. Higher concentrations of MBAm yielded crumbly polymers; lower charges resulted in tough, rubbery materials.

C. Thermal Stability Tests on FBA/Acrylamide Copolymers

Table 4 indicates weight loss of various copolymers after oven aging at 350°F; it will be noted that many copolymers of FBA are equivalent to poly FBA with respects to this particular test.

Rapid heating tests were considered somewhat more significant. Samples were evaluated on a small 1/4 inch aluminum hot plate under atmospheric conditions; the hot stage was heated at a rate of 20°C per minute to a temperature of 330°C (626°F). The FBA/Acrylamide polymers seemed to be unaffected to 200°C (392°F); however, decomposition ensued above 200°C. These results were only slightly better than were obtained for a control sample of poly FBA. The 75/25 FBA/FEAm polymer exhibited exceptional thermal stability. The polymer was converted to a viscous liquid at 230°C (446°F) which could be drawn into fibers. No darkening was noted to 330°C (626°F). This represents an increase of about 100°C (180°F) over the darkening and apparent decomposition point found for poly FBA. A similar performance was exhibited by the 90/10 sample, although with this composition smoke and vapour were observed at about 310°C (590°F). All copolymers evaluated in the rapid heating tests were considered superior in thermal stability to the control sample of poly FBA used. The group composed of FBA copolymers with N,N'-methylene-bisacrylamide, acrylamide, and methacrylamide exhibited the poorest stability. The N-*tert.*-butylacrylamide produced polymers of intermediate stability, while the fluorinated acrylamides were found to impart the highest thermal stability.

Although the results of the thermal stability tests appear encouraging, the polymers investigated were undesirable from other standpoints. Introduction of sufficient amounts of the acrylamide to significantly

affect thermal stability brought about considerable reduction in low temperature flexibility. In addition, the polymers became less elastic as the ratio of acrylamide to FBA was increased.

TABLE 4. WEIGHT LOSS OF POLYMER FILMS AT 350°F

A. Polymers Exhibiting Less than 10% Weight Loss

<u>Charged Monomer Ratios</u>		<u>Percent Weight Loss at 350°F After 20 Hours</u>	<u>40 Hours</u>	<u>60 Hours</u>
FBA/BAm	90/10	0.8	0.9	1.1
FBA/DAM	90/10	0.8	1.0	1.1
FBA/FBAm	90/10	1.0	1.1	1.2
FBA/MBAm	95/5	1.6	2.2	2.5
FBA/Am	90/10	2.4	2.5	2.8
FBA/BAm	75/25	1.5	2.3	3.0
FBA	100	1.1	2.1	3.1
FBA/MAm	90/10	3.3	3.3	3.5
FBA/DAM	95/5	2.7	3.1	3.3
FBA/MA	84/16	0.7	0.9	3.3
FBA/FBAm	75/25	1.3	1.6	5.5
FBA/EBA	95/5	2.4	3.1	5.4

B. Polymers Exhibiting Between 10% - 20% Weight Loss

FBA/EBA	90/10	5.2	10.0	12.0
FBA/THA	84/16	12.7	12.9	13.1
FBA/EBA	80/20	11.0	15.2	17.7

C. Polymers Exhibiting Weight Loss Greater Than 20%

FBA/VBE	75/25	8.2	28.1	34.4
FBA/MBAm	75/25	30	33	36
FBA/Am	75/25	32	37	41
FBA/CP	50/50	39	42	44
FBA/MAm	50/50	45	49	51
EBA	100	53	55	56

D. Compounding of FBA/Acrylamide Copolymers

Table 5 indicates experimental recipes used for a 75 FBA/25 FBAm copolymer; none of these yielded cures. In addition, neither sulfur monochloride nor triallyl cyanurate were effective in producing cures when incorporated into recipe B:

TABLE 5. COMPOUNDING RECIPES FOR FBA/FBAm COPOLYMERS

	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>
Polymer: FBA/FBAm (75/25 Charge)	100	100	100	100
MgO	25	25	-	-
PbO ₂	5	5	3	3
SAF Black	-	-	5	5
Tolyene diisocyanate	-	-	3	3
Trimene Base*	-	-	-	3
Halocarbon Oil**	-	12	-	-

Cure: 60 minutes at 310°F

* Naugatuck Chemical Company

** Halocarbon Products Company, North Bergen, New Jersey

FBA/MBAm copolymers were compounded and cured as indicated by Table 6; most of the vulcanizates were stiff and crumbly but those from recipes C and E were somewhat better and permitted evaluation of physical properties.

TABLE 6. COMPOUNDING RECIPES AND EVALUATION OF FBA/MBAm COPOLYMERS

	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>
Polymer: FBA/MBAm (Composition of polymer*)	100. (95/5)	100. (90/10)	100. (90/10)	100. (75/25)	100. (90/10)
Stearic Acid	1.	1.	2.	2.	1.
HAF Black	35.	20.	13.	13.	10.
TETA**	1.	1.	0.9	0.75	-
Sulfur	-	-	-	1.	-
MBTS***	-	-	-	-	1.4
Trimene Base	-	-	-	-	2.0

* i.e. monomer charge ratio in mole percent

** triethylene tetramine

*** Mercaptobenzothiazyl disulfide

Cure: 60 minutes at 310°F

Physical Data

<u>Sample</u>	<u>Modulus at 100% Elongation</u>	<u>Tensile (psi)</u>	<u>Elongation (Percent)</u>	<u>Permanent Set (Percent)</u>
C.vulcanizate	686	783	156	11
C vulcanizate	672	680	-	17

E. Copolymers of FBA and Unsaturated Acids

Several unsaturated acids were copolymerized with FBA so as to provide pendant carboxylic acid groups with the expectation that they could then be utilized in vulcanization reactions with common curing agents such as diamines; the effect of three such acids was investigated, namely acrylic acid, methacrylic acid and maleic acid. Table 7 lists the copolymer systems studied:

TABLE 7. COPOLYMERS OF FBA WITH UNSATURATED ACIDS

<u>Monomers</u>	<u>Mole % Charge</u>	<u>Polymers</u>
FBA/MA	83/17	Slightly snappier than poly FBA
FBA/MA	91/9	Appeared to be poly FBA
FBA/MA	72/28	Very tacky
FBA/AA	95/5	Somewhat tougher than poly FBA
FBA/AA	84/16	Cheesy elastomer
FBA/AA	70/30	Mud-like consistency
FBA/AA	50/50	Tough elastomer
FBA/AA	90/10	Tough elastomer
FBA/MAA	90/10	Very similar to 90 FBA/10AA
FBA/MAA	50/50	Cheesy elastomer

Upon coagulation, the 90/10 polymers of acrylic acid and of methacrylic acid with FBA yielded characteristic cheesy products. At this stage, the polymers appeared nonhomogeneous; however, after slight kneading, a homogeneous tough elastomer was obtained. The samples prepared with maleic acid on the other hand, produced softer polymers with more tack. Titration of the filtered FBA/maleic acid polymerization solutions, after coagulation, indicated that the majority of the acid remained unreacted. A similar titration in the case of the FBA/acrylic acid polymers indicated that more than 80% of the acid had entered into the polymerization.

Fairly good cures were obtained with those recipes of Table 8 which contained 1 part Trimene Base; 2 parts of the latter produced excessively stiff vulcanizates:

TABLE 8. COMPOUNDING RECIPES FOR FBA/AA COPOLYMERS

	A	B	C	D	E	F	G	H	J	K
Polymer: FBA/AA	100.	100.	100.	100.	100.	100.	100.	100.	100.	100.
(Polymer Composition*) (100/0) (84/16) (84/16) (84/16) (84/16) (95/5) (90/10) (90/10) (90/10) (90/10)										
MgO	1.5	5.	3.	3.	3.	3.	-	2.	1.5	1.5
SAF Black	-	5.	5.	-	-	-	-	-	-	-
HAF Black	15.	-	-	5.	10.	10.	25.	15.	15.	20.
Trimene Base**	-	2.	1.	1.	1.	1.	2.	-	-	-
Stearic Acid	1.	-	-	-	-	-	1.	1.	1.	1.
ZDEDTC***	1.	-	-	-	-	-	-	1.	1.	1.
Remarks	good cure	stiff cure	fair	fair	fair	fair	cured well badly knit	good cure	blistered cure	brittle porous

(Cure: 90 minutes at 310°F for A; 60 minutes at 310°F for others)

* i.e. monomer charge

** Naugatuck Chemical Company

*** Zinc diethyldithiocarbamate

Table 9 presents test data as obtained on selected FBA/AA vulcanizates from the above:

TABLE 9. EVALUATION OF FBA/AA VULCANIZATES

Original Properties

<u>Cure</u>	<u>Tensile psi</u>	<u>Elongation (Percent)</u>	<u>Permanent Set (Percent)</u>	<u>Modulus at 100% Elongation</u>
C	923	100	6	-
D	1345	245	22	-
E	1243	173	14	708
F	1174	216	14	456
H	1142	200	22	747

Properties after Aging in Diester Fluid (MIL-L-7808A) at 350°F for 280 Hrs.

E	520	0	0	-
F	880	60	-	-
G	0	0	-	-

Volume Swell after Aging in Diester Fluid (MIL-L-7808A) at 350°F.

	<u>Hours-% Swell</u>	<u>Hours-% Swell</u>	<u>Hours-% Swell</u>
A	115-5.7	280-10.8	790-28.0
C	90-9.0	264-12.4	458-16.6

Weight Loss on Air Aging at 350°F

<u>Polymer</u>	<u>Loss after 48 hrs</u>	<u>Loss after 100 hrs</u>
Poly FBA	12.9%	32.9%
Cure C	9.7%	16.2%

The aging of FBA/AA polymers in synthetic diester fluids left much to be desired. Although the samples exhibited low swells, physical properties were drastically impaired after the immersion period.

The thermal stability, as measured by weight loss, of the 84FBA/16AA polymers offered a considerable improvement over poly FBA, however, both poly FBA and the copolymers with AA attained approximately the same degree of hardness when aged at 350°F for the same period of time. Minnesota Mining and Manufacturing Company has determined that in curing poly FBA, 1,1 dihydroperfluorobutyl alcohol is split out. In the case of the FBA/AA copolymers, however, it is quite possible for the curing agent to preferentially react with carboxylic acid groups to eliminate water. Air aging (i.e. post curing conditions) would then be expected to result in weight-loss differences between poly FBA and FBA/AA copolymers such as have been observed because of the weight of a molecule of heptafluorobutanol compared to that of a molecule of water. The effect on physical properties, on the other hand, could be quite comparable under limited aging conditions.

F. Copolymers of FBA and 1,3 Dienes

Two monomers in the general class of 1,3 dienes, namely chloroprene and butadiene, have been copolymerized with FBA. It would be expected that the incorporation of large amounts of such monomers in copolymer structures would result in more readily curable polymers possessing improved low temperature flexibility. At the same time the new polymers would be expected to exhibit decreased fuel and oil resistance and decreased resistance to ozone attack.

Considerable work on the FBA-butadiene copolymer system has been reported by Minnesota Mining and Manufacturing Company (2). Efforts reported herein were directed toward introduction of relatively small amounts of butadiene with the hope that sufficient unsaturation could be introduced to facilitate conventional curing methods without adversely affecting fuel and oil resistance or substantially decreasing resistance to attack by ozone.

Table 10 presents compounding data on several FBA/BD copolymers prepared by Materials Laboratory (these copolymers were somewhat tougher than poly FBA; the product of the 93/7 polymerization was nonhomogeneous and probably contained considerable amounts of the two homopolymers along with any copolymer that formed.

TABLE 10. COMPOUNDING RECIPES FOR FBA/BD COPOLYMERS

	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>
90 FBA/10 BD	100.	-	-	-
95 FBA/5 BD	-	100.	-	-
93 FBA/7 BD	-	-	100.	100.
ZnO	5.	5.	5.	5.
Stearic Acid	1.5	1.5	1.5	1.5
Sulfur	2.	2.	1.5	2.
HAF Black	25.	25.	-	-
Altax*	2.	2.	1.5	2.
SAF Black	-	-	10.	12.

* R. T. Vanderbilt Company

Cure: 60 minutes at 310°F

Results of compounding and curing studies with the above polymers were discouraging in that only slight evidence of vulcanization was obtained. Additional sulfur and accelerator failed to increase the degree of vulcanization when employed in cure D, indicating that the butadiene, if present, was aiding little in attaining improved cures.

Initial preparations of FBA/Chloroprene copolymers were not very successful. The products discolored while being dried, and to a lesser extent, degraded even under atmospheric conditions. Considerable pre-coagulum was also formed in these preliminary runs. Satisfactory copolymers were finally obtained by an incremental addition of the chloroprene monomer to a polymerization emulsion which had been made slightly basic with NH_4OH . No pre-coagulum was observed and the polymers themselves possessed considerable strength and tack. Compounding data are presented in Table 11 (A represents a typical Neoprene recipe, B an FBA recipe, C an aromatic diene cure):

TABLE 11. COMPOUNDING RECIPES FOR FBA/CHLOROPRENE COPOLYMERS

	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>F</u>	<u>G</u>	<u>H</u>	<u>I</u>
Polymer: FBA/CP	100	100	100	100	100	100	100	100	100
(Monomer Charge)	(82/18)	(82/18)	(82/18)	(50/50)	(50/50)	(50/50)	(95/5)	(50/50)	(50/50)
ZnO	5	-	-	5	5	5	5	5	5
MgO	4	25	-	4	4	25	4	2	2
Na-11*	-	-	1	-	-	-	-	-	-
Na-22**	.5	-	-	.5	.5	-	.5	.5	.5
Stearic Acid	1	1	-	1	1	1	1	1	1
HAF Black	10	-	-	-	-	-	-	-	-
SAF Black	-	-	-	-	20	-	10	20	12
PbO ₂	-	5	-	-	-	-	-	-	-
Agerite Resin D***	-	-	-	-	-	-	-	1.	-
Time at 310°F (min.)	60	60	60	30	30	60	30	30	30

* p,p' - diamino diphenyl methane. E. I. duPont deNemours Co., Inc.

** 2-mercaptoimide azoline. E. I. duPont deNemours Co., Inc.

*** R. T. Vanderbilt Company, Inc.

Recipe J yielded the best vulcanizates in this series; recipes C and G, on the other hand, produced no observable cure while the other recipes yielded products which were rather hard, often blistered and generally had poor flexibility.

A typical vulcanizate from recipe J swelled about 65% after 70 hours in diester-base fluid (MIL-L-7808A) at 325°F; another swelled 47.5% in 70/30 isooctane/toluene and fell apart upon subsequent handling. These observations and other test data indicated that the FBA/Chloroprene copolymers offer no properties of interest for Air Force applications.

G. Copolymers of FBA and Vinyl Silanes

Several experimental polymers were prepared from FBA and vinyl triethoxy silane, using the standard emulsion procedure. However, those polymers prepared from monomer compositions containing five mole percent or more of the silane were fibrous, tough materials with no snap.

Small quantities of vinyl triallyl silane were also incorporated into the FBA polymer with the expectation that the pendant allyl groups could be further reacted through conventional curing procedures. However, as little as five mole percent of the silane yielded a white powdery product. With one mole percent of vinyl triallyl silane, a white, waxy, somewhat rubbery product was obtained which had very limited extensibility. Attempts to prepare polymers containing less than one mole percent of the silane resulted in low yields.

Compounding of the FBA/VES polymers was attempted with the recipes indicated in Table 12. Benzoyl peroxide proved ineffective as a curing agent (recipe C) and PbO_2 (recipe A) produced badly blown and porous cures but recipe B yielded a reasonably good cure:

TABLE 12. COMPOUNDING RECIPES FOR FBA/VINYL SILANE POLYMERS

	<u>A</u>	<u>B</u>	<u>C</u>
99 FBA/1 VES	100	-	-
95 FBA/5 VES	-	100	-
90 FBA/10 VES	-	-	100
PbO ₂	3	3	-
HAF Black	15	5	25
M. T. Black	-	10	-
HgO	-	5	-
Benzoyl Peroxide	-	-	10

(Cure: 60 minutes at 310°F)

A typical vulcanizate from recipe B yielded the following swelling data upon aging in synthetic diester engine oil (MIL-L-7808A) at 350°F:

<u>Time (hours)</u>	<u>Swell (%)</u>
111	0.6
148	3.2
280	8.2

Preliminary evaluation studies indicate that these FBA/Vinyl triethoxy silane copolymers have improved heat resistance over poly FBA but comparatively poor physical properties. Hydrolysis of ethoxy groups during polymerization (followed by premature cross-linking) is considered partially responsible for the effects on physical properties which have been observed.

H. Copolymers of FBA with Allyl Esters and Alcohols

FBA/Diallyl Maleate

Copolymerization of FBA with more than 10 mole percent of DAM yielded nonelastomeric products. A 95 FBA/5 DAM mole ratio produced a rubber crumb of low extensibility; smaller proportions of DAM yielded better elastomers but these were still quite short. A copolymer prepared from a 99.5 FBA/.5 DAM monomer mixture was a somewhat tougher elastomer than poly FBA itself.

Table 13 presents compounding data on selected FBA/DAM copolymers:

TABLE 13. COMPOUNDING RECIPES FOR FBA/DAM COPOLYMERS

Polymer: FBA/DAM	A	B	C	D	E	F	G	H
(Monomer charge ratio)	100	100	100	100	100	100	100	100
	(99/1)	(98/2)	(98/2)	(98/2)	(98/2)	(98/2)	(98/2)	(95/5)
HAF Black	5	10	10	10	10	10	10	5
PbO ₂	3	-	-	3	3	3	3	3
ZnO	-	5	5	-	-	-	-	-
Stearic Acid	-	1	1	-	-	-	-	-
Sulfur	-	1.5	3	-	-	-	-	-
Altex	-	1.5	1.5	-	-	-	-	-
MgO	-	-	-	-	-	3	8	-

Cure: All recipes 60 minutes at 310°F

A number of the above recipes containing just PbO_2 and black produced blistered vulcanizates although good cures were generally obtained; recipes D and G appeared to give the best results of the series. Although all of these vulcanizates were weak, some exhibited low volume swell and small weight losses upon aging in diester fluids. Table 14 presents typical heat aging test data:

TABLE 14. EVALUATION OF FBA/DAM COPOLYMERS

Oven Aging at 350°F:

Cure A:	Time (hours)	30	53	97	142	189
	Weight loss (%)	5.5	7.6	10.2	12.9	15.6

Aging in Diester Fluid (MIL-L-7808A) at 350°F:

Cure A:	Time (hours)	96	241	312	
	Swell (%)	5.5	7.7	8.2	
Cure D:	Time	94	239	434	556
	Swell	4.0	6.4	6.5	12.0
Cure E:	Time	73	145	239	
	Swell	5.8	5.8	4.8	
Cure F:	Time	73	145		
	Swell	53.3	brittle		
Cure G:	Time	73			
	Swell		brittle, surface blisters		

FBA/Diallyl Oxalate

No homopolymer of DAO was obtained with the standard emulsion recipe. Attempted copolymerization of FBA with DAO resulted in a reaction product which appeared to be only poly FBA. This was not surprising in view of the general sluggishness of the allyl group in polymerization reactions.

FBA/Allyl Alcohol

Polymerization of FBA in the presence of allyl alcohol was attempted. Allyl alcohol apparently acted as a modifier for the resulting polymers were viscous low molecular weight liquids and as such were of little interest to this investigation.

I. Copolymers of FBA with Selected Acrylates

FBA/Ethyl-Alpha-Bromoacrylate

Considerable effort was expended in copolymerizing FBA with ethyl-alpha-bromoacrylate for the purpose of introducing reactive halogen atoms which would be expected to facilitate vulcanization reactions with curatives such as amines. The homopolymer of ethyl-alpha-bromoacrylate was a white amorphous powder. Initial copolymerizations yielded considerable amounts of precoagulum. Later runs were found to be acid even after base had been added to the initial emulsion. Formation of HBr during polymerization, as HCl is formed in chloroprene polymerizations, was considered responsible for the production of acid solutions and the formation of precoagulum.

The polymers obtained had a tan color but otherwise appeared quite similar to poly FBA in properties. As the ratio of the haloacrylate was increased the thermal stability of the resulting polymer product was decreased (see Table 4) and elastomeric properties became poorer.

Selected compounding and test data on these copolymers are recorded in Table 15:

*

TABLE 15. COMPOUNDING AND TEST DATA ON FEA/EBA COPOLYMERS

	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>F</u>	<u>G</u>	<u>H</u>
Polymer (95/5)	100	100	100	100	-	-	-	-
Polymer (90/10)	-	-	-	-	100	100	100	100
Stearic Acid	1	1	1	1	1	1	1	1
Trimene Base*	3	3	3	4	3	3	3	3
Sulfur	.75	1	1	1.25	.5	0	.5	.5
MgO	-	-	-	-	20	20	20	20
SAF	10	10	20	20	-	-	-	-
Agerite Resin D	-	-	-	-	-	5	5	5
Stabilite Resin**	-	-	-	-	-	-	-	10
Cure: Minutes at 310°F	60	60	60	60	60	60	60	60
% Swell in Diester Fluid***	89	79	52	32	67	36	59	107

* Naugatuck Chemical Co.

** Hercules Powder Co.

*** After aging for 72 hours at 350°F in MIL-L-7808A fluid

Initial attempts at vulcanization were accompanied by considerable blowing in the molded compounds but the cures themselves were quite good. The incorporation of metallic oxides somewhat limited the tendency toward blowing.

These copolymers are considered to be of no potential value for Air Force applications. Swelling in fuels and oils is more than can be tolerated and elastomeric properties are poor after oil immersion. It was of interest, however, that the introduction of a reactive halogen atom into the polymeric structure made possible more effective amine cures than could initially be obtained with poly FBA.

FBA/2-Chloroethoxyethyl Acrylate

This monomer was homopolymerized to give a white rubbery polymer. When charged in 34 mole percent with FBA, a slightly translucent, fairly tough polymer was obtained. Compounding and evaluation data of interest are tabulated below:

TABLE 16. COMPOUNDING AND TEST DATA ON FBA/CEEA POLYMERS

<u>Recipe</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>
Polymer: 66 FBA/34 CEEA	100	100	100	100
Stearic Acid	1	1	1	1
HAF Black	25	25	-	10
SAF Black	-	-	25	-
TETA	1	1.5	-	-
Sulfur	1	1	-	-
MgO	-	-	25	25
PbO ₂	-	-	5	5

Cure: 60 minutes at 310°F

Physical Properties

Tensile (psi)	595	<500	1087	<500
Elongation (%)	100	<100	130	60
Permanent Set (%)	-	-	4	2

Moldings from the above recipes were poorly knit but showed evidence of strength and flexibility. Extensibility was quite low for all samples, and physical properties were generally inferior to those of poly FBA.

J. Copolymers of FBA with Unsaturated Ethers

The vinyl ethers are generally polymerized in systems employing ionic catalysts. Polymerization of vinyl ethers can be effected in emulsion systems employing peroxide catalysts providing the vinyl ether is a minor constituent of the copolymer system. Acidic conditions must be avoided to prevent hydrolysis of the ethers.

FBA/n-Butyl Vinyl Ether

The products resulting from the copolymerization of these monomers were soft and taffy-like. The poor thermal stability exhibited by the polymers in this class eliminated them from further study.

FBA/Allyl Glycidyl Ether

The polymer obtained from a 1:1 mole charge of these monomers was tacky, flowing material (75% yield). It exhibited properties similar to low molecular weight poly FBA and was of no particular interest to this study.

K. Miscellaneous Copolymerizations

FBA/2-Vinyl Pyridine

2 -Vinyl pyridine homopolymerized to form a brittle, light brown resinous material. However, when 2-vinyl pyridine was charged in the standard emulsion recipe with FBA, no polymer products were isolated with reaction times up to seven (7) days.

FBA/Triallyl Cyanurate

A charge of as little as one mole percent of this trifunctional monomer produced a rubbery crumb which was quite short. Higher ratios of TAC consistently formed precoagulums of highly crosslinked materials. Good latexes were formed with less than one mole percent TAC, but as little as 12 mgs. of TAC per five grams of FBA monomer curtailed the extensibility of the resulting polymer considerably.

It had been theorized that sufficient unreacted allyl groups would be present in the polymer product to permit better curing through the

unsaturated linkages. However, the amount of TAC that could be introduced into the system and still produce a raw polymer with acceptable elastomeric properties was apparently too minute to be effective in improving vulcanization reactions. All vulcanizates were weak, crumbly, and unsatisfactory for further evaluation.

FBA/Trihexylaconitate

A soft and very extensible copolymer was obtained with a 17 mole percent charge of the aconitate; this material was not investigated further.

FBA/Divinyl Sulfide

The homopolymer of DVS was a fine, white, crystalline material. FBA/DVS copolymers, as obtained from a 1/1 molar ratio of monomers, were stiff and very brittle. Tough elastomers were obtained with smaller quantities of DVS but these had very low elongations and were no doubt highly crosslinked because of the difunctional nature of DVS. No further investigation of this system was undertaken.

IV. SUMMARY AND CONCLUSIONS

Of the numerous systems of polymers based on FBA and described in this report, only those copolymers formed by addition of small quantities of acrylic acid, diallyl maleate, triethoxy vinyl silane or the fluoroacrylamides showed marginal improvement in some physical property (s) over the homopolymer FBA--and such marginal improvements were almost invariably accompanied by poorer properties in other important areas. For instance, acrylic acid copolymers seemed to perform better than poly FBA in the air aging tests at elevated temperatures, but worse in synthetic ester base oils (Table 9). Similarly, the fluoroacrylamides were found to increase thermal stability but sharply decrease elasticity and low-temperature performance. Diallyl maleate copolymers cured readily and showed improved aging properties but were generally weak rubbers. Vinyl triethoxy silane likewise gave improved thermal stability but greatly reduced strength and extensibility.

In no case was it observed that thermal stability, resistance to diester fluids, ease of vulcanization, and elastomeric properties were simultaneously improved over and above the corresponding properties of poly FBA. Improvements in one property area were always accompanied by deleterious effects in another.

This investigation confirms previous but tentative conclusions by other researchers that the FBA monomer can not readily be modified through copolymerization to yield a polymer with an improved balance of properties over poly FBA itself. However, copolymerization with other monomers will remain indefinitely an important potential field for the development of an improved FBA elastomer. Further screening preparations should be undertaken with other new monomers of interest as they become available and terpolymer systems should also be considered for investigation.

V. BIBLIOGRAPHY

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R. L. Frank, P. V. Smith, F. E. Woodward, J. Polymer Sci., 3; (1948)
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- (2) F. A. Bovey, Synthetic Rubber from Carbon-Fluorine Compounds, WADC
Technical Report 52-197, Part 3, September 1953, p. 131 ff.
- (3) Ibid., p. 118 ff.

APPENDIX I

Subsequent to this investigation, satisfactory amine recipes for curing poly FBA have been developed. Early recipes employing amines generally contained metallic oxides since these aided in processing the rubber. It has been found that by eliminating or greatly reducing the oxides from amine recipes, it is possible to produce rubbers with improved aging properties. These improved amine-cured rubbers have reduced the need for the introduction of small amounts of comonomer into the poly FBA structure for the sole purpose of aiding the vulcanization. It is entirely possible that recompoundng of previously prepared polymers, utilizing the new amine recipes, would improve their properties. However, it is not expected that these rubbers would provide more than marginal improvements over amine cured poly FBA.

Two representative amine recipes developed by Minnesota Mining and Manufacturing Company under Contract AF 33(038)515 are presented below (3):

	<u>Recipes</u>	
	<u>A</u>	<u>B</u>
Poly FBA	100.0	100.0
Stearic Acid	1.0	1.0
Sulfur	1.0	1.0
HAF black (Philblack 0)	35.0	35.0
Triethylenetetramine	1.0	-
Trimene Base	-	1.0
Cure, Minutes at 300°F	60.0	60.0

APPENDIX II

LIST OF ABBREVIATIONS

AA	Acrylic acid
Am	Acrylamide
BAm	N-tertiarybutyl acrylamide
BD	Butadiene
CEEA	2-Chloroethoxyethyl acrylate
CP	Chloroprene
DAM	Diallyl maleate
DAO	Diallyl oxalate
DVS	Divinyl sulfide
EBA	Ethyl- <u>alpha</u> -bromoacrylate
FBA	1,1-Dihydroperfluorobutyl acrylate
FBAm	N-1,1-Dihydroperfluorobutyl acrylamide
FEAm	N-1,1-Dihydroperfluoroethyl acrylamide
MA	Maleic acid
MAm	Methacrylamide
MAA	Methacrylic acid
MBAm	N,N'-Methylenebisacrylamide
TAC	Triallyl cyanurate
VES	Vinyl triethoxy silane
THA	Trihexyl aconitate
VBE	Vinyl n-butyl ether