WADC TECHNICAL REPORT 52-197
PART 5

SYNTHETIC RUBBERS FROM CARBON-FLUORINE COMPOUNDS

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APRIL 1956

MATERIALS LABORATORY
CONTRACT No. AF 33(038)-515
PROJECT No. 7340

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

Carpenter Litho & Prtg. Co., Springfield, O.
300 - June 1956

FOREWORD

This report was prepared by the Minnesota Mining and Manufacturing Company, under USAF Contract No. AF 33(038)515. This contract was initiated under Project No. 7340, "Rubber, Plastic and Composite Materials", Task No. 73405, "Compounding of Elastomers", formerly RDO No. 617-12, "Compounding of Elastomers", and was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with Major H. C. Hamlin acting as project engineer.

This report covers period of work from May 15, 1954 to April 15, 1955.

The monomers which constitute the raw material used in the work under the contract, viz., polymerization studies and evaluation of polymers, are available only through the use of contractor's personnel and facilities, and constitute approximately 48% of the effort involved in the contract during this period. This leaves approximately 52% of said effort as representing the actual polymerization studies and evaluation of polymers reported herein.

ABSTRACT

Fluorine containing elastomers, such as FBA (1, 1-dihydroperfluorobutyl acrylate), are being prepared for possible use in fuels, lubricants, and hydraulic fluids over the widest possible temperature range (<0°F to >350°F).

Fluorinated diene-vinyl ether type copolymers continue to present difficulties in preparation. Electron irradiation has been an effective means of vulcanization.

Copolymers of 1,1,2-trifluorobutadiene with FBA have good tensile strength, solvent resistance, and low temperature behavior but lack resistance to heat and ozone.

Certain antioxidants increase the resistance of FBA polymers to dry heat. Thioamines give promise as high temperature stabilizers for poly-FBA.

Traces of co-polymerized acrylic acid are important for optimum cured properties of poly-FBA.

Butyl carbitol formal is one effective non-fluorinated plasticizer for poly-FBA but is subject to solvent extraction. Only polymeric materials resist such solvent extraction. Marked plasticization can be accomplished with silicone polymers, but swelling is excessive. Blends of Teflon and poly-FBA appear promising in strength and solvent resistance, but poor in uniformity and high temperature properties.

The greatest improvement in low temperature flexibility, without sacrifice of other desirable properties as compared to poly-FBA, is achieved by incorporating ether oxygen links into the alcohol side chain of the acrylate structure.

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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INTRODUCTION

In the introduction to the second annual report, the role played by small rubber parts in the operation of modern aircraft was described. It was pointed out that in the development of synthetic rubbers up to the present, no material has been found which satisfies the extreme requirements of military aircraft for resistance to fuels, lubricants and hydraulic fluids, for low temperature flexibility, and for resistance to high temperatures.

Earlier work, reported in the second, third and fourth annual reports, showed that certain fluorine-containing polymers, chiefly the fluoroacrylates, had the necessary resistance to swelling by aircraft fluids, but required improvement in their low temperature flexibility and in their resistance to degradation at high temperatures. From the known properties of organic substances containing large proportions of fluorine it was to be expected that fluorine-containing synthetic rubbers would show high resistance to a variety of organic liquids, including those of interest in aircraft, and this has in fact been found to be the case. It has also been found that the presence of fluorine on polymer chains tends to reduce flexibility at low temperatures and is not necessarily helpful in resistance to degradation at high temperatures. However, it was found (fourth annual report) that by proper design of the molecular architecture of the polymers and by improved vulcanization methods the behavior both at low and at high temperatures could be improved. Introduction of ether oxygen atoms at appropriate points in the side-chains of the fluoroacrylate polymers accomplishes a significant improvement in low temperature properties, while the use of polyamines (such as triethylene tetramine) for vulcanization results in greatly improved high temperature resistance. This report describes further study of fluoroacrylate polymers and copolymers. Improvements have been sought in copolymerization with fluorinated dienes, by incorporation of plasticizers, and by addition of heat stabilizers. The presence of a small amount (0.15%) of copolymerized acrylic acid has been found to be important in obtaining the optimum cured properties for poly-FBA (poly-1,1-dihydroperfluorobutyl acrylate).

A new type of alkoxyalkyl acrylate has been developed which is more favorable economically than those previously studied but equally good in properties. This is 3-(ω-hydroperfluoroethoxy)-1,1-dihydroperfluoropropyl acrylate (H-FEFPA).

SUMMARY AND CONCLUSIONS

The object of the research described in this report is the preparation and evaluation of fluorine-containing elastomers with very wide useful temperature ranges and resistance to a wide variety of solvents, hydraulic fluids, lubricants, and other liquids.

Further study has been given to homopolymers and copolymers of fluorinated dienes. A copolymer of perfluorobutadiene and vinyl 1,1-dihydroperfluorobutyl ether prepared using a 3:1 molar charge ratio has been found to have good high temperature properties when compounded with carbon black alone and no vulcanizing agents. It retained useful properties after 400 hours heating in air at 400°F. It has been found that the perfluorobutadiene:vinyl 1,1-dihydroperfluoroalkyl ether copolymers can be readily vulcanized by irradiation with high speed electrons. This may be valuable in evaluation work, for previous study has shown that it is difficult to vulcanize these materials reproducibly.

Copolymers of 1,1,2-trifluorobutadiene with 1,1-dihydroperfluorobutyl acrylate (FBA) have been prepared. They have good tensile strength and solvent resistance but poor resistance to ozone and heat.

Traces of copolymerized acrylic acid have been found to be important for optimum cured properties in poly-FBA. Polymers containing about 0.15% give polyamine vulcanizates which have initial and oven-aged strength superior to that of polymers containing lesser or greater amounts.

Several advances have been made in the compounding of poly-FBA. It has been found that the super-abrasion furnace black, Philblack E, gives outstanding initial strength, but the aging qualities are inferior to those obtained with Philblack O. Compression set increases markedly with decreasing particle size of the furnace black. A surface-treated fine silica, Valron (duPont) has shown promise.

Of a large number of materials evaluated as high temperature stabilizers, Permalux gives the best retention of tensile strength at 350°F. in air. Another promising additive is Sulfasan R which improves initial tensile strength and retention of tensile strength on air aging, and likewise improves crush resistance. However, it tends to increase compression set and to decrease elongation upon aging and therefore its use must be carefully controlled. It appears to be equally effective in poly-γ-(perfluoromethoxy)-1,1-dihydroperfluoropropyl acrylate (poly-FMFPA). A number of other thioamines are also effective.

A further study of plasticizers for poly-FBA has disclosed one non-fluorinated material (butyl carbitol formal) which is effective, but only polymeric materials resist extraction by solvents. Marked plasticization can be accomplished with silicone polymers, but swelling is excessive. Blends of Teflon and poly-FBA appear promising in strength and solvent resistance, but poor in uniformity and high temperature properties.

The most important advance made during the contract year has been the development of a method for the production of an alkoxyalkyl acrylate, 3-(ω-hydroperfluoroethoxy)-1,1-dihydroperfluoropropyl acrylate (H-FEFPA), which is closely related and nearly equivalent in properties to the previously developed poly-FEFPA and poly-FMFPA. H-FEFPA-FEFPA combinations should be substantially less expensive than FMFPA or FEFPA alone. Poly-H-FEFPA has the solvent and heat resistance of poly-FBA but is 25-30°C. better in low temperature properties.

I. FLUORINATED DIENES

1. Perfluorobutadiene - Vinyl 1,1-dihydroperfluorobutyl ether copolymers

Several preparations of copolymers of perfluorobutadiene (FB) with vinyl 1,1-dihydroperfluorobutyl ether (VFBE) have been carried out. The following emulsion recipe was used:

Water	180 parts
Monomers	100
Aerosol OT	3
Borax	0.5
TDDM	0.4
Sodium persulfate	0.2

The perfluorobutadiene was treated with solid sodium hydroxide before using. The polymerization data are given in Table I.

TABLE I

Copolymerization of Perfluorobutadiene (FB) with Vinyl 1,1-dihydroperfluorobutyl ether (VFBE)

Run #	Mol % FB Charged	Reaction Time at 50°C.(hr.)	% Yield	Inherent Viscosity (vistex)*	% F in Copolymer	Mol % FB in Copolymer
1a	75	111	60	insol.	-	-
1b-4	75	71	37	0.33	62.7	42
5-8	75	79	47	.52	62.6	41
9	83	71	17	.46	62.4	39
10	83	184	42	.49*	63.6	50

* 0.1% solution in xylene hexafluoride

Run 1a was carried out separately. Runs 1b-4 and 5-8 were carried out in large ampoules and the latexes were combined before working up the polymer. The latex was coagulated by freezing, and the polymer was washed with water and dried in vacuum at 50°C.

Two small preparations (9 and 10) were made from 5:1 FB:VFBE charges. The products are much softer than the 3:1 products.

The product of Run 1a was found to require a closely controlled milling cycle. It will not mold without milling and it becomes excessively soft when milled too long. When properly milled it can be molded, and it can be vulcanized to a tensile strength of 1200 psi. when heated with carbon black for 24 hours at 400°F. Polyamines are excellent curing agents in very small amounts, but cause excessive shrinkage and poor molding. Sulfur:accelerator, oxide, or Polyac systems were ineffective.

The best stability at 400°F. in air was observed when only carbon black and no vulcanizing agents were present. Weight loss is 19% at 1000 hours, and the samples remain strong and flexible. Phenyl-β-naphthylamine is ineffective as an antioxidant.

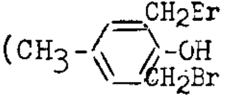
The copolymer has a T_{10} of +4°C. and a brittle point of +1°C. It has good resistance to aviation fuel, benzene, and diester lubricant, but disintegrates in acetone.

Upon exposure to 800 KV electrons, the 1:1 (molar charge ratio) FB:VFBE copolymer becomes vulcanized, reaching a maximum tensile strength of 680 psi. (with 140% elongation) at 3 megarep. Larger doses resulted in a further decrease of elongation with no increase in strength. The data are summarized in Table II, which includes data on a 3:1 FB:VFHE copolymer.

TABLE II

Effect of 800 KV Electron Radiation on Perfluorobutadiene Copolymers

	3:1 (molar charge ratio)FB:VFHE		1:1 (molar charge ratio) FB:VFBE				
Exposure, megareps.	0	52	0	12	25	52	100
Tensile strength, psi.	390	590	230	1000	730	780	Brittle
Ultimate elongation, %	160	10	410	80	40	0	
Weight loss after 100 hrs. at 350°F. in air	4.1	6.2	4.6	5.4	5.7	7.2	8.6
Weight loss after 100 hrs. at 400°F. in air.	5.7	13.4	7.5	10.2	11.4	14.0	15.6

The products of 1b-4 and 5-8 have likewise been evaluated, using information gained from 1a. The data of Table IIIa substantiate earlier results in bringing out large variations in properties between lots prepared identically. This behavior is independent of the curing system and processing. Both copolymer lots contained 41-42 mol % FBd. Lot 1 "cured" by carbon black alone shows quite good tensile properties on aging in air and in diester lubricant. Triethylene tetramine in addition to black overcures the stock but dibromomesitol () a curative for vinyl alkyl ethers, gives lot 2 remarkably good properties in aging.

Our limited volume swell data are consistently good for this type of copolymer. Gehman T_{10} values (23°F) and brittle points (18°F.) are also consistent but high. Although some samples indicate that extremely high temperature resistance is possible with this system, the lack of reproducibility of properties from batch to batch continues to hamper our progress. The data shown in Table IIIa were obtained from stocks loaded with 30 parts HAF black.

TABLE IIIa

Properties of Perfluorobutadiene (FB):Vinyl 1,1-Dihydroperfluorobutyl ether (VFBE) Copolymer Vulcanizates.

	Lot 1			Lot 2			FBA
Curing agent:	None	TETA	DBM	None	TETA	DBM	TETA
Originals							
T	430	930	320	70	840	Too weak	1100
E	325	95	355	680	260		300
PSB*	13	0	25	113	6		6
T_{10}, °F.		23			28		12
T_B		18			16		9
% Vol. Swelling							
70/30 Fuel					16		17
Benzene					22		26
Acetone					139		91
Water, 212°F					20		30
10% NaOH					3		220
Fum. HNO_3					?		75
100 hrs/350°F/air							
T	770	940	630	220	850	135	600
E	245	80	280	300	150	500	200
PSB*	6	0	3	6	0	100	3
% Wt. loss	2	4	3	2	3	3	4
100 hrs/400°F/Turbo Oil #15							
T	380	420	520	155	470	150	400
E	175	50	170	330	80	340	160
PSB*	3	6	0	6	6	13	
% Vol. Swelling	-6	0	0	0	0	+6	0

* % Set at Break

2. Perfluorobutadiene: FBA Copolymers

A series of copolymers of perfluorobutadiene with FBA were prepared. These are described in Table IIIb. A standard silicate cure was used for vulcanization. Analytical results indicate that little or no perfluorobutadiene entered the copolymers regardless of the proportion charged. No further work is planned on this system.

TABLE IIIb

Copolymers of FBA and Perfluorobutadiene

Sample #	Charge ratios Molar FBA:FB	Charge ratios Weight FBA:FB	% Yield (2 g. scale)	Analytical Results * % C	Analytical Results * % F	% Swelling Volumes** 70:30 Iso-octane: toluene	% Swelling Volumes** Benzene	% Swelling Volumes** Acetone	T_{10} (°C)
1	75:25	82.5:17.5	62	33.6	51.6	19	26	86	-2
2	50:50	61:39	40.5	33.1	52.1	17	22	85	-7.5
3	25:75	34:66	30.5	33.1	52.1	too soft,ran out of mold			

* FBA theo. 33.1% C, 52.4% F.
FB theo. 29.7% C, 70.4% F.

** 48 hrs. at room temperature.

3. 1,1,2-Trifluorobutadiene

a. Homopolymer

The preparation of resinous, extensible samples of poly-1,1,2-trifluorobutadiene were reported in WADC Technical Report 52-197, part 4. It was reported that the polymer softened at 70°C. and decomposed at about 200°C. Recent tests on a newer sample of the raw polymer, however, indicate much better thermal stability. The latest sample did not soften appreciably or lose weight upon heating in air to 200°C. The decomposition temperature was about 230°C.

b. Copolymer with Maleic Anhydride

It was reported in WADC Technical Report 52-197, part 4 (p. 27) that an attempted Diels-Alder reaction of equimolar amounts of trifluorobutadiene with maleic anhydride resulted in a small yield of a rubber containing 38% fluorine. The reaction was repeated this month, when a new sample of the monomer was received from J. D. Park (U. of Colorado).

The run was made on a 2 g. scale, using one part of 2,2-azobisisobutyronitrile as the initiator. A 70% yield of a tough, leathery rubber was produced in 15 hours at 50°. The product was soluble in acetone and dimethyl formamide. It analyzed for 34.5% fluorine and 45.0% carbon, corresponding to 63 mole % trifluorobutadiene. Another copolymer, prepared in a similar manner, was found to contain 67 mole % trifluorobutadiene. A Laue X-ray pattern of these samples stretched and tested at room temperature, disclosed a considerable degree of crystallite orientation.

It may be possible to make a more attractive rubber by reducing the crystallinity of the copolymer. Another approach may be the partial esterification of the anhydride groups with fluorinated alcohols.

c. Copolymers with Other Monomers

Copolymerizations of 1,1,2-trifluorobutadiene were carried out with vinyl acetate, styrene, vinyl n-butyl ether, vinyl 1,1-dihydroperfluorobutyl ether (VFBE), methyl methacrylate, and 1,1-dihydroperfluorobutyl acrylate (FBA). The runs were made in emulsion at 50°, using three parts Duponol ME. Products were obtained in good yields in each aase (estimated to be greater than 70%), except with VFBE. The latter run gave only about 20% conversion. The results are given in Table IV.

TABLE IV

Copolymers Based on 1,1,2-Trifluorobutadiene (TFB)

Run #	Comonomer	Reaction Time (Hrs.)	Fluorine %	Carbon %	Composition (Mole % TFB)	Nature of Product
TFB- 12	Vinyl Acetate	16	28.1	49.1	51	Short rubber; Insoluble but swells in benzene.
13	Styrene	16	21.4	72.0	41	Powdery resin. Soluble in C_6H_6
14	Vinyl n-butyl ether	16	41.8	49.2	80	Soft, short rubber, insoluble.
15	VFBE	88	53.8	37.4	ca. 60	Short rubber, insoluble
16	Methyl methacrylate	16	17.9	54.6	31	Powdery resin; soluble in C_6H_6
17	FBA	16	51.9	35.8	44	Tough, snappy rubber.

d. Copolymers with FBA

Because the copolymers of 1,1,2-trifluorobutadiene with FBA appeared attractive on the basis of the experiments described in (c), a more extensive series of preparation were carried out, using the following emulsion recipe:

Monomer	100 parts
Water	180
Duponol ME	3
Sodium persulfate	0.2
Borax	0.5

The experimental data are given in Table V. Polymerizations were carried out in ampoules. The first five were carried out on a 1 g. scale. The last two were carried out with total monomer charges of 8.5 g. and 24 g., respectively. The products were isolated by freezing the latex, washing the coagulum with water, and drying the polymer in vacuum. All polymers contained about the same percentage fluorine (TFB, 52.8%; FBA, 52.4%).

Also in Table V are shown the swelling and T_{10} values for vulcanized samples of the products. The 50:50 (molar charge) copolymer was vulcanized with amine, sulfur, and silicate cures containing 35 parts carbon black. Gehman T_{10} values for the three cured samples were as follows:

Amine cured:	-16°C.
Sulfur cured:	-16°C.
Silicate cured:	-20°C.

The sulfur cured sample appeared only slightly cured and flowed on the Instron tensile testing machine. The amine-cured sample broke at 500% elongation and 1750 psi. A set of 9% was observed.

Percent swelling volumes of the amine cured sample were measured in the following solvents:

70:30 Iso-octane:toluene	24-28	48 hrs. at rm. temp.
Benzene	54-69	"
Acetone	173-372	"
Ethyl alcohol	9-13.5	"
10% NaOH	2	"
H_2O	97-107	70 hrs. at 212°F.
Penola Turbo Oil	25-30.5	100 hrs. at 350°F.

After 100 hrs. air aging at 350°F. the amine cured sample had lost 21% of its weight and had become brittle. When subjected to 0.2 - 0.3 g. per hr. of ozone, a stressed sample of the amine cured polymer started to crack almost immediately. After standing overnight in conc. nitric acid the amine cured polymer had lost all its strength.

TABLE V

Copolymers of FBA and 1,1,2-Trifluorobutadiene

Sample #	Charge Ratios Molar FBA:TFB	Charge Ratios Weight FBA:TFB	Length of Reaction at 50°C.	% Yield	Analytical Results %C	Analytical Results Mol. ratio FBA:TFB	Analytical Results Wt. ratio FBA:TFB	% Swelling Volumes *70:30-Iso-octane: toluene	% Swelling Volumes *Ben-zene	% Swelling Volumes *Ace-tone	% Swelling Volumes **Penola Turbo Oil	T_{10} °C.
1-1	50:50	70:30	15 min.	38.5	38.3	33:67	54:46	35	81	567	-	-20
2-1	100:0	100:0	35 min.	52	33.5	-	-	21.5	31	-	1	-10
2-2	75:25	88:12	2 hrs.	83	33.8	87:13	94:6	17	24	-	2	-10.5
2-3	50:50	70:30	2 hrs.	100	*** 35.6	60:40	78:22	21	36.5	-	11	-15
2-4	25:75	44:56	35 min.	60	41.3	14:86	27:73	45	137	-	76	-22.5
3-1	50:50	70:30	40 min.	62	39.1	27:73	47:53	24-28	54-69	173-372	25-30	**** -19.5
	67:33	82:18	45 min.	60	35.9	57:43	75:25	-	-	-	-	-

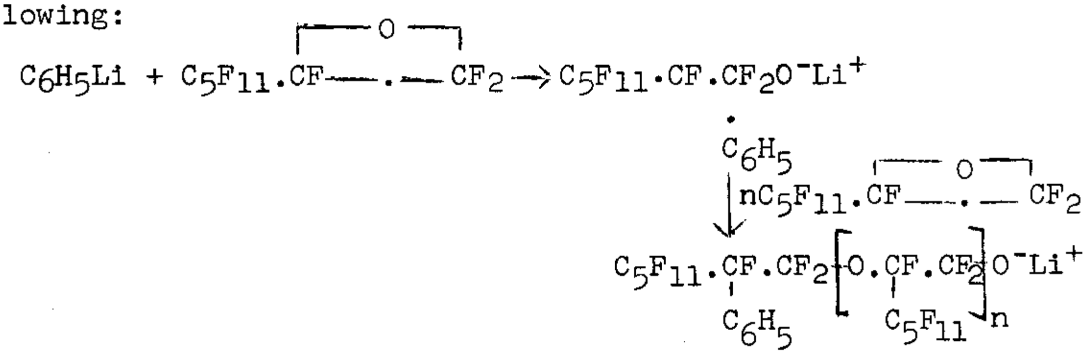
* 48 hrs. at room temperature
** 100 hrs. at 350°F.
*** Theoretical: 36.5%C. for 50:50 copolymer
**** Silicate cure. With amine cure -16°C.

The product containing 43 mol % TFB (last line of Table V) was given a more complete evaluation. This polymer had an intrinsic viscosity (by "Vistex" in 2:1 acetone:methyl perfluorobutyrate) of 0.77. As with the others, no adequate cure of this polymer was obtained with sulfur recipes, but good strength and rubbery qualities were achieved in the polyamine recipe. Properties of the polyamine vulcanizate are listed in Table VI. Low temperature flexibility of the copolymer is only slightly improved over poly-FBA, and swelling in solvents is generally higher. One notable exception is good resistance of the copolymer to alkali. The most important observation is that the -CF=CH double bond is highly vulnerable to oxidation, as evidenced by cracking of the rubber in ozone and by rapid embrittlement at high temperatures, both in air and in Turbo Oil. The results do not seem to hold much promise for trifluorobutadiene copolymers as oil resistant rubbers useful at high temperatures.

II. Anionic Polymerizations

1. 1,2-Perfluoroheptylene Oxide

An attempt was made to polymerize anionically this fluorinated epoxide using phenyllithium as the initiator. The desired reaction is the following:



$$C_6H_5Li + C_5F_{11}\cdot\overset{\overbrace{\quad O \quad}}{CF\text{—}\cdot\text{—}CF_2} \rightarrow C_5F_{11}\cdot\underset{\underset{C_6H_5}{\cdot}}{CF}\cdot CF_2O^-Li^+$$

$$\xrightarrow{nC_5F_{11}\cdot\overset{\overbrace{\quad O \quad}}{CF\text{—}\cdot\text{—}CF_2}} C_5F_{11}\cdot\underset{C_6H_5}{CF}\cdot CF_2\left[O\cdot\underset{C_5F_{11}}{CF}\cdot CF_2\right]_n O^-Li^+$$

TABLE VI

Properties of Amine-Cured FBA:Trifluorobutadiene (43 mole %) Copolymer

ORIGINAL PROPERTIES	
Tensile strength, psi.	1330
Ultimate elongation, %	260
Resilience, Bashore	8
Hardness, Shore A-2	60
Compression set (70 hrs. at 212°F.),%, post-cured 24 hrs. at 300°F.	37
Ozone resistance	very poor
Gehman T_{10}, °F.	+13
Brittle point, °F.	+3
Swelling, %, 48 hrs. in 70:30	
isooctane:toluene at 77°F.	25
benzene at 77°F.	43
acetone at 77°F.	180
10% NaOH at 77°F.	4
90% HNO_3 at 77°F.	disintegrates
water at 212°F.	30

PROPERTIES AFTER AGING	Wt. Loss %	Tens. Str. psi.	Ult. Elong. %
410 hrs. at 212°F. in air	1.7	1130	140
50 hrs. at 300°F. in air	2.8	680	130
50 hrs. at 350°F. in air	8.1	600	10
100 hrs. at 350°F. in air	-	brittle	
50 hrs. at 400°F. in Penola Turbo Oil #15	-	460	40
100 hrs. at 400°F. in Penola Turbo Oil #15	-	brittle	

The termination reaction would be expected to consist of an electron transfer from the oxygen ion to a fluorine atom. The substance would then be stabilized by the expulsion of a fluoride ion. T. F. McGrath and R. Levine[1] have reported that phenyllithium reacts with lithium

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[1] Paper presented at A.C.S. meeting in Kansas City (1954)

trifluoroacetate at 65°C. to yield 74% trifluoroacetophenone; whereas a complex mixture of products, containing a considerable quantity of lithium fluoride, was obtained at room temperature. Thus, it was thought best to carry out the present reaction at a very low temperature.

Phenyllithium was prepared in the conventional manner[2]. 0.7 g. (0.1 gram atom) of lithium shavings was added to 50 ml. of anhydrous ether in a 3-neck, 100 ml. flask. A purified nitrogen stream was run through the apparatus continuously. The flask was fitted with a mercury-sealed stirrer, a dropping funnel, a dry ice condenser with a calcium chloride drying tube, and the gas inlet tube. A solution of 8.0 g. (0.051 mole) of bromo-benzene in 25 ml. of ether was added dropwise to the flask while stirring. The phenyllithium solution was then cooled to -70°C. Five g. of the epoxide was added dropwise to the solution. A vigorous reaction started, and the addition rate had to be slowed considerably in order to permit better temperature control. Stirring was continued for one hour following the addition. The excess catalyst was destroyed by the addition of methanol. No polymeric product was obtained. A benzene-soluble compound (probably diphenyl) formed by the reaction of phenyllithium with bromobenzene was separated from the products. In addition, a large quantity of lithium fluoride was found.

An attempt to produce cationic polymerization fared no better. An attempt to polymerize this material with a BF_3.ethyl ether complex

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[2] Gilman and Blatt Organic Syntheses - Coll. Vol. 11, p. 517 (1941)

catalyst (0.5 and 2.0 part) failed to yield any high boiling material.

2. Other Anionic Polymerizations

The attempt has been made to polymerize several fluorinated monomers using typical anionic initiators. Acrylonitrile (control), butadiene (control); perfluoroacrylonitrile, perfluorobutadiene (already described, see WADC Technical Report 52-197, part 4, p. 24), vinyl 1,1-dihydroperfluorobutyl ether, $C_2F_5CF{=}CH_2$, and perfluorobutyraldehyde were studied. The results are given in Table VII.

Because of the failure to realize any promising polymers, the present study on anionic polymerization is to be discontinued. It should be borne in mind that the study was not intended to be exhaustive (either with respect to initiators or to fluorinated monomers) and therefore does not rule out all approaches. The anionic initiators usually show extraordinary specificity. For example, neither allyl sodium, sodium isopropoxide, nor sodium chloride can polymerize butadiene to any extent. A combination of all three (the Alfin catalyst) is necessary for the preparation of high molecular weight polybutadiene. Phenyl magnesium bromide, phenyl lithium and the Alfin catalyst were used in the present study mainly because these catalysts could be prepared and handled easily.

There was evidence that the desired initiation steps occurred in a number of the runs tried (e.g. perfluorobutadiene, FAN, 1,2-FHO and perfluorobutyraldehyde). Unfortunately, side reactions prevented the

TABLE VII

Attempted Anionic Polymerizations

Monomer	Initiator (Approx.parts)	Reaction Conditions	Results
FBA	3 PhLi	96 hrs. at 30°	No polymerization. No LiF formed.
Acrylonitrile	5 PhLi	1 hr. at -78°	Polyacrylonitrile formed in about 20% yield
Butadiene	5 PhLi	16 hrs. at 50°	Less than 5% of a soft rubber was formed. A water-insoluble unknown Li salt was also formed.
Butadiene	5 Alfin	1 hr. at 30°	About 90% of a tough resinous rubber was formed.
FAN	10 Alfin	1 hr. at -78°	About a 10% yield of an acetone-soluble tar was formed. Product is similar to that reported for reaction with PhMgBr (June).
FAN	10 PhLi	1 hr. at -78°	Same as above
VFBE	5 Alfin	18 hrs. at 50°	No reaction
VFBE	5 PhLi	18 hrs. at 50°	No reaction
$C_2F_5CF{:}CH_2$	5 Alfin	18 hrs. at 50°	No polymerization
$C_2F_5CF{:}CH_2$	5 PhLi	18 hrs. at 50°	A trace of an acetone-soluble tarry product was formed.
Perfluoro-butyraldehyde	5 PhLi	1 hr. at -78°	A colorless glass polymer was produced in high yield. Upon standing overnight in the unopened ampoule, the polymer had almost completely decomposed. A residue representing a 2% yield remained.

realization of high yields, or attractive polymers, in the first three cases, while the inherent instability of the polyaldehyde appears to preclude any preparation of a useful polymer in the latter case.

III. Fluorine-Containing Acrylates

1. Copolymer of FBA and Acrylamide

Two FBA:acrylamide copolymers were made by treating 1 g. FBA latex with concentrated aqueous ammonia at 50°C. The resulting products contained 11.8 mol % (3.6 wt.%) and 8 mol % (2.5 wt.%) acrylamide. Their vulcanization is discussed in Section IV, (p. 50).

2. Poly-γ-(perfluoromethoxy)-1,1-dihydroperfluoropropyl Acrylate (FMFPA)

A 187 g. quantity of poly-FMFPA has been prepared in emulsion, using Aerosol OT as emulsifier. Its vulcanization is discussed in Sec. IV (p. 56).

3. 1,1-Dihydroperfluorohexoxyethyl Acrylate (FHEA)

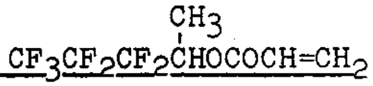
FHEA ($C_5F_{11}CH_2OCH_2CH_2OCOCH=CH_2$) is a higher homolog of FBEA ($C_3F_7CH_2OCH_2CH_2OCOCH=CH_2$), which was prepared and evaluated some years ago. (See WADC Technical Report 52-197, part 3, p. 78, for a summary of properties of poly-FBEA). It was hoped that the higher fluorine content and longer side-chain might improve the low temperature and swelling characteristics. The polymer was prepared in Duponol ME emulsion and vulcanized with a standard silicate cure. Results were as follows:

Conversion	95%
$\langle \eta \rangle$ (Vistex)	0.74
T_{10}	-21.5°C.
T_g	-52°C.
Volume swell in 30% aromatic fuel	11%
Volume swell in benzene	15%

Since the inherent viscosity of the polymer was quite low, attempts were made to increase it by washing the monomer, using other emulsifiers, lowering the catalyst concentration, and lowering the temperature of polymerization. (All of these methods have been successful in increasing the inherent viscosity of FBA.) Results of these experiments are reported in Table VIII. It was not possible to prepare polymers of higher viscosity in this way. However, it is probable that the molecular weight of the product prepared with Duponol ME is quite high.

Eighteen grams of poly-FHEA were then prepared in Duponol ME emulsion at 40°C. using 0.05 parts catalyst. Polymerization reached a conversion of 96%. The polymer had an inherent viscosity of 0.60. The attempt to vulcanize it in the polyamine recipe was unsuccessful. No satisfactory cure resulted. It is not known whether this is because amide formation did not occur or because the polyamine was used up in some side reaction. The data for the "vulcanized" product are given in Sec. IV (p. 53).

4. 1-Methyl-1-Hydroperfluorobutyl Acrylate,



$$CF_3CF_2CF_2\overset{CH_3}{\overset{|}{C}}HOCOCH=CH_2$$

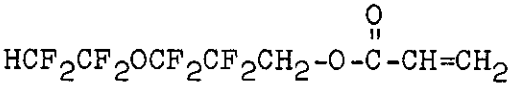
Five grams of this monomer was polymerized to complete conversion in Duponol ME emulsion. The polymer had an inherent viscosity of 1.03 in 2:1 acetone:methyl perfluorobutyrate. The latex was coagulated by freezing, giving a polymer somewhat similar to poly-FBA, but somewhat tougher and more leathery. The properties of its vulcanizate are discussed in Sec. IV (p. 56).

TABLE VIII

1,1-Dihydroperfluorohexoxyethyl Acrylate

Sample #	Monomer Washed	Emulsifier	Parts emulsifier	Parts $K_2S_2O_8$ catalyst	Temperature of polymerization, °C.	$\langle\eta\rangle$ (vistex)
1-1	yes	Duponol ME	3	0.25	50	0.74
2-1	no	"	3	0.25	50	0.68
2-2	no	Aerosol OT	3	0.25	50	0.53
2-3	no	F126 (ammonium perfluoro-caprylate)	6	0.25	50	0.45
3-1A	no	Duponol ME	3	0.25	50	0.49
3-2A	no	"	3	0.10	50	0.48
3-3A	no	"	3	0.05	50	0.48
3-1B	no	"	3	0.25	35	0.51
3-2B	no	"	3	0.10	35	0.56
3-3B	no	"	3	0.05	35	0.54
4-1	yes	"	3	0.05	40	0.60

5. 3(ω-Hydroperfluoroethoxy)-1,1-dihydroperfluoropropyl Acrylate (H-FEFPA)



A new perfluoroalkoxy acrylate, $HCF_2CF_2OCF_2CF_2CH_2\text{-}O\text{-}\overset{\underset{\|}{O}}{C}\text{-}CH{=}CH_2$ has been prepared. The new monomer differs from FEFPA (previously reported) only in having a terminal hydrogen atom. For economic reasons and probably for best balance of properties as well, H-FEFPA and FEFPA will be used together either as copolymers or as a mixture of polymers. The ratio in which the two components will be used has not yet been established. It is expected that the H-FEFPA-FEFPA system will be substantially less expensive than FMFPA or FEFPA alone and may make possible the practical utilization of the perfluoroalkoxyalkyl acrylate polymers.

The monomer (H-FEFPA) was polymerized in emulsion using the standard Duponol-persulfate recipe. A 98% yield was obtained after 3.75 hrs. at 50°C. The vistex viscosity of the polymer in 2:1 acetone:MFB was 2.7. The polymer is a soft rubber, resembling the other alkoxy acrylates.

Physical properties of a silicate-cured sample are:

T_{10} = -39°C.
T_b = -48°

Volume Swell: Acetone, 48 hr., 25° = 450%
Benzene " " = 27
70:30 Iso-octane:
Toluene, " " = 5
Iso-octane " " = 3
Water, 70 hr., 100°C. = 330

The swelling in acetone is higher than for other alkoxyalkyl acrylates, but the swelling in hydrocarbons is about the same and the low temperature behavior is certainly at least as good as that of poly-FMFPA and poly-FEFPA. Corresponding data on poly-H-FEFPA are reported in Sec. IV (p. 57). Its copolymers with FEFPA are being prepared and their properties will be described in a later report.

IV. Vulcanization and Physical Testing

1. Quality Control of Poly-FBA Preparation

In the previous Quarterly Report (No. 22, August 15 - November 15, 1954, p. 9) it was mentioned that FBA monomer prepared using Sulfan (sulfur trioxide) rather than trifluoroacetic anhydride catalyst in the final esterification step gives polymer which shows retarded cure in the standard polyamine cure. An increase in triethylene tetramine is necessary to achieve a normal curing rate, but initial strength remains somewhat below normal.

It has now been found that the monomer prepared using the Sulfan process is actually exceptionally pure. It contains only 0.02-0.08% acrylic acid (the principal contaminant) rather than 0.1-0.5%, as with the monomer prepared using trifluoroacetic anhydride. It appears that the presence of the larger proportion of copolymerized acrylic acid accounts for the superior performance of the present standard polymer, using the polyamine cure.

In order to determine the effect of copolymerized traces of acrylic acid on the vulcanization rate and properties of poly-FBA, two independent determinations were made on three series of polymers made from Sulfan-processed monomers to which 0.0-0.8 weight per cent of acrylic acid were added. Since the initial acid content of the monomers was not accurately known in all cases, no correction was applied. The actual amount of acid which entered the polymer was also unknown. All cures were carried out in the standard polyamine recipe, and a summary of results is presented in Table IX and in Figures 1, 2, and 3.

It is apparent that best initial and oven-aged strength is developed when about 0.15% of acrylic acid are added to the monomer, but data after Turbo Oil aging are scattered. Curing rate, typified by elongation and hardness data, increases sharply with increasing acid content; again, 0.15% acrylic acid gives good values of about 320% and 60, respectively. The acrylic acid content in this range has no appreciable effect on low temperature flexibility or on swelling in solvents, but resistance to boiling water improves strikingly as more acrylic acid is added. This is an unexpected result for which no explanation can be offered. Minimum compression set occurs at about 0.15% acrylic acid, again indicating the best state of cure for this composition.

The results of these experiments explain many of our past observations, such as the generally better quality of pilot plant batches over laboratory polymers, the relationship between induction period in polymerization and polymer quality, and performance variations from lot to lot. The data will provide a basis for better future quality control of poly-FBA manufacture.

TABLE IX

Effect of Copolymerized Acrylic Acid on Cure and Properties of Poly-FBA

Wt. % of Acrylic Acid to Sulfan-processed Monomer	PROPERTIES OF STANDARD POLYAMINE VULCANIZATE								
					%, Swelling, 48 hrs. at 77°F. in				
	Shore Hardness	Compression set,% (post-cured)	Gehman T_{10} °F.	T_B °F.	70:30 Iso-octane: toluene	benzene	acetone	ethyl acetate	% Swelling in water, 70 hrs. at 212°F.
0.0	47	25	18	5	13	16	63	91	60
0.048	49	24	18	3	16	23	69	95	52
0.096	51	22	18	7	16	26	79	86	48
0.14	60	17	18	5	14	21	68	90	41
0.195	65	21	16	7	14	24	63	82	38
0.3	68	24	14	7	13	21	82	95	21
0.8	80	37	12	5	13	19	73	82	6

FIG. 1. PROPERTIES OF POLY-FBA MADE BY SULFAN PROCESS

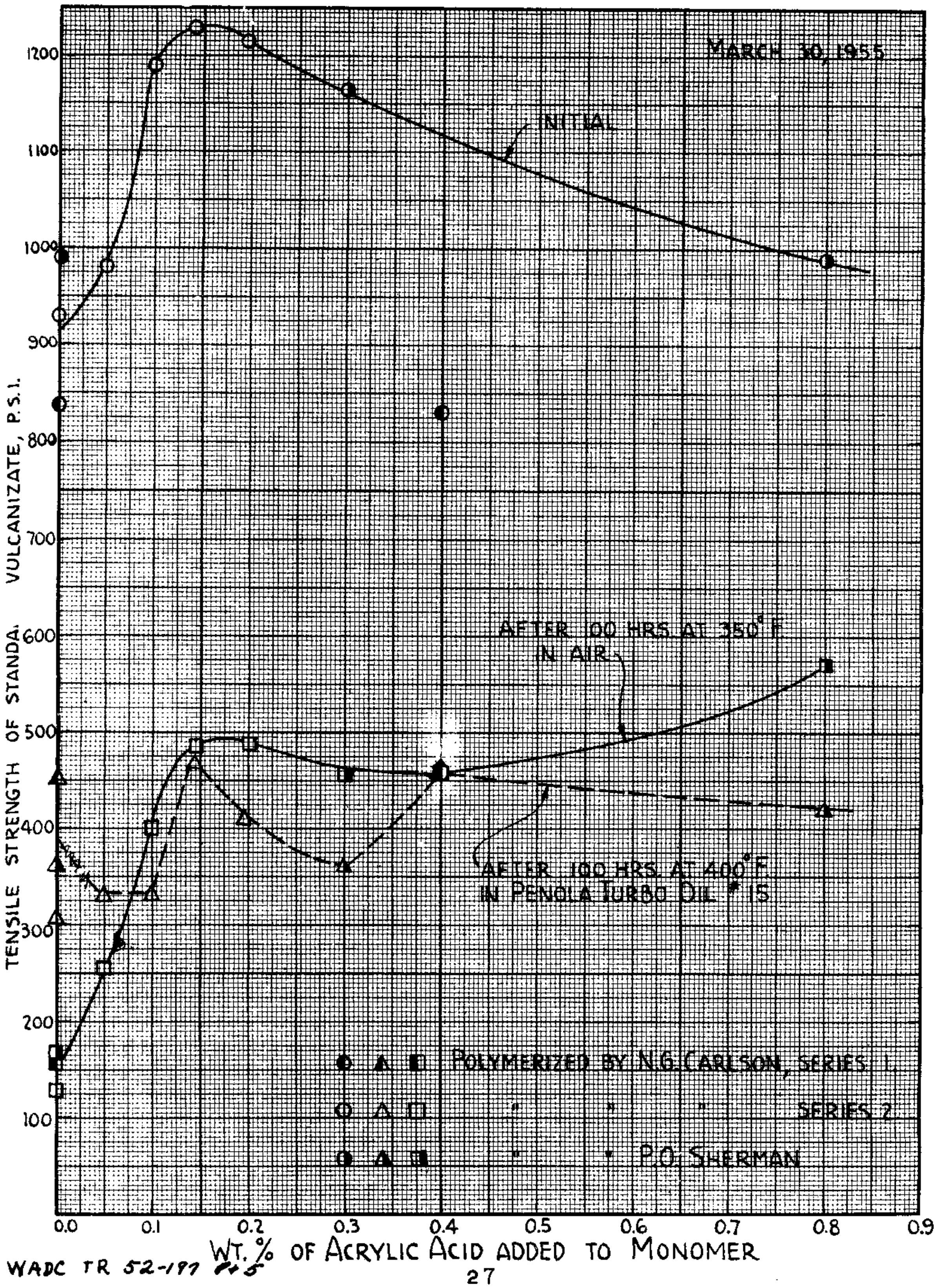
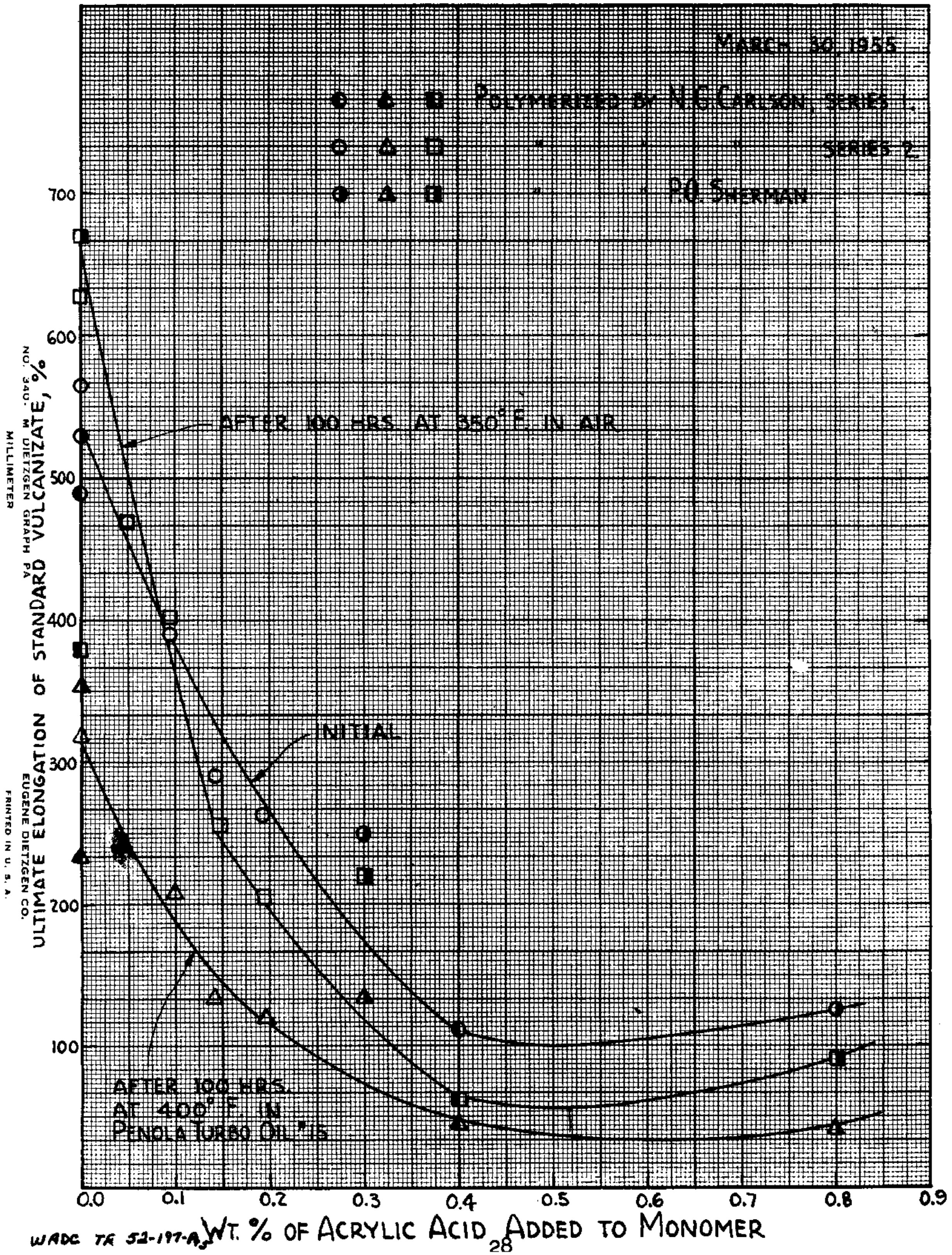


FIG. 2. PROPERTIES OF POLY-FBA MADE BY SULFAN PROCESS



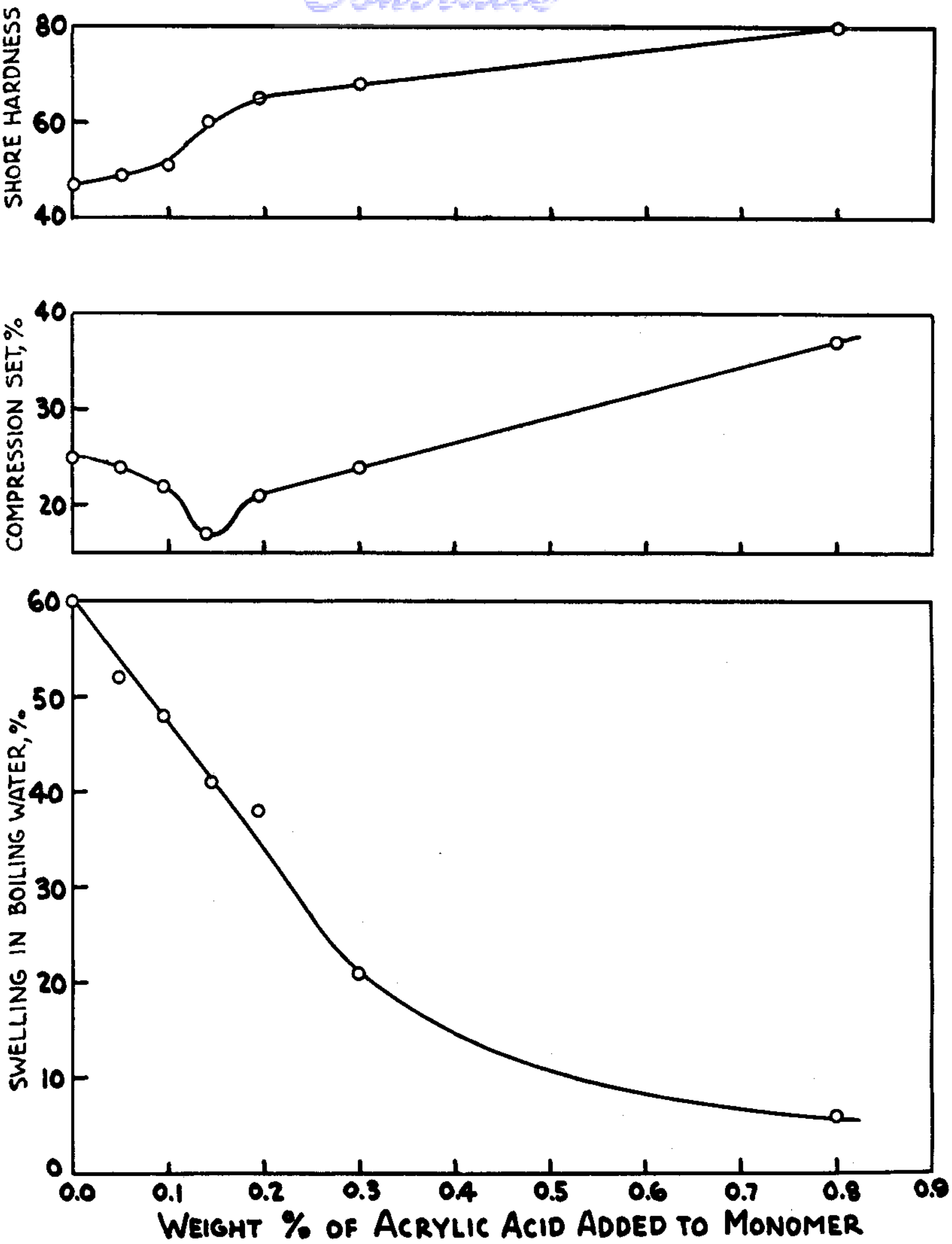


Figure 3. Properties of Standard Vulcanizate

As described in previous reports, four methods of coagulating poly-FBA latex have been studied:

(1) Low temperature alum method
(2) Room temperature alum method
(3) "Creaming" with alum (similar to U.S. Patent # 2,562,191)
(4) Block freezing

Neutralization of the latex above pH 6 is required before coagulation. The first two methods were dropped from consideration because of poor processing and high free acid content of the resulting gum rubber (above 0.02 meq. H^+ per gram). Residual acid interferes with the alkaline curing systems for poly-FBA. The "creaming" method is much more suitable for scale-up and gives a polymer acceptably low in free acid, but high in gel and poorly soluble. More recent work has shown that solubility can be greatly improved by brief milling, and tests performed at the Materials Laboratory indicated that high gel does not interfere with extrudability.

Nevertheless, the block freezing process was found to give the highest quality polymer most consistently, and is being used in current pilot plant production. This method requires excessive handling and its cost is very high, making it entirely unsuitable for larger scale manufacture. Therefore, two additional methods are being investigated:

(5) continuous film freezing
(6) continuous hot air drying

Both processes reduce or entirely eliminate washing of the polymer, thus effecting a great reduction in handling cost. Since they do not use a source of anions, the polymer has very low free acid content. The level of other impurities is relatively high (0.6 to 1.0% ash), but thus far it appears that polymer quality is not affected. The solubility characteristics have been variable, but the presence of some gel is no longer considered to be highly objectionable. More experimental work will be necessary before these processes can be considered for use in production.

2. Reinforcing Agents for poly-FBA

A study of carbon black reinforcement of poly-FBA has been carried out and the effects of varying the fast extrusion furnace black (Philblack A) content are shown in Table X. Excellent reinforcement and optimum strength retention after oil aging were obtained with only 20 parts of the black. As expected, hardness and compression set increased with increased loading.

Evaluation of several other reinforcing pigments is summarized in Table X. The super-abrasion furnace black, Philblack E, gives outstanding initial strength when used at low loading, but the aging qualities of the compounds are poor. Though this black is alkaline, it was found advantageous to use more amine with it. Other furnace blacks are generally inferior to Philblack E, in line with their larger particle size. Good reinforcement can be obtained with channel black if the TETA content is increased to compensate for its acidity. The fine-particle silica, Aerosil, is equivalent to carbon black in rein-

TABLE X

Compounding Study of Poly-FBA:Evaluation of Reinforcing Agents

Poly-FBA 100
Sulfur 1

Cure: 30 min. at 310°F.

REINFORCING AGENT	PHILBLACK A(FEF)			PHILBLACK E(SAF)			FURNEX(SRF)			SPEERON #9 (EPC)		AEROSIL			HI-SIL C	
Amounts (parts)	20	30	40	20	30	40	20	30	40	30	40	20	30	40	20	30
Triethylene tetramine (parts)	1.25	1.25	1.25	1.5	1.5	1.5	1.25	1.25	1.25	1.5	1.5	1.5	1.5	1.5	2.0	2.0
ORIGINAL PROPERTIES																
Tensile strength, p.s.i.	1040	1130	1070	1450	1180	1200	910	930	960	1020	1140	1220	1210	920	820	1770
Ultimate elongation, %	440	350	270	460	410	330	520	360	320	470	340	380	360	150	120	130
Bashore resilience, %	5	6	6	5	6	9	4	5	5	6	7	9	10	12	13	15
Shore A-2 hardness, as molded	45	56	63	50	64	81	43	53	55	51	64	56	63	79	68	78
Shore A-2 hardness, post-cured 24 hrs. at 300°F.	49	61	70	58	74	91	46	60	63	60	76	65	74	90	80	93
Compression set (70 hrs.at 212°F.) as molded	52	49	50	53	67	77	53	52	50	55	77	64	70	81	75	85
Compression set (70 hrs.at 212°F.) post-cured 24 hrs.at 300°F.	15	18	21	25	40	54	18	18	16	27	36	43	53	66	50	62
PROPERTIES AFTER 100 HRS.AT 350°F. IN AIR																
Weight Loss, %	4.0	4.1	4.0	4.9	5.2	5.4	3.9	4.2	4.1	5.4	5.7	6.6	6.8	7.9	14.2	12.8
Shore A-2 hardness	56	64	74	62	78	94	51	63	64	60	78	68	73	92	81	92
Tensile strength, p.s.i.	380	360	310	180	180	470	490	470	460)	very	300	440	350	530	500	560
Ultimate Elongation, %	360	290	250	300	100	20	360	220	220)	low	20	200	70	10	20	10
PROPERTIES AFTER 100 HRS.AT 400°F. IN PENOLA TURBO OIL 15																
Shore A-2	55	63	74	60	73	84	60	68	63	59	79	63	72	90	85	92
Tensile Strength, p.s.i.	590	680	930	700	840	830	580	730	670	520	690	580	550	620	660	910
Ultimate elongation, %	160	130	130	140	150	100	160	90	110	190	90	110	110	30	25	20

forcing power but imparts no outstanding properties. The two inorganic pigments are also acidic and require an adjustment in curative addition.

Compression set measurements are also shown in Table X. The set increases markedly with decreasing particle size of furnace black, particularly at high loadings. Furnex (SRF), the largest in particle size and poorest in reinforcing power of the carbon blacks tested, gives the best compression set and crush resistance. Both silica pigments cause a very high set.

Attempts were made to prepare compounds with higher hardness and improved crush resistance. High loadings of thermal black or combinations of thermal and furnace blacks were tried. Though tensile strengths were generally low, it was encouraging to find that compression sets of less than 15% could be achieved even with 100 parts of black. The stocks prepared thus far are still too soft and have poor crush resistance.

We are now using the standard A.S.T.M. test for measuring the compression set of poly-FBA. The values obtained are lower (favorable) than in the micro-test previously used. The standard TETA formula gives sets of 12-18% after oven post-cure.

Interesting results have been obtained with duPont Valron as reinforcing agent. This material is described as "a finely divided surface-esterified amorphous silica", formerly called duPont Fine Silica, and differs from other reinforcing silicas in being especially hydrophobic, said to arise from alkoxy groups on the surface of the particles.

Three recipes utilizing Valron in poly-FBA are shown in Table XI for comparison with our standard Philblack recipe. The A and B formulations, in spite of their high hardness, show improved resilience, decreased volume swelling and better Gehman T_{10} values than black-loaded stock. Their deficiencies lie in poor compression set, short elongations on aging, and high hardness. It should be noted that brittle points do not show the same improvement as T_{10} values.

Whatever may be the reasons, it is clear that "surface-esterification" has rendered these particles very organophilic, so that the network formed is strong enough to restrict normal elongation and recovery. WADC reports covering Hycar 4021 apparently support this type of behavior. Blends of carbon black and minor amounts of Valron are planned to improve the strength of poly-FBA during heat aging.

3 Antioxidants and Stabilizers for Poly-FBA

Of 33 materials evaluated as possible high temperature stabilizers for poly-FBA, only four were effective in recent tests: (1) Neozone D (phenyl-β-naphthylamine); (2) Agerite Resin D (polymerized trimethyl dihydroquinoline); (3) Permalux (di-o-tolylguanidine salt of dicatechol borate); (4) Sulfasan R (4,4'-dithiodimorpholine). Agerite has received a thorough evaluation previously, and was judged to be unsuitable for various reasons. Permalux gives good protection during oven aging. A poly-FBA sample containing 2 parts of Permalux retained a tensile strength of 540 psi at 65% elongation after 265 hrs. at 350°F. in air, whereas the control lost all of its rubbery properties.

TABLE XI

Initial Evaluation of Valron in Poly-FBA

Recipe:

	A	B	C	D
Poly-FBA	100	100	100	100
Valron	30	30	30	
Philblack O	-	-	-	35
Sulfur	1	1	0.5	1
TETA	1.25	1.25	0.5	1
Neozone D	1	-	-	-

cure: 30'/310°F.

Original Properties

	A	B	C	D
Tensile, psi.	1020	975	660	1250
Elongation, %	225*	210*	860*	260
F_{100}, psi.	640	650	160	320
Break set, %	50	37	133	6
Hardness, A	86	90	67	54
Resilience, %	25	23	13	6
Gehman T_{10}, °F.	1	-2	11	12
ASTM T_B, °F.	2	8	18	9
Compression set, original, %	94**	94**	103	69
post-cured, %	57	56	77	23
Volume swell, %				
70/30 fuel	9	9	22	17
benzene	15	12	20	26
acetone	48	48	56	91
water, 212°F.	4	3	11	30
Turbo Oil, 350°F.	0	0	13	3

* definite yield point at F_{20}

** bleeds oily substance during test.

Aged 100 hrs./air/350°F.

	A	B	C	D
Hardness, A	94	98	94	-
Wt. Loss, %	9	9	8	5
Tensile, psi.	1355	1000	390	350
Elongation, %	10	5	0	320
Break set, %	0	0	0	20

Aged 100 hrs/Turbo Oil/400°F.

	A	B	C	D
Hardness, A	91	95	78	-
Tensile, psi.	790	900	330	860
Elongation, %	10	5	35	150
Break set, %	0	0	0	6

Another promising additive for improving the properites of poly-FBA vulcanizates is Sulfasan R (N,N'-dimorpholine disulfide). This compound is known to decompose into sulfur, morpholine, and other fragments at curing temperatures. The best dry aging properties are obtained by adding 1 to 3 parts to the standard triethylene tetramine recipe. The results of aging experiments are shown in Table XII and can be summarized as follows:

(1) Increases initial tensile strength by 200-300 psi.

(2) Improves crush resistance, but not sufficiently to pass the Air Force test.

(3) Greatly improves the retention of tensile strength during oven aging, despite somewhat increased weight loss and hardness and decreased elongation.

(4) Increases compression set, particularly when used in excess of one part.

(5) Decreases elongation and increases hardness during Turbo Oil aging without affecting tensile strength.

The protective action of Sulfasan R against oxygen degradation continues for long periods of oven aging. Samples have maintained reasonably good properties after 505 hrs. in air at 350°F. Retention of tensile strength improves with increasing Sulfasan R content, but hardening is also increased. After 505 hrs. in Turbo Oil at 400°F., samples containing Sulfasan swell more and are weaker than the control.

Sulfasan R has similar activity in poly-FMFPA; it improves initial tensile strength and aging in air at 350°F. Data are not extensive due to shortage of polymer.

TABLE XII
Effect of Sulfasan on Poly-FBA Aging

Poly-FBA 100 Philblack O 30 Cure: 30 min. at 310°F.

Sulfur	1	1	1	1	1	1	0	2	0	0
Sulfasan R	0	1	2	3	5	10	2	2	2	2
Triethylene Tetramine	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	0.75	1.0
ORIGINAL PROPERTIES						porous spongy				
Tensile strength, psi	1080	1410	1380	1390	1020		1290	1340	1100	1420
Ultimate Elongation, %	340	330	350	380	400		200	260	450	310
Shore A-2 Hardness	57	57	56	55	51		64	61	54	60
Comp.Set "B"(70 hrs.at 212°F) as molded	53	69	71	79	88		70	64	80	70
Comp.Set "B"(70 hrs. ")post cured*	18	19	28	29	41		28	32	37	35
PROPERTIES AFTER AGING IN AIR AT 350°F.										
100 Hrs. Weight Loss, %	5.6	7.4	8.7	9.8	12.2	13.2	10.8	10.5	7.9	9.1
Tensile Strength, psi	140	430	640	770	810	-	730	710	390	650
Ultimate Elongation	250	170	140	90	60	-	100	110	240	140
Shore A-2 Hardness	61	72	85	83	90	-	84	81	72	75
265 Hrs. Weight Loss, %	13.0	13.8	14.9	17.1	19.1	19.7	17.3	17.5	14.6	15.0
Tensile strength, psi.	necks	110	310	400	670	-	460	390	120	310
Ultimate Elongation, %	-	130	70	60	20	-	50	50	160	90
Shore A-2 Hardness	48	68	80	84	89	-	88	80	70	80
505 Hrs. Weight Loss, %	24.6	26.8	26.3	28.4	31.4	29.3	27.9	33.3	26.7	27.9
Tensile Strngth, psi.	220	360	360	610	790	-	590	580	350	450
Ultimate Elongation, %	30	10+	20+	10+	0+	-	0+	0+	10	10
Shore A-2 Hardness	60	76	86	92	98	-	91	84	78	87
PROPERTIES AFTER AGING IN PENOLA TURBO OIL #15 at 400°F.										
100 Hrs. Tensile Strength, psi.	730	750	810	780	740	-	550	740	760	670
Ultimate Elongation, %	150	85	65	50	50	-	25	50	115	70
Shore A-2 Hardness	62	74	79	81	81	-	84	81	78	77
265 Hrs. Tensile Strength, psi.	470	430	430	360	220	-	250	260	330	290
Ultimate Elongation, %	110	70	60	60	50	-	40	40	100	60
Shore A-2 Hardness	56	61	68	57	64	-	72	80	60	75
505 Hrs. Tensile Strength, psi.	360	150	130	120	40	-	crum- bles	80	270	100
Ultimate Elongation, %	80	30	35	30	20	-		30	60	30
Shore A-2 Hardness	47	31	38	32	0	-	0	0	30	23
Volume Change, %	+ 19	+ 22	+25	+32	+43	-	+40	+25	+43	+43

* Post Cure: 24 hrs. at 300°F.

\+ Brittle

A thorough evaluation of Permalux (di-o-tolyl guanidine salt of dicatechol borate) has been completed, but it is apparent from data in Table XIII that the optimum compound has not as yet been prepared. The accelerating activity of Permalux necessitates a decrease in curative content for best results. Permalux appears to be a better stabilizer than Sulfasan R for the first 100 hrs. in air at 350°F., but Sulfasan gives slightly better results on longer aging. Both give poly-FBA compounds with a service life of about 500 hrs. in air at 350°F., and both increase the compression set. Permalux, however, has much less detrimental effect on Turbo Oil aging. These antioxidants will be valuable compounding ingredients for certain uses, but obviously they are not universally applicable.

Since Sulfasan R improves the dry heat resistance of poly-FBA, some other rubber chemicals of this type have been tested. Tetrone A, dipentaminethylene thiuram tetrasulfide, shows some promise. N,N'-dimorpholine diselenide, the selenium analog of Sulfasan' R, obtained from Wright Field, materially improves strength retention of amine-cured poly-FBA after heat aging for 100 hrs. at 350°F. in air. The effect is very similar to that observed with Sulfasan R (morpholine disulfide). The data in Table XIV were obtained using 5 parts of the diselenide.

TABLE XIII

Compounding Study of Poly-FBA:Evaluation of Permalux

Poly-FBA 100 Philblack 0 30 Cure: 30 min. at 310°F.

Sulfur		1	1	1	1	1	1	0	0	0	1	2
Permalux		0	0	1	2	3	5	2	2	2	2	2
Triethylene tetramine		1.25	0.75	0.75	0.75	0.75	0.75	0.75	1.0	1.25	1.25	1.25
ORIGINAL PROPERTIES												
	Tensile strength, psi.	1240	430	1130	1040	1045	1020	1255	1255	1145	1200	1160
	Ultimate elongation, %	400	780	570	540	520	610	305	160	90	140	145
	Shore A-2 hardness	55	42	48	50	50	51	59	68	76	74	71
	Comp.Set "B" (70 hrs.at 212°F.), as molded	56	86	81	81	80	81	70	68	69	66	63
	Comp.Set "B" (70 hrs. at 212°F), post-cured	20	43	30	32	35	41	32	35	40	38	37
PROPERTIES AFTER AGING IN AIR AT 350°F.												
100 hrs.	Weight loss, %	5.3	5.2	4.5	4.6	4.8	4.9	5.2	6.4	8.5	6.5	6.8
	Tensile Strength, psi.	160	soft	190	355	440	485	740	820	880	865	850
	Ultimate elongation, %	330	stringy	320	300	240	225	180	110	50	70	80
	Shore A-2 hardness	60	27	50	62	68	74	62	72	84	84	81
265 hrs.	Weight loss, %	12.8	11.8	9.9	9.4	8.8	8.1	9.8	12.3	15.3	11.4	11.8
	Tensile Strength, psi.	60	60	90	120	130	180	310	480	630	560	580
	Ultimate elongation, %	40	20	35	50	50	30	155	80	40	60	60
	Shore A-2 hardness	64	0	50	71	76	79	69	80	91	89	84
505 hrs.	Weight loss, %	27.0	21.5	19.6	16.3	16.5	13.4	16.4	18.6	22.4	18.5	20.7
	Tensile strength, psi.	150	150	190	170	240	240	290	400	610	530	565
	Ultimate elongation, %	40	0	10	20	10	10	30	10	10	25	20
	Shore A-2 hardness	47	39	59	71	79	84	75	86	93	92	92
PROPERTIES AFTER AGING IN PENOLA TURBO OIL #15 at 400°F.												
100 hrs.	Volume change, %	-3	+2	-1	-3	-6	-8	0	-2	+5	-3	-2
	Tensile strength, psi.	685	400	670	695	705	665	730	845	740	615	770
	Ultimate elongation, %	130	290	210	190	190	200	90	70	40	50	60
	Shore A-2 hardness	59	42	58	49	50	57	64	75	84	79	77
265 hrs.	Volume change, %	-2	0	-1	-3	-6	-8	0	-2	+6	-4	0
	Tensile strength, psi.	540	290	425	410	480	540	520	430	620	620	540
	Ultimate elongation, %	130	290	150	130	140	140	80	40	25	40	40
	Shore A-2 hardness	64	49	62	57	55	64	63	78	84	84	81
505 hrs.	Volume change,	+2	0	0	0	-4	-5	+5	0	*22	-1	+5
	Tensile strength, psi.	335	335	330	350	400	270	260	20	190	280	335
	Ultimate elongation, %	120	230	120	110	80	100	50	20	190	10	30
	Shore A-2 hardness	62	59	66	64	62	71	70	79	81	85	85

TABLE XIV

N,N'Dimorpholine Diselenide as Stabilizer for Polyamine-cured Poly-FBA

	Tensile Strength, psi.		Ultimate Elongation, %	
	Control	With M.D.	Control	With M.D.
Original	1170	1260	260	265
After 100 hrs. at 350°F. in air	540	970	210	75
After 100 hrs. at 400° in Turbo Oil	640	590	115	40

Eight research samples of various thioamines were obtained through the courtesy of Monsanto Chemical Co. These were evaluated as possible high temperature stabilizers for poly-FBA by adding 2 parts to the polyamine curing recipe. As shown in Table XV, most of these compounds improved the tensile strength after 100 hrs. at 350°F. in air. The data are not fully representative, because the control batch had unusually low elongation. Compounds of this class, which includes Sulfasan R, appear to be universally effective.

TABLE XV

Thioamines as Stabilizers for Polyamine-Cured Poly-FBA

	After 100 hrs. at 350°F. in air			After 100 hrs. at 400°F. in Penola Turbo Oil #15	
STABILIZER	Wt.Loss %	Tens.Str. psi.	Elong. %	Tens.Str. Psi.	Elong. %
None - Control	4.9	490	185	610	95
4,4'-dithiodimorpholine (Sulfasan R)	6.3	620	190	790	75
dibutylamine disulfide	6.3	700	105	680	60
4,4'-tetrathiodimorpholine	6.3	720	135	710	75
2,2'-dithiodianiline	5.7	390	165	650	100
N,N'-dithiobisdiethylamine	7.8	800	90	920	55
N,N'-dithiobispiperidine	8.2	780	60	640	20
N,N'-dithiobispipecoline	7.9	740	50	815	30
N,N'-dithiobispyrrolidine	6.2	510	100	670	60
Rx 2,5-dimethylpiperazine + S_2Cl_2	7.5	810	60	810	40

4. New Curatives for Poly-FBA

Several new materials were tried as possible curatives. Dihydrazides appear to be effective but cause excessive bubbling in the mold. A reaction product of zinc salicylate and ethylene diamine gives a similar result. Melamine and Naugatuck's mixed amines (Beutene, Hepteen Base) did not cause vulcanization. Carbide and Carbon's new polyamines (Polyamine H Special, Polyamine T) proved to be excellent curatives, and properties of the vulcanizates will be determined.

A series of Monsanto N,N'-dithioamines were evaluated for curing activity. Previous data had shown these materials to accelerate the TETA cure. N,N'-dithiobispipecoline continues to act this way with only small amounts of TETA. Only the reaction product of 2,5-dimethyl piperazine and S_2Cl_2 cured well alone. These materials might be useful to shorten the curing cycle for poly-FBA.

5. Plasticizers for Poly-FBA

A number of substances have been tested as plasticizers for poly-FBA, including silicone rubbers, silicone oils, acrylate polymers, polyethylene, and a polyether compound, butyl carbitol formal: $CH_3(CH_2)_3OCH_2CH_2OCH_2CH_2OCH_2OCH_2CH_2OCH_2CH_2O(CH_2)_3CH_3$, obtained from Thiokol Corp. and designated TP90B. The last of these is the only non-fluorinated liquid found so far which is an effective plasticizer for poly-FBA. A brittle point of -26°C. and a Gehman T_{10} of -20°C were found for a composition containing 15 parts of TP90B. Unfortunately, it is extracted by solvents and is nearly completely evaporated after 100 hrs. at 300°F.

Table XVI shows the swelling of poly-FBA blends in several solvents.

TABLE XVI

Swelling of Poly-FBA Blends

	% Volume Swell				
Solvent Temperature, °C.	70:30 iso-octane: toluene 25	acetone 25	benzene 25	water 100	dioctyl sebacate (48 hrs.) 188
Composition					
20 parts polybutylacrylate	71	162	112	257	50
20 " Silastic X3867	73	81	61	103	8
36 " DYLT polyethylene	23	45	27	53	5
15 " Silicone Oil	94			115	
15 " TP90B	6				
Poly-FBA	17	91	26	30	3

Some additional data on blends containing large proportions of Dow-Corning 410 silicone polymer and Teflon are shown in Table XVII.

TABLE XVII

% Volume Swell after 48 Hours Immersion of Poly-FBA Blends

Medium:	70% isooctane 30% toluene	acetone	10% NaOH	Water
Temperature, °C:	25	25	25	100
Composition:				
Poly-FBA control	21	82	135	38
50 FBA/50 DC 410	122	41	0	28
66 FBA/33 Teflon	9	28	17	14
DC 410	196	25	0	13

Teflon, incorporated by coagulating mixed latexes, reduces swelling of the poly-FBA substantially; silicone blends swell prohibitively in the hydrocarbon solvent, but show reduced swelling in the other solvents.

Stress-strain data, Gehman stiffness, brittle temperature, swelling and aging results on several blends of poly-FBA with DC-410 silicone polymer have been obtained.

The curing recipe was as follows:

	Parts
polymer blend	100
coated Hi-Sil	40 (includes 8.3% LM-3 silicone oil)
sulfur	1.0
triethylene tetramine	1.25
Captax	0.5
methyl tuads	3.0

Cure: 25 min. at 310°F.

Because the cures (polyamine) used were probably not optimum, only the volume swell and low temperature properties are reported here. These are summarized in graphical form in Figs. 4 and 5. Compositions containing 30% or less of the silicone polymer appear promising.

6. Teflon:Poly-FBA Blends

A series of experiments with thin films in open aluminum dishes were performed to find optimum cure and fusion conditions for several compositions prepared by coprecipitation of poly-FBA latex and Teflon dispersion. Results indicated limited interaction of the two polymeric species, since little fusion took place at temperatures much below the normal fusion temperature of Teflon (∼ 700°F.)

POLY-FBA-DC410 BLENDS

3-10-55

RECIPE

POLYMERS	100 PARTS	
COATED HI-SIL	40	-INCLUDES 8.3% LM-3 SILICONE OIL
SULFUR	1.0	
TRIETHYLENE TETRAMINE	1.25	
CAPTAX	0.5	
METHYL TUADS	3.0	

CURE: 25'/310° F.

DC 410 IS DOW CORNING SULFUR-CURABLE SILICONE GUM RUBBER.

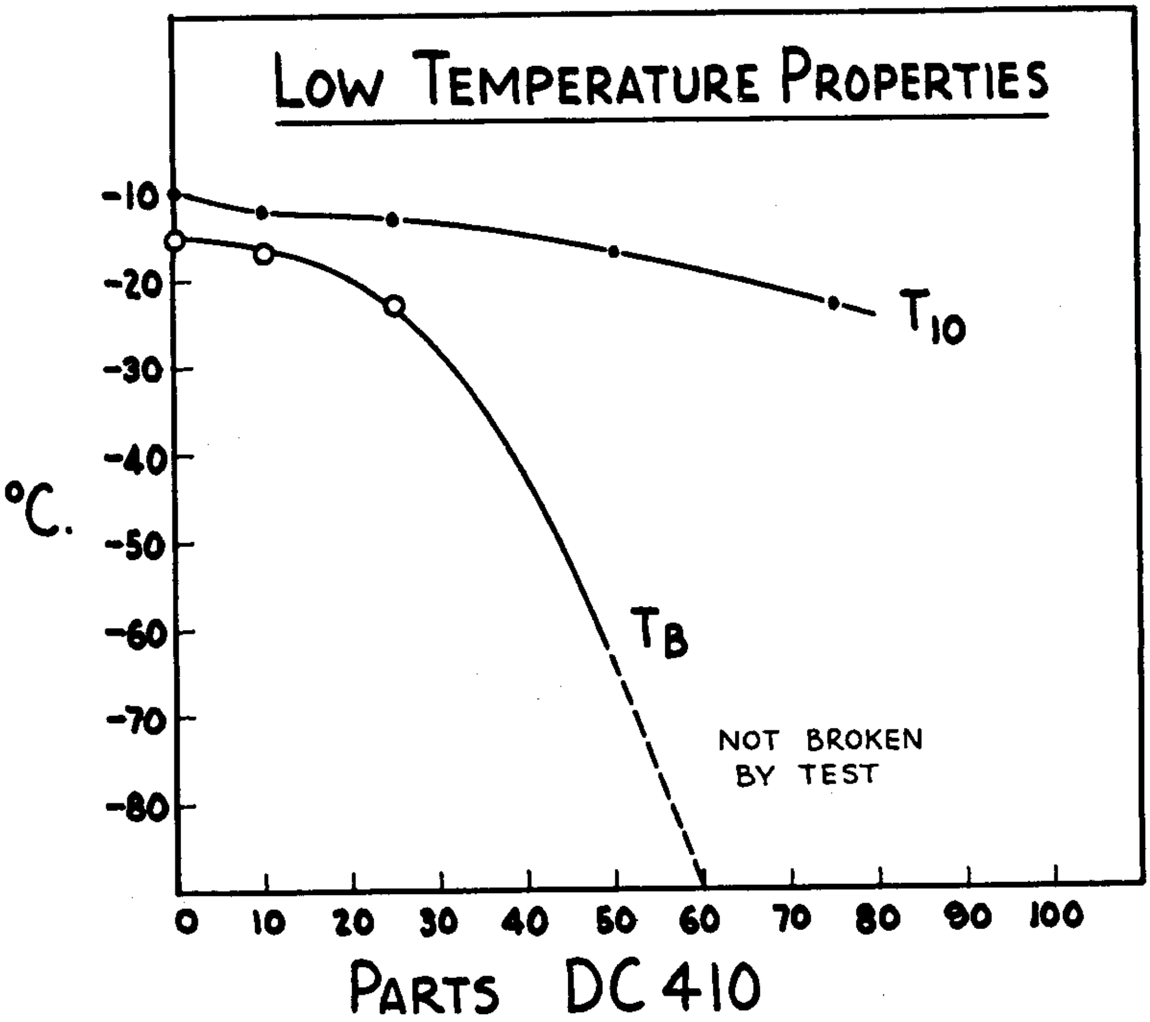


FIGURE 4

3-10-55

VOLUME SWELL OF FBA-DC410 BLENDS

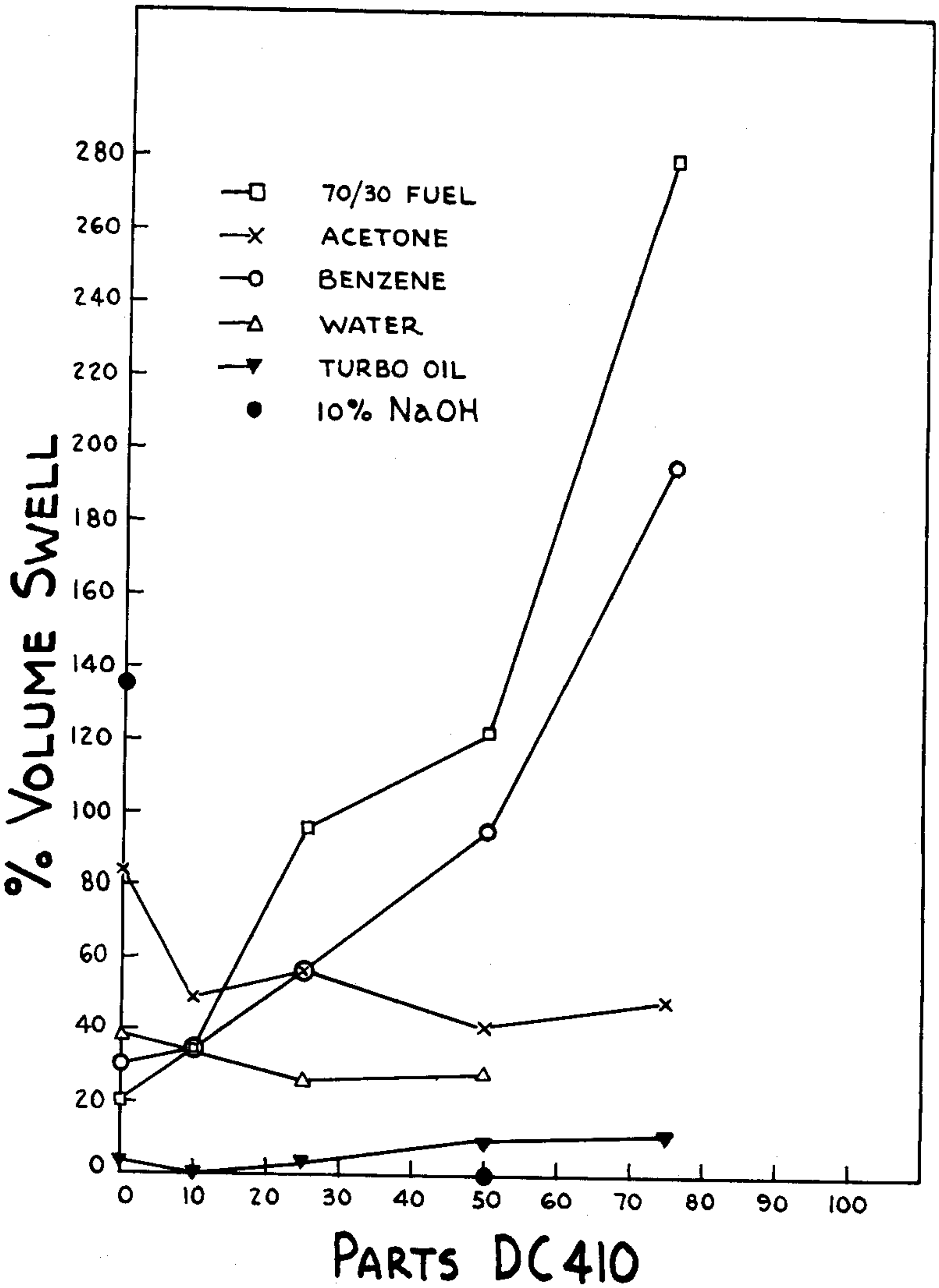


FIGURE 5

At this temperature poly-FBA gum degrades rapidly to a discolored melt. Blends of 23 and 66 wt. % Teflon with no curative fuse to give firm stocks without cold flow. With 10 parts TETA/100 parts blend, cured reinforced samples are obtained in less than a minute at 650°F. for a 13 mil film. Results are summarized in Table XVIII.

TABLE XVIII

Heat Treatments of Teflon/Poly-FBA Blends

Wt % Teflon	Min./°F.	Tensile, psi.	Elongation, %
26	3/700	85	300
26	7/700	160	60
26	2/650	65	160
33[a]	0.5/650	450	120
33[a]	1.5/650	270	1080
33[a]	none	110	>1000
66	3/700	1260	370
66	7/700	1400	360
66	2/650	1100	300
66	2/600	870	320
66	3/550	145	>800
66	3/500	105	>800

[a] Ten parts TETA/100 parts solids added to latex.

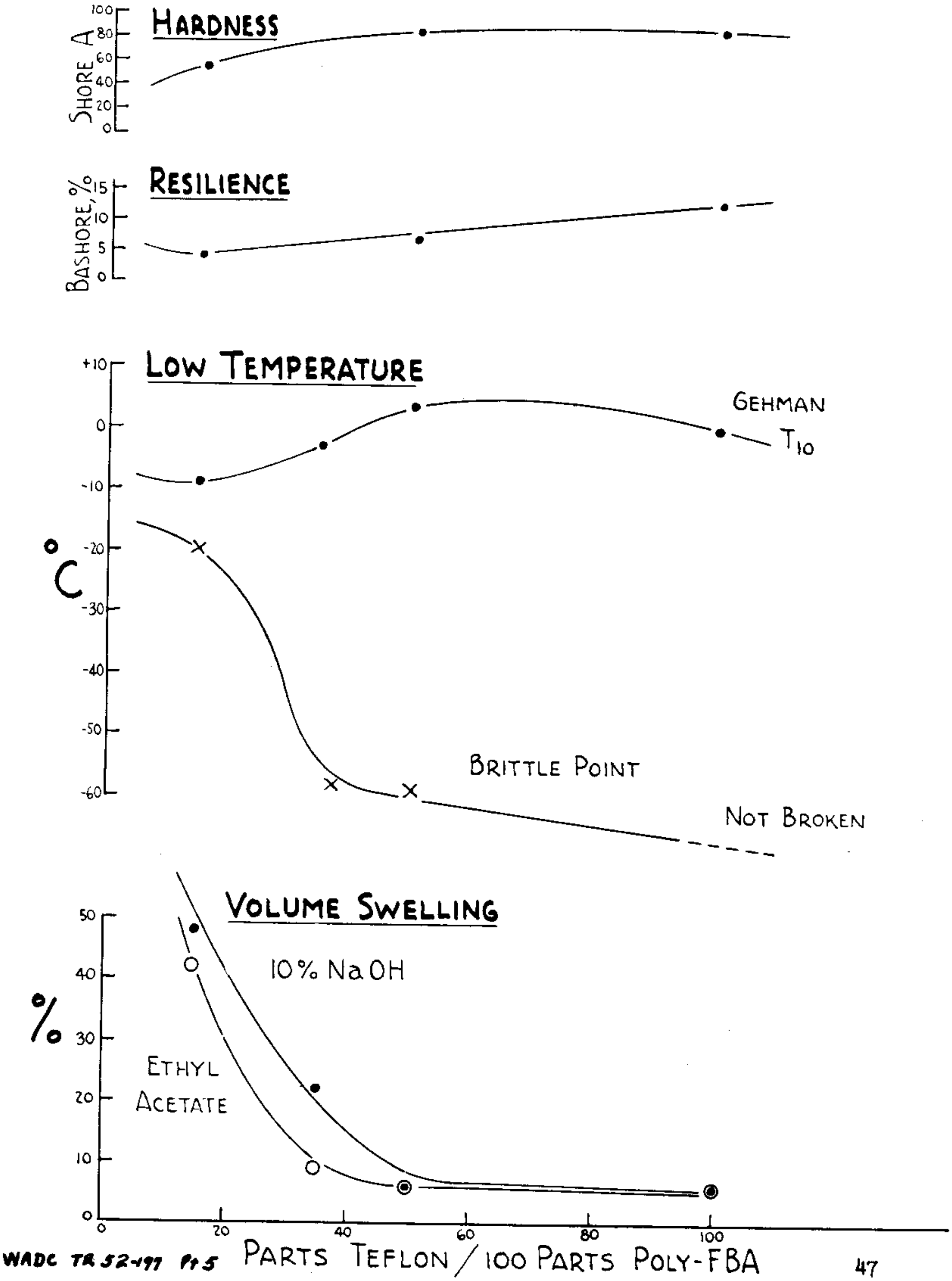
Further data were then obtained for a series of blends prepared using a polyamine curing recipe:

	Parts
Polymer blend	100
Philblack	0
TETA	0.5
Phenothiazine	0.5

Cure: 30 or 60 min., 310°F.

Results are shown in Figure 6.

FIG 6 TEFLON - POLY-FBA BLENDS



Very short cures at 650°F. were tried with several compositions but were fairly successful only for the (highest) 66% Teflon sample. All samples molded as irregular laminates whenever milled prior to molding. Apparently the Teflon particles are matted together during milling, orienting in the mill direction to form layers. Fig. 6 shows a peculiar variation of low temperature stiffening with composition, probably due to poorer knitting of layers as Teflon content increases. The lower brittle points reflect toughness rather than flexibility but may also be misleading due to laminar flexure.

Attempts have been made to devise a method for reducing this difficulty.

Method one: Carbon black and triethylene tetramine were added to the blended latices before freezing and drying. This stock can be milled without difficulty but the mouldings are undercured, apparently because most of the water-soluble amine is lost to the water phase in preparation. Mouldings by this method are seldom laminated and, therefore, gave more reproducible stress-strain curves than previous samples.

Method two: A blend of polytetrafluoroethylene latex and poly-FBA was freeze-coagulated and dried. After a waxy oil was milled out and removed, carbon black and TETA could be added readily. The mouldings were not laminated but exhibited lower strength and higher elongations than blends with duPont Teflon latex.

Method three: Blend latices and black, freeze, wash and dry. Add TETA to the dry blend on the mill and again cure 30 minutes at 310°F. as with poly-FBA.

The last method is the most satisfactory and will be followed to prepare any future blends.

7. Evaluation

The Navy H-cell for measurement of nitric acid permeability was modified by the addition of a magnetic stirrer to the water side. This change shortened the life of a 17-mil poly-FBA membrane (standard reinforced compound) from 7 hours to 20 minutes, in agreement with results reported by Wright Field. With a 50-mil poly-FBA film, about 2 hours were required for the water to reach a pH value below 2.0. Gum poly-FBA fails at about the same rate.

In contrast, a 40:60 polyethylene:Vistanex sheet obtained from Wright Field is still satisfactory after 200 hours. It was thus confirmed that poly-FBA forms a very poor barrier to penetration by fuming nitric acid.

We continue to observe that poly-FBA vulcanizates swell greatly in Turbo Oil at 400°F. when immersed for long periods in sealed containers No such swelling takes place when the oil surface is exposed to air. We have no explanation for this behavior at the present time.

8. Adhesion of Poly-FBA to Metal

Equipment for evaluating rubber-to-metal adhesion by Method A of ASTM D429 is now available. In this test, the rubber compound is vulcanized in contact with two steel plugs with smooth and parallel surfaces. The surfaces are prepared and treated in any desired manner. The assembly is pulled apart in tension and adhesion reported in pounds per sq. in. Values approaching 1000 psi. are considered to be excellent.

The standard poly-FBA compound bonded to cleaned, but untreated steel has an adhesion of about 120 psi. This can be improved somewhat by coating the metal with a compounded poly-FBA solvent cement. Several commercial adhesives were also evaluated. Best results were obtained with Goodrich's Plastilock 604, which is a ketone dispersion of Buna N rubber and a heat advancing phenolic resin. In testing the assembly, the rubber failed by tearing at 310 psi., but the bond did not rupture The method of adhesive application and the curing procedure were found to be very important. Further work will be done, but it appears that bonding of poly-FBA to metal will present no unusual problems.

9. Vulcanization of FBA Copolymers

a. FBA:acrylamide: The copolymer containing 11.8 mol % acrylamide (described in Sec. III, p. **20**) was evaluated. It crosslinks spontaneously on heating, possibly by imide formation. The best cures were obtained with triethylene tetramine and toluene diisocyanate. The properties of these vulcanizates initially and after 100 hrs. in air and Turbo Oil are summarized in Table XIXa. These results suggested that 11.8 mol % acrylamide was somewhat too high, particularly for best low temperature properties. A similar evaluation was therefore carried out on the 8 mol % copolymer, but here the aging was extended to 510 hours. An improvement over

TABLE XIX-a

Properties of FBA:Acrylamide (12 mole %) Copolymer

	Best TETA Cure	Best TDI Cure
ORIGINAL PROPERTIES		
Tensile strength, psi.	1170	680
Ultimate elongation, %	105	140
Shore A-2 hardness	69	-
Bashore resilience	10	-
Compression set "B" (70 hrs. at 212°F.)		
as molded	62	-
Post-cured 24 hrs. at 300°F.	31	-
Gehman T_{10}, °F.	+18	-
Brittle point, °F.	+14	-
Swelling after 48 hrs. in 70:30		
isooctane:toluene at 77°F.	16	-
benzene at 77°F.	19	-
acetone at 77°F.	71	-
ethyl acetate at 77°F.	66	-
10% NaOH at 77°F.	56	-
90% HNO_3 at 77°F.	29	-
water at 212°F.	11	-
PROPERTIES AFTER 100 HRS. AT 350°F. IN AIR		
Weight loss, %	7.8	8.6
Tensile strength, psi.	590	890
Ultimate elongation, %	70	50
PROPERTIES AFTER 100 HRS. AT 400°F. IN PENOLA TURBO OIL #15		
Tensile Strength, psi.	780	-
Ultimate elongation, %	65	-

poly-FBA in resistance to dry heat became apparent after this longer aging period, but aging in Turbo-Oil proved to be inferior to that of poly-FBA, so the polymer does not appear to be of real interest. The results for the 8 mol% copolymer are summarized in Table XIX-b.

TABLE XIXb

Properties of FBA:Acrylamide (8 mole %) copolymer

Curing Recipe:

FBA:acrylamide copolymer	100
Philblack O	20
Sulfur	1
TETA	0.75

30 min. at 310°F.

Tensile, psi.	980
Elongation, %	175
T_{10}	+19°F.(-7°C)
Brittle point	0°F.(-18°C)
Hardness, Shore-A-2	47
Resilience, Bashore	7

Compression set (70 hrs. at 212°F.)	
as molded	51
post-cured 24 hrs. at 300°F.)	26

Swelling	
70:30 iso-octane:toluene (48 hrs. at rm.temp.)	17
benzene " "	20
acetone " "	82
water (48 hrs. at 212°F.)	6
Turbo Oil (48 hrs. at 350°F.)	5

Aging in air at 350°F.	Tensile strength, psi.	Ultimate Elongation %	% Wt. Loss
100 hrs.	350	180	4.8
275 "	130	120	7.7
510 "	120	175	16.3
Aging in Turbo Oil at 400°F.			
100	670	100	-
275	330	85	-
510	205	75	-

b. FBA:acrylonitrile

Two high molecular weight copolymers were evaluated with the results shown in Table XX. The copolymers require a relatively low amount of curative for optimum properties. As in previous samples, acrylonitrile was found to increase compression set and swelling in oxygenated solvents, and to decrease low temperature flexibility. Aging in hot air was poor, but retention of properties in Turbo Oil was superior to the homopolymer; this is just the opposite of previous results. Milling degrades the copolymer rapidly, similarly to poly-FBA. The value of acrylonitrile as a comonomer, if any, has not been clearly established.

c. FBA:Chlorinated Monomers

Four copolymers of FBA with vinyl-β-chloroethyl ether (VClEE) and with β-chloroethyl acrylate (ClEA) also develop optimum properties with lower amine content than poly-FBA (Table XX). Remarkably, the polymers had very good initial strength despite apparently low molecular weight, particularly in case of the chloroethyl acrylate samples. Otherwise, low temperature properties were similar to those of poly-FBA, swelling in solvents was somewhat higher, and heat aging qualities were poor both in air and in oil.

10. β(1,1-Dihydroperfluorobutoxy)-ethyl Acrylate (FBEA) and β(1,1-Dihydroperfluorohexoxy)-ethyl Acrylate (FHEA).

A sample of poly-FBEA of low viscosity, $\langle\eta\rangle = 0.83$, was vulcanized in polyamine recipes. Handling and molding properties were very poor,

TABLE XX

EVALUATION OF FBA COPOLYMERS

COMONOMER	An	An	VClEE	VClEE	ClEA	ClEA
Mole percent of comonomer	10	19	7.5	15	11	20
Inherent viscosity (vistex)	3.76	3.56	1.57	1.39	0.59	0.36
Parts of TETA used	0.76	0.50	0.75	0.75	0.75	0.75
ORIGINAL PROPERTIES						
Tensile strength, psi.	1080	1120	1170	1150	1250	1290
Ultimate elongation, %	290	270	330	330	210	210
Set at break, %	6	6	13	19	0	6
Bashore resilience, %	8	9	9	10	10	10
Shore A-2 hardness	62	71	61	62	65	67
Compression set+, as molded	47	56	60	65	32	37
Compression set+, post-cured*	25	38	32	32	21	23
Gehman T_{10}, °F.	33	45	27	28	19	23
Brittle point, °F.	15	26	5	12	8	11
Swelling, %, 48 hrs. in 70:30 isooctane:toluene at 77°F.	12	16	18	28	20	18
benzene at 77°F.	20	29	22	41	24	38
acetone at 77°F.	115	162	97	131	107	112
ethyl acetate at 77°F.	70	154	-	-	-	-
fuming (90%) HNO_3 at 77°F.	56	79	106	-	31	31
water at 212°F.	14	13	33	45	24	40
PROPERTIES AFTER 100 HRS. AT 350° IN AIR						
Weight loss, %	5.5	5.9	5.9	10.5(?)	4.5	4.3
Shore A-2 hardness	68	83	62	74	84	
Tensile strength, psi.	100	470	very soft	very soft	380	somewhat
Ultimate elongation, %			& stringy	& stringy	40	brittle
PROPERTIES AFTER 100 HRS. AT 400°F. IN PENOLA TURBO OIL 15						
Shore A-2 hardness	63	72	56	55	71	72
Tensile strength, psi.	840	900	610	550	260	190
Ultimate elongation, %	300	250	150	140	short	short

\+ 70 hrs. at 212°F.
* 24 hrs. at 300°F.

and 5 parts of TETA had to be added before a sample suitable for testing could be obtained. Strength was low (410 psi.) and heat stability was poor. In comparison with poly-FBA, swelling in solvents was about doubled and low temperature properties were no better (T_{10} = -8°C. = 18°F.). The polymer showed no promise.

Alcohols containing the $-CF_2OCH_2-$ ether group apparently are not split off readily by polyamines, and polyacrylates with corresponding side chains crosslink with difficulty. Poly-FHEA (See Sec. III, p. 20) was somewhat cured by 5 and 10 parts of TETA but mechanical properties were poor. Vulcanizates were prepared using Philblack O; the results are shown in Table XXI.

TABLE XXI

Properties of Poly-FHEA

Curing recipe:

Poly-FHEA	100
Philblack O	35
Sulfur	1
TETA	6.25

30 min. at 310°F.
(Very poor cure)

Swelling (48 hrs. at room temperature)

70:30 iso-octane:toluene	28
benzene	33
acetone	59
ethyl acetate	73
10% NaOH	210 (cheesy)
90% HNO_3	68
H_2O (70 hrs. at 212°F.)	170

Low temperature properties:

T_{10}	-8°C.
B.P.	-12°C.

No satisfactory cure was achieved, and the tensile properties were poor. In comparison with poly-FBA, the vulcanized polymer swelled slightly more in hydrocarbons, but less in oxygen-containing solvents, and was highly water sensitive. The T_{10} was -8°C., about the same as for poly-FBA. As pointed out in Report No. 21 (p. 24), neither poly-FHEA nor its butoxy homolog poly-FBEA, when vulcanized in the polyamine recipe, show the improvement over poly-FBA in T_{10} which is observed using the silicate curing recipe.

11. Poly-1-hydro-1-methyl Perfluorobutyl Acrylate

This polymer did not cure in polyamine recipes, and its mechanical properties could not be measured. An approximate Gehman determination gave a T_{10} of + 58°F., indicating very poor low temperature flexibility. The following swell data were obtained on the compounded stock:

Solvent	Temp. °F.	Time, Hrs.	Volume Swell,%
70:30 isooctane:toluene	77	48	33
benzene	77	48	46
acetone	77	48	51
ethyl acetate	77	48	42
10% sodium hydroxide	77	48	4
water	212	70	164
Penola Turbo Oil #15	400	100	0

12. γ-(Perfluoromethoxy)-1,1-dihydroperfluoropropyl Acrylate (FMFPA).

A preparation of poly-FMFPA has been carried out (Sec. III, p. 20). The polyamine vulcanizate was found to have lower tensile strength (780 psi.) than previous lots, despite apparently higher molecular weight ($\langle \eta \rangle = 2.97$). About 300 g. of poly-FMFPA are now on hand.

Sulfasan R appears to have the same beneficial effect in the alkoxy acrylate as in poly-FBA.

13. 3(ω-Hydroperfluoroethoxy)-1,1-dihydroperfluoropropyl acrylate (H-FEFPA).

A small quantity of the homopolymer (3.3 g.) was compounded in the polyamine recipe. The properties of the vulcanizate are given in Table XXII, with those for poly-FBA included for comparison. Low temperature flexibility is much improved over poly-FBA and is at least as good as that of poly-FEFPA and poly-FMFPA. Judging from preliminary data, mechanical properties and heat stability in air and in Turbo Oil are comparable to poly-FBA. The terminal hydrogen increases swelling in oxygenated solvents but not in hydrocarbons -- the results for the polyamine vulcanizate paralleling those for the silicate vulcanizate (p. 23). Somewhat surprisingly, the swelling in 10% sodium hydroxide is markedly less than that of poly-FBA; the effect is doubtless chemical rather than purely physical in both cases.

Copolymers of H-FEFPA and FEFPA monomers are now under study, and results obtained so far are favorable. The development of this new and more practical class of alkoxyalkyl acrylates represents the most significant advance made during the present contract year.

TABLE XXII

Properties of Poly-H-FEFPA

ORIGINAL PROPERTIES	H-FEFPA	FBA
Tensile strength, psi.	900	1100
Ultimate elongation, %	300	300
Gehman T_{10} °F.	-24	+20
Brittle point, °F.	-39	+12
Volume Change, 48 hrs. at 77°F.		
isooctane:toluene, 70:30	16	16
benzene	34	30
acetone	330	90
ethyl acetate	345	100
water (70 hrs. at 212°F.)	64	20
10% NaCH	6	100
PROPERTIES AFTER 100 HRS. AT 350°F. IN AIR		
Weight change, %	-4.8	-5
Tensile strength, psi.	250	400
Ultimate elongation, %	220	200
PROPERTIES AFTER 100 HRS. AT 400°F. IN PENOLA TURBO OIL #15		
Volume change, %	+3	0
Tensile strength, psi.	320	700
Ultimate elongation, %	140	160

APPENDIX I

Standard Polyamine Recipe

Poly-FBA	100 parts
Philblack O (HAF)	35
Sulfur	1.0
Triethylene tetramine	1.0

Cure: 30 minutes at 310°F.