

WADC TECHNICAL REPORT 52-197
Part 3

Part 3 SYNTHETIC RUBBERS FROM CARBON-FLUORINE COMPOUNDS

F. A. Bovey

Minnesota Mining and Manufacturing Company

September 1953

Materials Laboratory
Contract No. AF 33(038)-515
RDO No. 617-11

Wright Air Development Center
Air Research and Development Command
United States Air Force
Wright-Patterson Air Force Base, Ohio

FOREWORD

This report was prepared by the Minnesota Mining and Manufacturing Company, under USAF Contract No. AF 33(038)515. The contract was initiated under Research and Development Order No. 617-11, "Synthesis and Evaluation of New Polymers", and was administered under the direction of the Materials Laboratory Directorate of Research, Wright Air Development Center, with Dr. R. N. Evans and Major W. H. Ebelke acting as project engineers.

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 67% of the effort involved in the contract during this period (see Appendix C). This leaves approximately 33% of said effort as representing the actual polymerization studies and evaluation of polymers reported herein.

ABSTRACT

This report describes the preparation and properties of fluorine-containing rubbers. The object of the work is the development of elastomeric materials which are resistant to the fuels, lubricants, and hydraulic fluids used in military aircraft and which are serviceable over the widest possible temperature range.

Of the materials under development, the following appear to be of chief interest:

- A. Perfluorobutadiene Copolymers. Copolymers of perfluorobutadiene with 1,1-dihydroperfluoroalkyl vinyl ethers offer excellent high temperature resistance, low swelling in aircraft fluids, and high resistance to ozone.
- B. Fluoroacrylates. In addition to the 1,1-dihydroperfluoroalkyl acrylates, which have been described in earlier reports and which have outstanding solvent resistance but limited low temperature flexibility, newer classes of fluoroacrylates have been synthesized. Of particular interest are the γ -(perfluoroalkoxy)-1,1-dihydroperfluoropropyl acrylates, which offer solvent resistance at least equal to that of the earlier series but are flexible at temperatures 25°C. lower than the polymers

of the 1,1-dihydroperfluoroalkyl acrylate.


In the compounding and vulcanization of fluoroacrylate polymers, the most striking accomplishment has been the development of polyamine curing systems which give greatly improved resistance to aircraft fluids such as diester lubricants at temperatures as high as 350°F., better compression set and other mechanical properties, and greatly improved resistance to nitric acid and to alkali.

Fundamental studies of the copolymerization behavior of the fluoroacrylates, of their swelling in organic liquids, and of their molecular weights are presented.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:


M. E. SORTE
Colonel, USAF
Chief, Materials Laboratory
Directorate of Research

Contrails

TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION	1
SUMMARY AND CONCLUSIONS	3
I. VINYL ETHERS	13
A. β -Hydroperfluoroalkyl Vinyl Ethers	13
B. 1,1-Dihydroperfluoroalkyl Vinyl Ethers	13
II. PERFLUORO-OLEFINS	
A. Perfluorocyclohexene	19
B. Perfluoropropylene	20
III. PERFLUOROACRYLONITRILE	25
IV. PERFLUOROACRYLYL FLUORIDE	29
V. PERFLUOROBUTADIENE AND COPOLYMERS	
A. Perfluorobutadiene:Ethylene	30
B. Perfluorobutadiene:1,1-Dihydroperfluoroalkyl Ethers	38
1. Preparation	38
2. Aging at Elevated Temperatures	45
3. Pyrolysis	53
4. Use of Other Emulsion Recipes	56
5. Compounding and Vulcanization	59
C. Copolymers of Perfluorobutadiene With Hydrocarbon Vinyl Ethers	63

Contents

	<u>Page</u>
D. Copolymers of Perfluorobutadiene and 1,1-Dihydroperfluorobutyl Acrylate (FBA)	66
E. Miscellaneous Copolymerizations of Perfluorobutadiene	67
F. Homopolymer of Perfluorobutadiene	67
VI. FLUORINE-CONTAINING ACRYLATES	
A. New Monomers and Their Polymers	72
1. 1,1-Dihydroperfluoroamyl Acrylate (FAA)	73
2. 1,1,5-Trihydroperfluoroamyl Acrylate (FAH ₃ A)	73
3. 1,1,3-Trihydroperfluorobutyl Acrylate (FBH ₃ A)	74
4. β-(1,1-Dihydroperfluoroethoxy) Ethyl Acrylate (FEH ₂ EA)	74
5. β-Hydroperfluoroethoxyethyl Acrylate (FEHEA)	75
6. β-Hydroperfluoroethyl Diethylene Glycol Acrylate (FEHE ₂ A)	75
7. (1,1-Dihydroperfluorobutoxy)Ethyl Acrylate, (FBEA)	75
8. β-(Perfluorofuryl)-1,1-Dihydroperfluoroethyl Acrylate (FFEA)	76
9. γ-(Perfluoroalkoxy)-1,1-Dihydroperfluoropropyl Acrylates, R _f OCF ₂ CF ₂ CH ₂ OCOCH:CH ₂	77
B. Copolymers of Fluoroprene (FP) with FHA and γ-(Perfluoroethoxy)-1,1-Dihydroperfluoropropyl Acrylate (FEFPA)	93
C. Poly-1,1-Dihydroperfluorobutyl Acrylate (Poly-FBA)	95

Contents

1.	Preparation of Poly-FBA	95
2.	Copolymerization of FBA and FHA	
	a. Copolymers with Chloroprene	98
	b. Copolymerization of FBA with Non-Fluorinated Alkoxyalkyl Acrylates	100
	c. Copolymers of FBA with Vinyl Triethoxysilane	103
	d. Copolymers of FHA and Acrylic Acid	105
3.	Fundamental Copolymerization Studies	106
4.	Compounding and Vulcanization of Poly-FBA and Poly-FHA	
	a. Vulcanization in Silicate and Oxide Recipes:Effect of State of Cure	112
	b. Vulcanization With Polyamine Recipes	118
5.	Heat Stability of Poly-FBA and Poly-FHA	122
6.	Copolymers of FBA and FHA with Butadiene	131
7.	Plasticizer Studied	145
8.	Compression Set and Relaxation	152
9.	Fundamental Swelling Studies With Poly-FBA	166
10.	Determination of Molecular Weight of Poly-FBA by Light Scattering	181
VII.	TESTING METHODS AND EQUIPMENT	187
	APPENDIX	189

LIST OF ILLUSTRATIONS

	<u>Page</u>
FIGURE 1 STIFFENING OF PERFLUOROBUTADIENE (FB): ETHYLENE POLYMERS AT 200°C	37
FIGURE 2 RATE OF WEIGHT LOSS OF 1:1 FB:VFHE COPOLYMER AT 200°C	47
FIGURE 3 RATE OF STIFFENING OF PERFLUOROBUTA- DIENE COPOLYMERS AT 200°C.	48
FIGURE 4 RATE OF WEIGHT LOSS OF 3:1 FB:VFHE COPOLYMER AT 200°C.	49
FIGURE 5 RATE OF WEIGHT LOSS AT 200°C. OF POLY- MERS STABILIZED WITH ONE PART PBNA	52
FIGURE 6 GEHMAN T ₁₀ VS. PERCENT SWELLING IN 70:30 ISO-OCTANE TOLUENE	87
FIGURE 7 COPOLYMERIZATION CURVES FOR FBA WITH BUTADIENE, METHYL METHACRYLATE, AND STYRENE	110
FIGURE 8 EFFECT OF CURE ON TENSILE AND MODULUS OF POLY-FBA VULCANIZATES	114
FIGURE 9 EFFECT OF CURE ON COMPRESSION SET AND SHORE HARDNESS OF POLY-FBA VULCANIZATES	115
FIGURE 10 EFFECT OF CURE ON SWELLING OF POLY- FBA VULCANIZATES	116
FIGURE 11 HEAT AGING OF POLY-FBA	124
FIGURE 12 PERCENT SWELLING IN 70:30 ISO-OCTANE: TOLUENE OF COPOLYMERS OF FBA, FHA, AND ACRYLONITRILE WITH BUTADIENE	142
FIGURE 13 PERCENT SWELLING IN BENZENE VS. GEHMAN T ₁₀ OF COPOLYMERS OF FBA, FHA, AND ACRYLONITRILE WITH BUTADIENE	143
FIGURE 14 STRESS DECAY IN COMPRESSION AT 25°C.	160
FIGURE 15 STRESS DECAY IN COMPRESSION AT 100°C.	161

Contracts

LIST OF ILLUSTRATIONS (Continued)

	<u>Page</u>
FIGURE 16 COMPRESSION STRESS RELAXATION OF POLY-FBA (OXIDE) CURE	164
FIGURE 17 COMPRESSION STRESS RELAXATION OF POLYACRYLATE RUBBERS	165
FIGURE 18 PERCENT SWELLING OF SILICATE CURED FBA VS. SOLUBILITY PARAMETER	167
FIGURE 19 PERCENT SWELLING OF SILICATE CURED POLY-FBA VS. SOLUBILITY PARAMETER OF MIXED SOLVENTS	170
FIGURE 20 PERCENT SWELLING OF SILICATE CURED FHA VS. SOLUBILITY PARAMETER OF SOLVENT	174
FIGURE 21 PERCENT SWELLING OF SILICATE CURED FBA:BD COPOLYMERS VS. SOLUBILITY PARAMETER	175
FIGURE 22 PERCENT SWELLING OF FHA AND FBA:BD. VS. SOLUBILITY PARAMETER OF MIXED SOLVENTS	180
FIGURE 23 INTRINSIC VISCOSITY VS. MOLECULAR WEIGHT FOR FRACTIONATED FBA	182

LIST OF TABLES

TABLE I COPOLYMERIZATION OF C_3F_6 WITH STANDARD MONOMERS	21
TABLE II COPOLYMERIZATION OF C_3F_6 AND ISOBUTYLENE	23
TABLE III PERFLUOROACRYLONITRILE - VINYL ETHER COPOLYMERS	27
TABLE IV SWELLING OF PERFLUOROBUTADIENE: ETHYLENE COPOLYMER	33

Contrails

LIST OF TABLES (Continued)

		<u>Page</u>
TABLE V	AGING OF PERFLUOROBUTADIENE: ETHYLENE (FB-C ₂ H ₄) AND OTHER POLYMERS AT 200°C.	35
TABLE VI	BULK PREPARATION OF PERFLUORO- BUTADIENE:1,1-DIHYDROPERFLUORO- ALKYL VINYL ETHER COPOLYMERS	40
TABLE VII	EMULSION COPOLYMERIZATION OF PER- FLUOROBUTADIENE AND VINYL 1,1-DI- HYDROPERFLUOROBUTYL ETHER (VFBE) AT 50°C.	42
TABLE VIII	POLYMERIZATION OF PERFLUOROBUTA- DIENE AND VFHE IN VARYING RATIOS	44
TABLE IX	REDOX RECIPES USED IN THE PREPAR-- ATION OF PERFLUOROBUTADIENE:VFHE COPOLYMERS	57
TABLE X	PROPERTIES OF PERFLUOROBUTADIENE: VFHE COPOLYMERS	61
TABLE XI	PERFLUOROBUTADIENE (FB):HYDROCAR- BON VINYL ETHERS (VE) COPOLYMERS	65
TABLE XII	PERFLUOROBUTADIENE COPOLYMERS	68
TABLE XIII	PROPERTIES OF FLUOROACRYLATE HOMOPOLYMERS	78
TABLE XIV	FLUORINATED ALKOXY-ACRYLATE: BUTADIENE POLYMERS	82
TABLE XV	PROPERTIES OF VULCANIZED FMFPA AND FEFPA HOMOPOLYMERS, COMPARED TO POLY-FBA AND POLY-FHA	88
TABLE XVI	PREPARATION OF BUTADIENE:FEFPA COPOLYMERS.	91
TABLE XVII	PROPERTIES OF BUTADIENE:FEFPA COPOLYMERS.	92

Contrails

LIST OF TABLES (Continued)

		<u>Page</u>
TABLE XVIII	COPOLYMERS OF FLUOROPRENE (FP) WITH 1,1-DIHYDROPERFLUOROHEXYL ACRYLATE (FHA) AND γ -(PERFLUOROETHOXY) 1,1-DIHYDROPERFLUOROPROPYL ACRYLATE (FEFPA)	94
TABLE XXIX	FBA:2-CHLOROBUTADIENE COPOLYMERS	99
TABLE XX	COPOLYMERS OF FBA AND ALKOXY-ALKYL ACRYLATES	102
TABLE XXI	COPOLYMERS OF FBA AND VINYL TRI-ETHOXYSILANE	104
TABLE XXII	COPOLYMERS OF 1,1-DIHYDROPERFLUOROHEXYL ACRYLATE (FHA) AND ACRYLIC ACID (AcAc)	107
TABLE XXIII	COPOLYMERIZATION OF FBA WITH BUTADIENE	108
TABLE XXIV	COPOLYMERIZATION OF FBA WITH METHYL METHACRYLATE	108
TABLE XXV	COPOLYMERIZATION OF FBA WITH STYRENE.	109
TABLE XXVI	REACTIVITY RATIOS AND $Q - e$ VALUES FOR FBA	109
TABLE XXVII	PROPERTIES OF POLYAMINE VULCANIZATES OF POLY-FBA	120
TABLE XXVIII	EFFECT OF BLACK LOADING IN RECIPE A, 45 MIN. CURE	121
TABLE XXIX	PYROLYSIS OF POLY-FBA - PO 227, LOT 3	127
TABLE XXX	PYROLYSIS OF POLY-FBA VULCANIZATE - PO 227, LOT 3	127
TABLE XXXI	AIR OVEN AGING	128
TABLE XXXII	RETENTION OF PROPERTIES AT 350°F.	129

Contrails

LIST OF TABLES (Continued)

		<u>Page</u>
TABLE XXXIII	FBA AND FHA COPOLYMERS OF BUTADIENE	133
TABLE XXXIV	SWELLING OF VULCANIZATES IN "SKYDROL"	135
TABLE XXXV	EVALUATION OF FBA AND FHA COPOLYMERS OF BUTADIENE	136
TABLE XXXVI	COMPARISON OF T_{10} 's AND BRITTLE POINTS OF FHA: BUTADIENE AND FBA: BUTADIENE VULCANIZATES IN VARIOUS CURING SYSTEMS	139
TABLE XXXVII	TENSILE PROPERTIES OF FHA: BUTADIENE AND FBA: BUTADIENE VULCANIZATES	140
TABLE XXXVIII	EFFECT OF SOLVENT UPON PHYSICAL PROPERTIES	146
TABLE XXXIX	PLASTICIZERS FOR POLY-FBA	148
TABLE XL	COMPOUNDING OF POLY-FBA WITH THIOKOL LP-3	151
TABLE XLI	COMPRESSION SET OF OIL RESISTANT COMPOUNDS	154
TABLE XLII	COMPRESSION SET AT -20°C	156
TABLE XLIII	STRESS RELAXATION DATA, FIGS. 14 & 15	159
TABLE XLIV	SWELLING OF POLY-FBA	168
TABLE XLV	SWELLING OF POLY-FBA IN MIXED SOLVENTS	171
TABLE XLVI	SWELLING OF SILICATE CURED POLY-FBA AND POLY-FBA:BD SWOLLEN 160 HRS.	176
TABLE XLVII	MOLECULAR WEIGHTS AND INTRINSIC VISCOSITIES OF POLY-FBA FRACTIONS	184

Contrails

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 yet 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 and third annual reports has shown 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 appeared to us that by proper

Contrails

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. During this fourth year of this contract, both of these hopes have been shown to be well founded. This report describes the work leading to improvements in the fluoroacrylate polymers, and also describes the preparation and properties of certain copolymers of perfluorobutadiene having unusual resistance to high temperatures.

Although the ultimate goal in low temperature flexibility has not yet been reached, a long step in this direction has been taken with the development of the fluoroalkoxy-alkyl acrylate monomers. The butadiene copolymers of two of these represent the closest approach to satisfying the Air Force's original low temperature and solvent resistance requirements of any materials so far prepared in this program. This, together with the polyamine cure, appears to have extended the useful temperature range of the fluoroacrylate polymers by nearly 100°F. The possibility of still further improvements in high temperature behavior is offered by the perfluorobutadiene copolymers which require and deserve considerable further study.

SUMMARY AND CONCLUSIONS

During this fourth year of the contract, emphasis has been placed on developing rubbers having better properties at low temperatures and particularly at high temperatures. The original aim of the program was the development of fluorine-containing synthetic rubber which would resist swelling in fuels, lubricants, and hydraulic fluids and which would have satisfactory flexibility at low temperatures, the ultimate objective being serviceability at -65°F . Since the original undertaking of this program, there has been added to this objective the somewhat more pressing one of developing a rubber useful in contact with these fluids at temperatures of 350°F . or higher. Work has continued and progress has been made along both of these lines.

Although considerable effort has been given to the preparation of new monomers during this contract year, we are beginning to center our attention more and more on certain specific polymer types. These are chiefly:

- A. Perfluorobutadiene Copolymers. These have been found to have excellent high temperature properties if properly compounded.
- B. The fluoroacrylates, both the 1,1-dihydroperfluoroalkyl

Contracts

type, which has been the subject of much investigation in the past, and the newer alkoxyalkyl types having better low temperature flexibility. Improved cures of the acrylate polymers by means of polyamine recipes have resulted in much improved high temperature properties as well.

The work of this contract year may be summarized as follows:

1. Vinyl Ethers

The β -hydroperfluoroalkyl vinyl ethers, $R_fCFHCF_2OCH:CH_2$, give plastic polymers having only limited elastic behavior and no further work with these is contemplated. The 1,1-dihydroperfluoroalkyl vinyl ethers, $R_fCH_2OCH:CH_2$, can be polymerized by both free radical and Friedel-Crafts catalysts. The butyl ether yields a rubbery polymer which, however, is not stable at high temperatures. The hexyl ether gives a semi-liquid polymer. This class of vinyl ethers is chiefly of interest as comonomers with perfluorobutadiene.

2. Perfluoro-Olefins

Perfluorocyclohexene, 1,1-dihydroperfluorobutene-1 and perfluoropropylene have been investigated. The last of these gives a liquid homopolymer of very low molecular weight when exposed to Co 60 gamma radiation.

Contrails

Its copolymerization with isobutylene has been carefully studied but the products do not appear to have interesting physical properties. The other two do not homopolymerize under ordinary conditions, but will copolymerize with vinyl acetate and certain other comonomers. None of the products appear to be of particular interest in this program.

3. Perfluoroacrylonitrile and Perfluoroacrylyl Fluoride

Perfluoroacrylonitrile and perfluoroacrylyl fluoride have been investigated. The first of these has been the subject of previous study and the subsequent investigation of further copolymer systems has not produced any products which appear to be of interest for Air Force use. Its homopolymer can be prepared by gamma irradiation, but is a granular material. Perfluoroacrylyl fluoride shows copolymerization behavior similar to that of perfluoroacrylonitrile and has so far given no products of interest.

4. Perfluorobutadiene

The copolymers of perfluorobutadiene and ethylene reported earlier have been studied further. Their preparation in emulsion has been carried out but it has been found that rubbery products cannot be obtained in

Contrails

yields much beyond 20-30%. In addition, these products, although showing considerable stability at elevated temperatures, are distinctly inferior in this respect to the copolymers with the vinyl ethers, and therefore no further study of them is contemplated.

With the 1,1-dihydroperfluorobutyl and -hexyl ethers, perfluorobutadiene copolymerizes both in bulk and in emulsion to give polymers which are rubbery even at relatively high conversions. These products when properly stabilized show weight losses of only about 8% and only slight stiffening after 500 hours at 200°C. (390°F.), and they are highly resistant to ozone. Considerable study has been given to the behavior of these materials at elevated temperatures, and it has been shown that while HF is liberated, together with other products, the chief loss in weight is probably due to the splitting out of the side-chain of the vinyl ether. Despite this, the copolymers having higher proportions of vinyl ether appear to be somewhat more stable at high temperatures. More careful study of this system, both of the preparation of the polymers and of their compounding and vulcanization, appears to be warranted.

The homopolymer of perfluorobutadiene has been

Contrails

prepared by Co 60 gamma irradiation and also by emulsion polymerization. The emulsion polymer, which was evidently higher in molecular weight, was a white resinous material which appeared to contain some material volatile at 200°C., but which did not undergo any evident degradation.

5. Fluorine-Containing Acrylates

A considerable number of fluorine-containing acrylates have been prepared during this contract year. Of these, the alkoxyalkyl acrylates are of chief interest. These have been made with the object of obtaining better low temperature flexibility without too great sacrifice in resistance to fuels and lubricants. A number of different types of these have been prepared. Some of these show no particular improvement in balance of low temperature flexibility and resistance to aircraft fluids. One type, however, has shown an outstanding improvement in this respect. These are the γ -(perfluoroalkoxy)-1,1-dihydroperfluoropropyl acrylates, $R_fO(CF_2CF_2CH_2)OCOCH:CH_2$. Four of these, the perfluoromethoxy, -ethoxy, -propoxy, and -butoxy have been prepared. Their homopolymers and copolymers with butadiene have been made and their properties studied. The homopolymers exhibit about a 25°C. improvement in low

Contrails

temperature flexibility over the corresponding 1,1-dihydroperfluoroalkyl acrylates, which have been the object of most of our previous investigations, and of which the butyl member, FBA, has been most studied. In the butadiene copolymers, a corresponding improvement over the butadiene copolymers of the earlier acrylates has been realized. As an example of the properties observed, the homopolymer of γ -(perfluoromethoxy)-1,1-dihydroperfluoropropyl acrylate, poly-FMFPA, shows a Gehman T_{10} of -32°C . (-7°C . for poly-FBA), and shows very low swelling in aircraft fluids. A butadiene copolymer of this acrylate vulcanized in a gum stock, exhibits a Gehman T_{10} of about -46°C ., with a swelling of about 60% in both 30% aromatic fuel and in benzene. This represents the closest approach to satisfying the Air Force's original requirements for solvent resistance and low temperature flexibility of any material so far developed in this program. The further study of this series of acrylates, particularly FMFPA, is being very actively pursued.

Copolymerization of the 1,1-dihydroperfluoroalkyl acrylates, chiefly 1,1-dihydroperfluorobutyl acrylate (FBA), with a number of comonomers has been carried out: fluoroprene, ethoxyethyl acrylate, methoxypropyl acrylate,

Contrails

vinyl triethoxysilane, and acrylic acid. These studies have been carried out with the objective either of obtaining products having an improved balance of low temperature flexibility and solvent resistance, or products which could be vulcanized by other methods than the silicate and oxide cures. These copolymerizations have not produced products of any particular interest.

The copolymerization of FBA has been studied from a fundamental viewpoint, and the reactivity ratios so far obtained have shown that the perfluoroalkyl group exerts a powerful electronegative effect.

Much study has been given to the effect of cure on the mechanical properties of FBA and FHA vulcanizates, using the silicate and oxide curing systems. As a result of study of a wide range of curing times, it has been concluded that the times arbitrarily chosen for single cures in our earlier work did not result in misleading conclusions.

The most striking achievement in the study of the vulcanization of the acrylate homopolymers has been the development of polyamine curing recipes which permit the preparation of vulcanizates having

Contrails

greatly improved stability at temperatures as high as 350°F. in contact with diester lubricants and other aircraft fluids, which show considerably improved compression set properties, and improved resistance to nitric acid and to alkali. This development, together with that of the γ -(perfluoroalkoxy)-1,1-dihydroperfluoropropyl acrylates, which are vulcanizable by the same means, appears to increase the useful temperature range of the fluoroacrylates by nearly 100°F.

Further study has been given to copolymers of FBA and FHA with butadiene. Careful measurements have been made of the swelling and low temperature properties of these families of copolymers, and results are presented in comparison to those with butadiene: acrylonitrile copolymers.

A study of plasticizers for poly-FBA has been carried out. A considerable number of fluorine-containing esters and polyesters of adipic, phosphoric, perfluorosuccinic and perfluoroadipic acids, as well as perfluoro ethers, amines, amides, fluorocarbons, low molecular weight poly-FBA and liquid Thiokol LP-3 have been evaluated. It has been found that those materials which serve as effective plasticizers are

Contrails

readily extracted by the aircraft fluids, whereas those which are not extracted are not effective plasticizers.

Using the Instron stress-strain relaxometer and the Hi-Po-Log stress relaxometer, both of which have been fitted for use at elevated temperatures, attention has been given to the relaxation properties of the fluoroacrylate polymers both in compression and in tension. An effort has been made to interpret the results in terms of recognized relaxation mechanisms. Such studies should assist us in the development of compounds for use in gaskets, O-rings, and other types of seals.

The swelling of poly-FBA, poly-FHA and an FBA:butadiene copolymer has been studied from a fundamental viewpoint. The Hildebrand solubility parameter has been deduced for each of these by measuring the swelling in a series of solvents of varying solubility parameter. The results indicate that poly-FBA has the relatively low parameter of 6.7 and that the poly-FHA and FBA:butadiene copolymers have values somewhat lower and somewhat higher, respectively. It has also been demonstrated that the simple

Contrails

solubility theory breaks down very badly when applied to these systems.

The molecular weight of poly-FBA has been measured by light scattering in benzotrifluoride and in methyl perfluorobutyrate. The molecular weights are surprisingly high for the intrinsic viscosities observed. The polymer as usually prepared has an intrinsic viscosity of about 1.8 and a molecular weight close to 10,000,000.

Contrails

I. VINYL ETHERS

A. β -Hydroperfluoroalkyl Vinyl Ethers

It has been shown in earlier reports that the β -hydroperfluoroalkyl vinyl ethers, $R_fCFHCF_2OCH:CH_2$, give plastic polymers having only limited elastic behavior. For this reason, no further work has been done with this class of monomers. It was found that, in contrast to the hydrocarbon vinyl ethers, these monomers do not polymerize with Friedel-Crafts catalysts, such as boron trifluoride, but polymerize readily with free radical initiators.

B. 1,1-Dihydroperfluoroalkyl Vinyl Ethers

As reported earlier, the 1,1-dihydroperfluoroalkyl vinyl ethers, $R_fCH_2OCH:CH_2$, can be polymerized by both free radical and Friedel-Crafts catalysts. Evidently, in the β -hydroperfluoroalkyl vinyl ethers the presence of fluorine next to the ether oxygen reduces its basicity to such a degree that Lewis acids do not interact appreciably with it. In the hydrocarbon vinyl ethers, the alkoxy groups are so highly electropositive, and the double-bond in consequence so negative, that radical-monomer interaction cannot occur, and free radical polymerization does not take

Contrails

place. In the 1,1-dihydroperfluoroalkyl vinyl ethers, the charge distribution is such that both free radical and ionic polymerization are possible. The free radical homopolymerization and copolymerization of vinyl 1,1-dihydroperfluorobutyl (VFBE) and -hexyl (VFHE) ethers were attempted in two emulsion recipes,

designated A and B:

	<u>Parts by Weight</u>	
	<u>A</u>	<u>B</u>
Monomer	100	100
Water	180	180
Duponol ME	3	---
Ammonium perfluoro-octanoate	---	6
Na ₂ S ₂ O ₈	1	1
Na ₂ HPO ₄	---	0.5

In both recipes the VFBE failed to homopolymerize or to copolymerize with styrene. Although the analytical results were not conclusive, it appeared that VFBE did copolymerize with 1,1-dihydroperfluorobutyl acrylate (FBA).

VFHE appears somewhat more reactive and homopolymer latexes of good yield were obtained in both recipes. The coagulated polymers were soft and evidently of low molecular weight. Again, in recipe B copolymerization with styrene was not achieved, but a charge of equal molar quantities of FBA and the VFHE polymerized to a product with a fluorine

Conrails

analysis corresponding to 28 mole % of the ether. Similarly, it was found that both the butyl and hexyl ethers could be copolymerized with acrylonitrile in emulsion, giving products analyzing for about 40 mole % of acrylonitrile in each case.

The copolymerization of fluorine-containing vinyl ethers with perfluorobutadiene is described in the following section on perfluorobutadiene.

Homopolymers of the 1,1-dihydroperfluoroalkyl vinyl ethers are best prepared by ionic catalysis. The highest molecular weight polymers obtained so far have been prepared in bulk at low temperatures, using boron trifluoride as catalyst. VFHE was polymerized in bulk and in solution, using BF_3 gas or BF_3 -diethyl ether complex. Propane, chloroform, and methyl chloride were the solvents used. Although the products prepared at -80°C . appeared to have the highest molecular weight, no rubbery products were obtained in a total of sixteen runs. There appeared to be little difference, however, between products prepared in bulk or in solution at this temperature. All of the products were

Contrails

too soft to be useable, even when the low molecular weight fraction was removed.

In contrast to VFHE, VFBE can be polymerized to a rubbery product by the action of BF_3 at -80°C . Four small ampoules were charged with one gram of VFBE and 0.003 g. BF_3 , and allowed to stand 24 hours at -80°C . The products were treated with ammonium hydroxide, washed with acetone, and dried. A total of three grams of polymer was thus obtained. It was a very soft, tacky material. Samples were heated at 200° , after the polymerization of BMA, a combination of sulfur, Altax and Toluene (essentially the same recipe as on page 34), and a combination of Lavantol Stabilizer E-6B and phenyl- β -naphthylamine. The results of measurements of weight loss with 1 part phenyl- β -naphthylamine are shown in Figure 5, and shows the typical behavior. The stability of all these samples on heating in air is extremely poor, with each sample losing more than 70% of its original weight within 100 hours. It is interesting, however, that the heat stability of the unstabilized copolymer in vacuum is a great deal better than in the presence of air, indicating that the degradation is probably

Conclusions

a free radical process, initiated by peroxides. In 332 hours at 200°C. at 8 mm. pressure, an unstabilized sample lost 25% of its initial weight. 1,1-Dihydroperfluorobutyl alcohol was identified by infrared analysis as a major constituent of the volatile degradation products. No HF was detected. The fluorine content of the degraded residue was found to decrease from 60.0% (58.9% theo.) to 55.8%; the carbon content increased from 32.3% (31.8% theo.) to 34.0%. These analytical results indicate that 25-35% of the original $C_3F_7CH_2$ -groups were split out of the polymer probably chiefly as the alcohol, leaving an unsaturated chain. If this were assumed to be the sole process occurring, 29% of the original $C_3F_7CH_2$ -groups must be split out to account for the observed weight loss. A separate sample of "stabilized" polymer, which lost 80% of its weight on heating in air, was found to have undergone a decrease in fluorine content to 30%. This would indicate the loss of 87% of the $C_3F_7CH_2$ -groups, which is in close agreement with the weight loss.

Thus, there is little doubt that the weight loss is largely due to splitting out of alcohol. Oxidation and cross-linking of the resulting

Contrails

unsaturated chain may account for the stiffening observed. Although these homopolymers do not appear to be useful at high temperatures, these results no doubt have a bearing on the behavior of their more useful copolymers with perfluorobutadiene, described in a later section.

II. PERFLUORO-OLEFINS

- A. Perfluorocyclohexene was studied, with regard to both homopolymerization and copolymerization. Likewise, 1,1-dihydroperfluorobutene-1, $\text{CH}_2=\text{CFCF}_2\text{CF}_3$ was examined using the same conditions. On heating at 50°C . with acetyl peroxide or under ultra-violet light with benzoyl peroxide, no homopolymer was obtained from either olefin. It was found that both monomers could be copolymerized in bulk with vinyl acetate. When equal molar charges were used, the perfluorocyclohexene copolymer was found by analysis to contain fluorine corresponding to 18 mole percent perfluorocyclohexene. The corresponding copolymer of vinyl acetate with 1,1-dihydroperfluorobutene-1 contained 18 % fluorine, corresponding to 16 mole percent of the butene.

The copolymerization of 1,1-dihydroperfluorobutene-1 with several fluorinated monomers was attempted in both bulk and emulsion systems. With vinyl 1,1-dihydroperfluorohexyl ether (VFHE) viscous liquid products were obtained. With perfluoroacrylonitrile, trifluorochloroethylene, and

Contrails

perfluorobutadiene, only trace amounts of polymeric products were recovered. It seems that the 1,1-dihydroperfluorobutene is similar to the completely fluorinated analog in its polymerization behavior.

- B. Perfluoropropylene has been copolymerized in bulk at 50°C. with four standard monomers for the purpose of determining its reactivity ratios. Acetyl peroxide was employed as initiator. The results of these experiments are tabulated in Table I.

It is interesting to note from the data of Table I that Run No. 7 produced a copolymer containing more than 50 mole percent C_3F_6 , indicating some addition of C_3F_6 radicals to C_3F_6 monomers. This had been observed earlier in copolymers of $n-C_4F_8-1$ with vinyl ethers. In none of the other systems, however, was more than 50 mole % of C_3F_6 found in the copolymers.

In the copolymer systems studied in this series, C_3F_6 entered the copolymer to an appreciable extent. It appears from the present data that

TABLE I
COPOLYMERIZATION OF C₃F₆ WITH STANDARD MONOMERS

Tube No.	Comonomer M ₁	M ₂ (C ₃ F ₆), Charge Ratio	Reaction Conditions	Ac ₂ O ₂ Catalyst %	Conversion %	Copolymer Analysis	Wt. % C ₃ F ₆	Mol % M ₁	Mol % C ₃ F ₆
1	Vinyl Acetate	11-89	18 hrs. @ 50°	1	17	39.4% C	51.6	62.1	37.9
2	"	50-50	6 hrs. @ 50°	1	34	47.5% C	26.1	79.3	20.7
2A	"	50-50	2 hrs. @ 50°	1	11	48.7% C	19.2	88.0	11.95
3	Isobutylene	10-90	5 hrs. @ 50°	2	1.0	42.0% C	71.0	52.5	47.5
4	"	50-50	72 hrs. @ 50°	2	7	46.0% C	64.3	59.8	40.2
5	Vinyl Chloride	10-90	3 hrs. @ 50°	1	2				
6	"	50-50	4 hrs. @ 50°	1	12	42 % Cl	26.0	87	13
7	Vinylidene "	10-90	4 hrs. @ 50°	1	3.5	27 % Cl	63.1	47	53
8	"	50-50	4 hrs. @ 50°	1	1.5	68 % Cl	7.0	95	5

Contrails

isobutylene may alternate with C_3F_6 . In future work, the systems studied here will be investigated more fully in order to obtain copolymerization curves from which the reactivity with other monomers, as yet untested, can be predicted.

A few additional copolymerizations of C_3F_6 and isobutylene were carried out. The object was to test other conditions of polymerization to determine if higher molecular weights could be obtained. Details of the polymerizations and results are shown in Table II. Yields were lower than have been obtained under more rigorous conditions. Molecular weights appeared quite low, the products varying from viscous liquids to weak, flexible materials. No further work on this copolymer system is planned.

Perfluoropropylene has been submitted to approximately 200 megaroentgens of the gamma radiation from Co 60, by arrangement with the Brookhaven National Laboratory. The results were similar to those reported in the last annual report (p. 16 et. seq.), but the yield of product was higher because of the much longer exposure. About 3.0 g.

TABLE II
COPOLYMERIZATION OF C₃F₆ AND ISOBUTYLENE

<u>Mol Ratio C₃F₆-iC₄H₈</u>	<u>Catalyst</u>	<u>Reaction Conditions</u>	<u>% Conversion</u>	<u>Mol% C₃F₆ in Polymer</u>	<u>Nature of Polymer</u>
1-1	Ac ₂ O ₂ , 1%	20 days at 50°	9	35.1	Clear, flexible
1-2	Ac ₂ O ₂ , 1%	20 days at 50°	10	34.7	Soft, tacky rubber
1-1	Bz ₂ O ₂ , 1%	20 days at 50°	11	30.9	Soft wax
1-1	*	7 days at 50°	Exploded	--	--
1-1	*	14 days at 50°**	5	9.7	White wax
1-1	Bz ₂ O ₂ , 1%	14 days at 50°**	2	--	Viscous liquid

* Standard emulsion recipe
 ** 0.05% primary dodecyl mercaptan added.

Contrails

(30% yield) of a high boiling (175-180°C.), viscous liquid was produced. The infrared curve was like that of the earlier product, showing unsaturation at 5.57 μ and 5.75 μ . The product was probably a trimer or tetramer, or a mixture of these.

- 24 -

WADC TR 52-197 Pt 3

III. PERFLUOROACRYLONITRILE

In the last annual report, some copolymerization studies with perfluoroacrylonitrile were reported. These concerned chiefly butadiene, and it was concluded that the copolymers of butadiene with perfluoroacrylonitrile do not show any advantage over butadiene:acrylonitrile copolymers in balance of solvent resistance and low temperature flexibility.

With the object of seeing whether perfluoroacrylonitrile can be copolymerized to yield rubbers for high temperature use, this monomer was copolymerized with a number of halogenated monomers using both acetyl peroxide at 50°C. and benzoyl peroxide with ultra-violet light as initiating systems. Perfluoroacrylonitrile failed to copolymerize with vinylidene fluoride and with trifluorochloroethylene by both methods. With vinyl 1,1-dihydroperfluorohexyl ether (VFHE) it copolymerized to give a soft plastic product which did not seem sufficiently elastic to be of interest. This product contained 44 mole % perfluoroacrylonitrile. With vinylidene chloride, perfluoroacrylonitrile gave a white powdery product in a yield of less than 50%. This material softened at 150-170°C. and appeared to be

Conclusions

resistant to most solvents; however, it contained only about 10 mole % perfluoroacrylonitrile.

With vinyl n-butyl ether (VNBE) and vinyl isobutyl ether (VIBE), perfluoroacrylonitrile was also copolymerized. The conditions and results of these experiments are summarized in Table III. The copolymerizations were carried out in bulk at 50°C. with either acetyl peroxide or benzoyl peroxide with ultra-violet light.

A maximum of slightly less than 50 mole % perfluoroacrylonitrile can be incorporated into the copolymers. The polymers are fairly strong and the plastic ones give clear, flexible films. They are, however, soluble in acetone and benzene so there seems to be little use in investigating the system further.

Perfluoroacrylonitrile has been copolymerized with perfluorobutadiene in bulk, using benzoyl peroxide or acetyl peroxide as catalysts. Only very low yields of a weak plastic were obtained after 18 days at 50°C. The product from an equimolar charge of monomers and 1% acetyl peroxide contained 24 mole % copolymerized perfluoroacrylonitrile.

When perfluoroacrylonitrile was exposed to 200 megareontgens of Co 60 gamma radiation at Brookhaven

TABLE III
PERFLUOROACRYLONITRILE - VINYL ETHER COPOLYMERS

<u>Tube</u>	<u>Vinyl Ether</u>	<u>Perfluoroacrylonitrile:Vinyl Ether Charge Ratio, Molar</u>	<u>Nature of Polymer</u>	<u>% Yield</u>	<u>% F</u>	<u>Mole % perfluoroacrylonitrile</u>
1	VNBE	1:1	Slightly elastic, slow recovery.	78	22.2	40
2	VIBE	1:1	Hard plastic.	86	25.6	46
3	VNBE	1:1	Like Tube 1, somewhat more rubbery.	92	23.6	43
4**	VIBE	1:1	Soft plastic.	84	--	--
5 & 6	VNBE	3:1	Elastic, slow recovery.	30-45	25.6	46
7 & 8**	VNBE	3:1	Viscous liquids.	--	--	--
9 & 10	VIBE	33:1	Hard inflexible plastic.	45-48	24.3	44
11 & 12	VNBE	3:1	Elastic, more rubbery than others.	42-48	21.8	39

* All tubes used bulk system; 11 and 12 polymerized with Ac_2O_2 ; all other tubes polymerized with Bz_2O_2 + ultraviolet light.

** Contained a trace of DDM.

Conclusions

it gave a 20% yield of an orange powder which is soluble in xylene hexafluoride, methyl perfluorobutyrate, acetone, and ethyl acetate. It softens at 90-100°C. An inherent viscosity determination in acetone gave the very low value of 0.02. The infrared spectrum showed the presence of $-C\equiv N$, a broad unsaturation band at 5.85 μ , and some acidic OH groups. Since perfluoroacrylonitrile is known to be very unstable to water, the latter two features may be due to hydrolysis products. The polymer had a nitrogen content of 13.1%, the same as the theoretical value.

From the work that has been done so far, it appears unlikely that perfluoroacrylonitrile will find use in rubbery polymers of interest for Air Force requirements. Certain copolymerization studies remain to be completed. This is chiefly a matter of fundamental interest, the purpose being to determine the reactivity and charge distribution in a monomer of this structure.

IV. PERFLUOROACRYLYL FLUORIDE

The behavior of perfluoroacrylyl fluoride, $CF_2=CFCOF$, in homopolymerization and copolymerization was investigated. This monomer is interesting only as the first example of the series of acrylate monomers in which the carbon atoms of the double bond have all the available positions filled by fluorine rather than by hydrogen. Attempts to homopolymerize this monomer in bulk have so far been unsuccessful. Emulsion polymerization is impossible because the monomer is very readily hydrolyzed. Peroxide catalysts, ultra-violet light and ionic catalysts (BF_3 and $AlCl_3$) were tried as initiators without success.

Copolymerizations with butadiene, styrene, and vinyl acetate in bulk were also tried. With butadiene, and styrene, less than 10% of the fluorinated monomer was incorporated in the polymer. With vinyl acetate, a tough plastic containing 25% F. (32 mole % perfluoroacrylyl fluoride) was produced. This material was insoluble in benzene and acetone but dissolved slowly in dilute base. When heated, it became rubbery at $75^\circ C$. and charred above $250^\circ C$. without softening further.

V. PERFLUOROBUTADIENE

In the last annual report, copolymers of perfluorobutadiene with ethylene were described. It was pointed out that the high temperature properties of these materials, properly stabilized, are quite good, but that the yield in the bulk polymerization used tends to be low. During the present contract year some further work on this system has been carried out, but it has been found that copolymers of perfluorobutadiene with 1,1-dihydroperfluoroalkyl vinyl ethers are more readily prepared and have better properties, and chief attention has therefore been given to them. In addition, certain other copolymers of perfluorobutadiene have been investigated, and these will be described briefly.

A. Perfluorobutadiene:Ethylene

The copolymerization of perfluorobutadiene and ethylene in bulk has been carried out in the Magne-Dash autoclave, in which a vertical stirring action is provided by a dasher activated by a solenoid. The charge contained:

Perfluorobutadiene	-	46.8 g.
Ethylene	-	8.1
Benzoyl peroxide	-	0.6

Contrails

The product after 48 hours at 80-85°C. was rubbery but was formed in only 20% yield. It contained 55% fluorine, corresponding to 78 weight % or 38 mole % perfluorobutadiene.

Part of this polymer was compounded with sulfur and accelerator and molded. The extent to which vulcanization actually occurred is unknown since with the small amount of material available, only ozone and heat resistance tests were possible. After 15 hours at 25% elongation in 350 ppm ozone atmosphere, the sample showed no cracking or other deterioration. Under the same conditions, GR-S, Buna-N, and natural rubber failed in a few minutes.

Emulsion polymerizations have been carried out in the following recipe, in which the monomer phase was composed of 20 g. of perfluorobutadiene and 3.5 g. of ethylene:

Water	- 180 parts
Monomers	- 100
Ammonium perfluoro-octanoate	- .6
$\text{Na}_2\text{S}_2\text{O}_8$	- 1
NaHSO_3	- 0.5
Borax	- 0.5
t-C ₁₂ mercaptan	- 1.0

Two polymerizations were carried out. One

Contrails

reaction was discharged after 24 hours at 60-70°C. The polymer at 39% yield was a non-rubbery powder. The second charge was maintained at 95-100°C. for 22 hours. A rubbery polymer in 18% yield was obtained. Lower conversion in this case was probably due to an oxygen induction period. The polymer from this second preparation was used in the heat stability experiments described later.

It was found that better yields resulted if the mercaptan concentration was increased to about 1.5%; mercaptan was also helpful in obtaining rubbery products at higher yields. In the absence of mercaptan the powdery form of the copolymer was always obtained.

In one case, after 42 hours at 95°C. and 600 psi, a 22% yield of a rubbery product was obtained. This material was used for the swelling studies reported below. In two other cases, yields of 45% and 55% were obtained. Although semi-rubbery, these products were much less extensible than the sample obtained at 22% conversion.

The results of swelling measurements on ethylene copolymer prepared at 22% yield are

tabulated in Table IV.

TABLE IV

SWELLING OF PERFLUOROBUTADIENE:ETHYLENE COPOLYMER

<u>Solvent</u>	<u>δ</u>	<u>Swelling %</u>
c-C ₈ F ₁₆ O	5.9	0
Iso-octane	6.85	37
Benzotrifluoride	8.2	370
Cyclohexane	8.2	7
Ethyl Acetate	8.95	575
Benzene	9.15	60
Acetone	9.9	800

On the basis of these results, it is difficult to assign any value for the cohesive energy density of the copolymer. Swelling in ethyl acetate is unexpectedly high. As in the case of poly-FBA, the cyclic C₈ ether, c-C₈F₁₆O, was a poor swelling agent, indicating that the assumed low cohesive density of poly-perfluorobutadiene has probably been shifted upwards by incorporation of ethylene. The high swelling in acetone and ethyl acetate may result from a specific interaction between carbonyl groups and hydrogens on

Conclusions

the copolymers. These hydrogens may be positive because of their proximity to carbon atoms bearing fluorine.

A portion of a copolymer prepared in the above emulsion recipe from a 1:1 molar monomer charge was molded into strips of the type used for the Gehman torsional modulus test. These strips were heated at 200°C. and the relative modulus determined at intervals by removing a specimen from the oven, cooling to room temperature, and testing at room temperature in the Gehman device.

Specimens were compounded in the following recipe, designated the "sulfur" cure in Table V.

Copolymer	-	100.0
ZnO	-	5.0
Stearic acid	-	1.0
Sulfur	-	1.5
Altax	-	1.5
Tuads	-	0.15

Various antioxidants were also tried, and these are indicated in the third column of Table V. A bulk copolymer was included in the study, both the material as obtained from the reactor and the same material after extraction with methyl ethyl ketone to remove residual peroxide, which might speed the degradation. Samples of poly-FBA

Contrails

TABLE V

AGING OF PERFLUOROBUTADIENE:ETHYLENE (FB-C₂H₄) AND OTHER POLYMERS AT 200°C.

Polymer	Cure	Anti-oxidant	Time of Wt. Loss %		Relative Moduli								
			Hardening Hours ¹	Loss %	21 Hrs.	42 Hrs.	64 Hrs.	87 Hrs.	110 Hrs.	162 Hrs.	185 Hrs.		
FB:C ₂ H ₄ Bulk	None	None	75	11%	18%	2.47	3.18	7.56	78.0	114			
FB:C ₂ H ₄ Bulk	Sulfur	None	155	8	11	1.12	1.26	1.67	4.55	6.96	8.45	18.1	65.7
FB:C ₂ H ₄ Bulk	None	None	65	10	19	3.34	4.83	16.8	254	300			
Extracted FB:C ₂ H ₄ Bulk	Sulfur	None	95	7	14	1.46	1.87	3.14	37.6	66.5			
Extracted FB:C ₂ H ₄	None	None	175	15	20	1.18	1.52	2.10	2.86	4.80	4.94	7.95	18.1
FB:C ₂ H ₄	None	PBMA	190	15	19	1.12	1.37	1.68	2.42	2.88	3.10	3.88	
FB:C ₂ H ₄	None	Agerite D + PEA	165	16	20	2.67	2.78	3.58	6.83	7.80	8.35	10.6	23.1
FB:C ₂ H ₄	Sulfur	None	110	18	26	3.92	5.32	8.32	8.88	18.9			
FB:C ₂ H ₄	Sulfur	PBMA	70	16	23	4.85	6.05	8.30	32.0	68.0	109	437	595
FB:C ₂ H ₄	Sulfur	Agerite D + PEA	70	16	24	4.15	5.56	8.40	50.7	127			
pFBA	M ₀ g	None	70	22	39	--	0.20	8.15	38.0				
Paracrill 18	Sulfur	None	2	--	--	1 Hr.	3 Hrs.						
Paracrill 18	Sulfur + Carbon Black	PBMA	3	--	--	1.53	89.5						
Hycar OR-15	Sulfur	Agerite B	2	--	--	0.95	9.50						

¹The approximate time at which the polymer became inflexible by hand test.

Contrails

cured with magnesium oxide and no litharge (the best heat-resistant cure known at the time of this work) and of sulfur-cured Buna-N were included for comparison.

The results of the study of weight loss and stiffening of these compounds at 200°C. are summarized in Table V. The increase in relative modulus (i.e., compared to the initial modulus) is plotted in Figure 1. It will be observed from Table V that the loss in weight of the perfluorobutadiene:ethylene copolymers was in all cases large (about 20%) after 140 hours, and that this was not remedied by any of the antioxidants or accelerators used. With regard to the stiffening of these polymers, the following observations can be made:

(1) The emulsion copolymer of perfluorobutadiene:ethylene is superior to poly-FBA in heat resistance. Both are superior to the sulfur-cured Buna-N compound tested. The Buna-N embrittlement can be retarded by using a non-advancing cure, as was done for the tests plotted in Figure 13 (see Appendix A and the section on fluoroacrylates); it is still much more rapid than for the perfluorobutadiene copolymers.

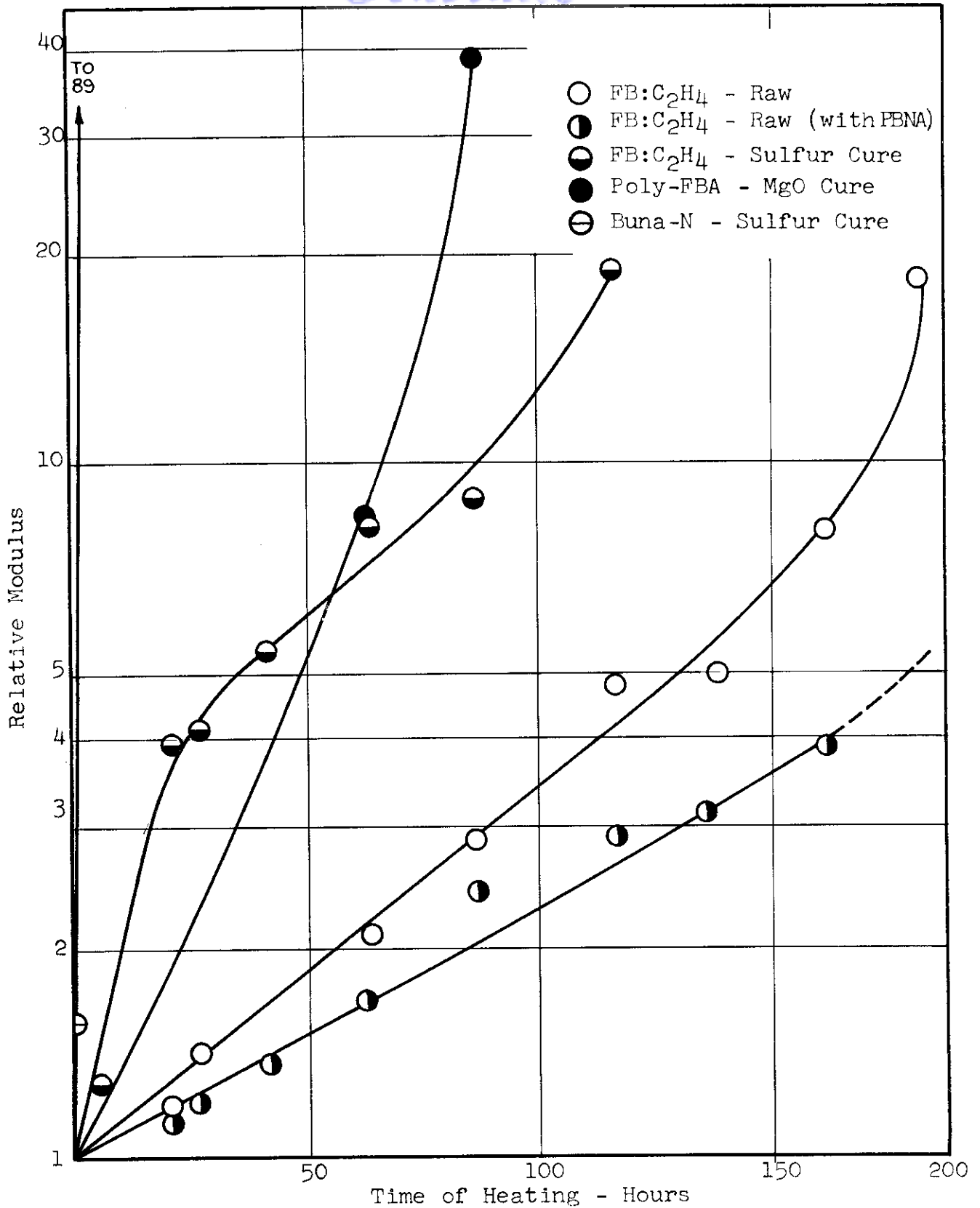


FIGURE 1

STIFFENING OF PERFLUOROBUTADIENE (FB):ETHYLENE POLYMERS AT 200°C.

perfluorobutadiene copolymers.

(2) Phenyl β -naphthylamine stabilized the raw copolymer against stiffening. The other two-anti-oxidants were ineffective.

(3) With sulfur and accelerators, there is a period of rapid stiffening on heating, suggestive of vulcanization. This is followed by a rate of modulus increase about equal to that for the raw polymer.

(4) The emulsion copolymer appears superior to the bulk copolymer even when the latter was extracted.

Despite these rather promising results, work on this copolymer system has been stopped because of the difficulties, indicated above, of obtaining elastic products at conversions above 20-25%.

B. Perfluorobutadiene:1,1-Dihydroperfluoroalkyl Ethers

1. Preparation

Initial preparations of copolymers of perfluorobutadiene with 1,1-dihydroperfluorobutyl vinyl ether (VFBE) and with 1,1-dihydroperfluorohexyl vinyl ether (VFHE) were carried out in a bulk system similar to that used for the

Contrails

copolymers. Because of the relatively low pressures required, sealed ampoules were used, and the Magne-Dash autoclave was not necessary. Typical preparations with acetyl peroxide (Ac_2O_2) and with ultra-violet light and benzoyl peroxide as sensitizer are shown in Table VI.

The calculated compositions are subject to very large errors because of the nearly equal fluorine contents of perfluorobutadiene and the fluorine-containing vinyl ethers. Properties of these rubbers were examined qualitatively because of the small amounts available. The stiffening range was estimated by bending samples by hand. The decomposition range was observed by heating the specimens on a bronze block at the rate of about 5° per minute. The samples darkened at 200°C . and decomposed rapidly above 275°C . On aging at 200°C ., even the best specimens became brittle or retained only slight elasticity after 24 hours.

TABLE VI

BULK PREPARATION OF PERFLUOROBUTADIENE:1,1-DIHYDROPERFLUORO-
ALKYL VINYL ETHER COPOLYMERS

<u>Run No.</u>	<u>Charge (Molar Ratio)</u>	<u>Catalyst</u>	<u>Reaction Time and Conditions</u>	<u>Fluorine (%)</u>	<u>Composition (Wt.% FBd) (Mol.% FBd)</u>	<u>Nature of Product</u>
FB-1A	1:1 FB:VFBE	1% Ac ₂ O ₂	25 hrs., at 50°	62.2	28.1 35.2	Soft, non-tacky rubber
1B		1% Fz ₂ O ₂	40 hrs., U.V.	64.6	49.2 57.5	Cheesy rubber
FB-2A	1:1 FB:VFHE	1% Ac ₂ O ₂	25 hrs. at 50°	64.2	1.6 3.2	Good rubber
2B		1% Bz ₂ O ₂	40 hrs. U.V.	66.1	32 49	Fair rubber

Contrails

Copolymerization of equimolar amounts of perfluorobutadiene and VFHE was repeated on a five-gram scale at 50°C. with 1% acetyl peroxide. The product was a soft, non-tacky rubber which softened still further on milling. The raw polymer was found to exhibit poor heat stability upon aging at 200°C. However, a number of materials, notably phenyl- β -naphthylamine and Altax (benzothiazyl disulfide) were discovered to be effective stabilizers for the rubber. The results of these heat aging tests will be given in detail in a later section (p.45 et. seq.).

Emulsion polymerization being in general a better method of preparing rubbery polymers, the copolymerization of perfluorobutadiene 1,1-dihydroperfluorobutyl vinyl ether (VFBE) was attempted by this means, using the same recipe as was used with the perfluorobutadiene:ethylene system (p. 31), except that the mercaptan content was varied. In Table VII are shown the results obtained in the initial experiments:

Contrails

TABLE VII

EMULSION COPOLYMERIZATION OF PERFLUOROBUTADIENE AND
VINYL 1,1-DIHYDROPERFLUOROBUTYL ETHER(VFBE) AT 50°C.

<u>Tube No.</u>	<u>Mercap- tan %</u>	<u>Reaction Time (Hours)</u>	<u>Yield %</u>	<u>Nature of Polymer</u>
1	0	360	12	Rubbery, soft
2	0	120	44	Rubbery but short
3	0.1	44	93	Boardy
4	0.1	18	78	Rubbery, stiff
5	0.1	18	78	Rubbery, stiff
6	0.5	44	90	Rubbery but short
7	0.5	18	73	Rubbery, rather soft
8	0.5	18	73	Rubbery, rather soft
9	1.0	18	84	Rubbery, soft, slow recovery
10	1.0	44	100	Rubbery, soft, slow recovery

The effect of mercaptan is very evident. At least in this recipe, it appears to have not only a chain transfer function, resulting in a softer polymer, but also seems to have an accelerating effect reminiscent of that of mercaptans in the emulsion polymerization of butadiene. With no mercaptan present, the rate of polymerization is very small.

Contrails

Another series of experiments was carried out using the following similar recipe, and with VFHE:

	<u>Parts</u>
Perfluorobutadiene	100
VFHE	180
H ₂ O	3
DuPont ME	1
Na ₂ S ₂ O ₈	0.5
NaHSO ₃	0.5
Borax	0.2
n-C ₁₂ Mercaptan	50°
Température	

In these experiments the perfluorobutadiene:VFHE molar ratio was varied from 2:1 to 4:1. The results of these experiments are shown in Table VIII. It is of interest to note that polymers can be prepared from charges containing very high molar ratios of perfluorobutadiene. As the perfluorobutadiene ratio increases, the polymers tend to become softer. From the appearance of the products, they seem to be of lower molecular weight and also may be less branched or cross-linked (or both) with larger proportions of perfluorobutadiene. In a separate experiment a copolymer was prepared from a charge containing a 1:2 molar

TABLE VIII
POLYMERIZATION OF PERFLUOROBUTADIENE AND VFHE IN VARYING RATIOS

Tube No.	Amt.		Molar Charge Ratio FBd:VFHE	Length of Reaction at 50°C.	Yield		Nature of Polymers
	FBd	VFHE			Gms.	%	
1	0.5g.	0.5g.	2:1	17 hrs.	0.57*	57	Elastic but short
2	0.5g.	0.5g.	2:1	24 hrs.	0.32	32	Elastic but short
3	0.75g.	0.5g.	3:1	17 hrs.	0.32*	26	Stronger, good rubber
4	0.75g.	0.5g.	3:1	41 hrs.	0.71	57	Stronger, good rubber
5	0.75g.	0.5g.	3:1	100 hrs.	0.78	62	Stronger, good rubber
6	1.0g.	0.5g.	4:1	17 hrs.	0.63*	42	Soft but strong
7	1.0g.	0.5g.	4:1	41 hrs.	0.76	51	Good, slightly soft
8	1.0g.	0.5g.	4:1	100 hrs.	0.87	58	Good, slightly soft

*Some polymer was lost in washing, yields were actually higher.

perfluorobutadiene:VFHE ratio. Surprisingly, this material was not rubbery but resinous and gave some indication of being highly cross-linked. The reason for the formation of resinous products at this ratio of monomers is being investigated further.

The 3:1 perfluorobutadiene:VFHE copolymer, as first prepared, appears to have the best elastic properties of the series. As will be shown later, however, it breaks down readily on milling, and becomes appreciably softer. Its breakdown seems to be more rapid than that of the copolymers of lower perfluorobutadiene content.

2. Aging at Elevated Temperatures

Extensive aging tests have been carried out at 200°C. on samples of the 1:1 copolymer prepared in bulk and the 3:1 and 3:2 perfluorobutadiene:VFHE copolymers prepared in the Duponol-persulfate-bisulfite emulsion system. In all of these tests it appeared that these polymers are quite good with respect to stiffening rate. It seems, however, that the

Contrails

relatively high weight loss rates shown by them poses the more serious problem.

The weight loss rates of a number of stabilized samples of the 1:1 copolymer are shown in Figure 2. (The rate curve for a stabilized sample of a 1:1 perfluorobutadiene:ethylene copolymer is also included to permit comparison.) The most heat stable sample in this group proved to be the rubber compounded with the sulfur-Altax-Tuads "cure" recipe described previously (p.34). This sample underwent a weight loss of 7% in the first 500 hours at 200°. At 1000 hours the weight loss rose to 22%, which of course is much too high. The study indicated that Altax was the most effective ingredient in the "cure" recipe. The inclusion of one part of phenyl- β -naphthylamine in this recipe failed to affect the stability of the compounded rubber.

In Figure 3, the rate of stiffening of the 1:1 copolymer compounded with the sulfur-Altax-Tuads recipe is shown in a semi-log plot, with similar samples of Buna-N, poly-FBA and

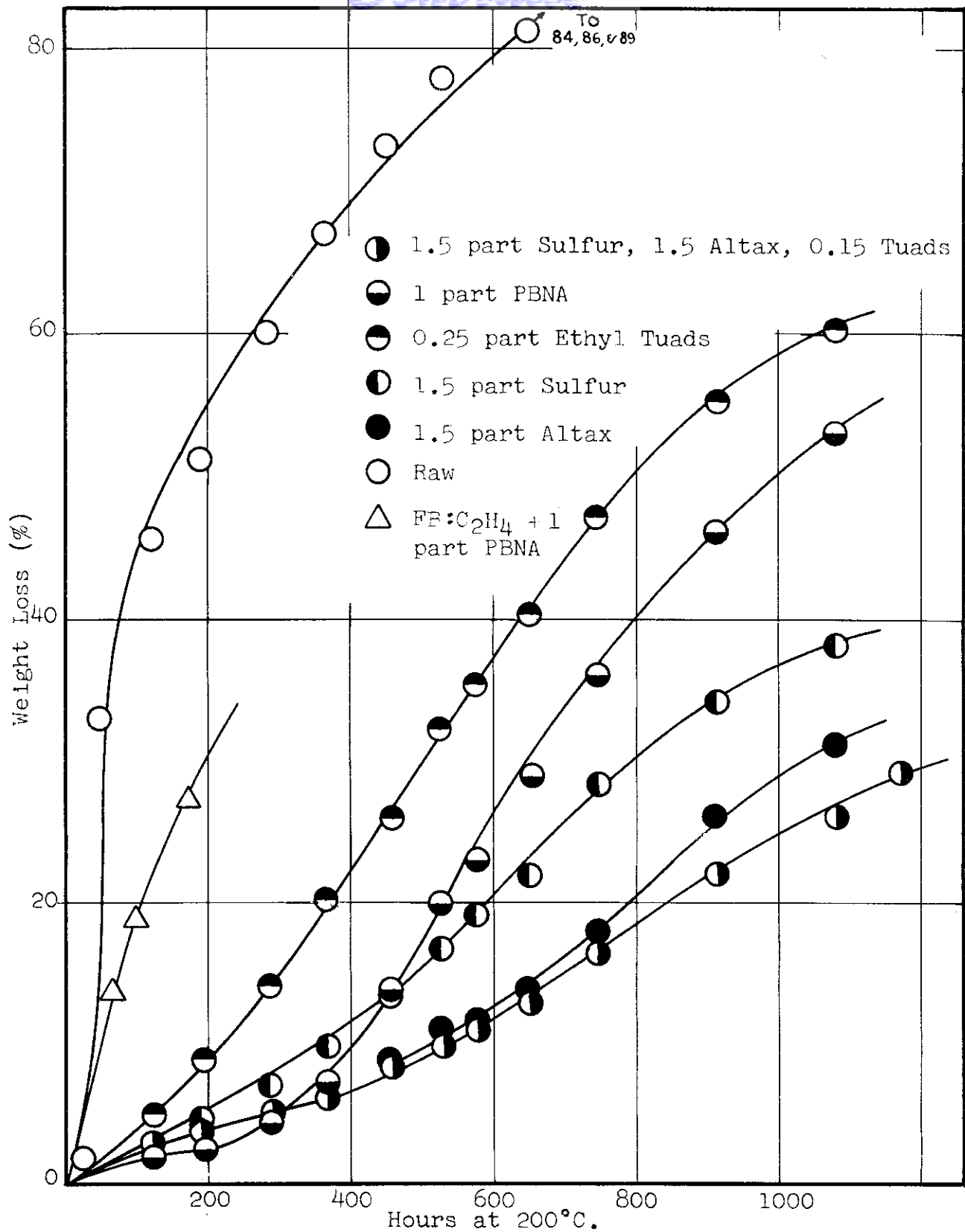


FIGURE 2

RATE OF WEIGHT LOSS OF 1:1 FB:VFHE COPOLYMER AT 200°C.

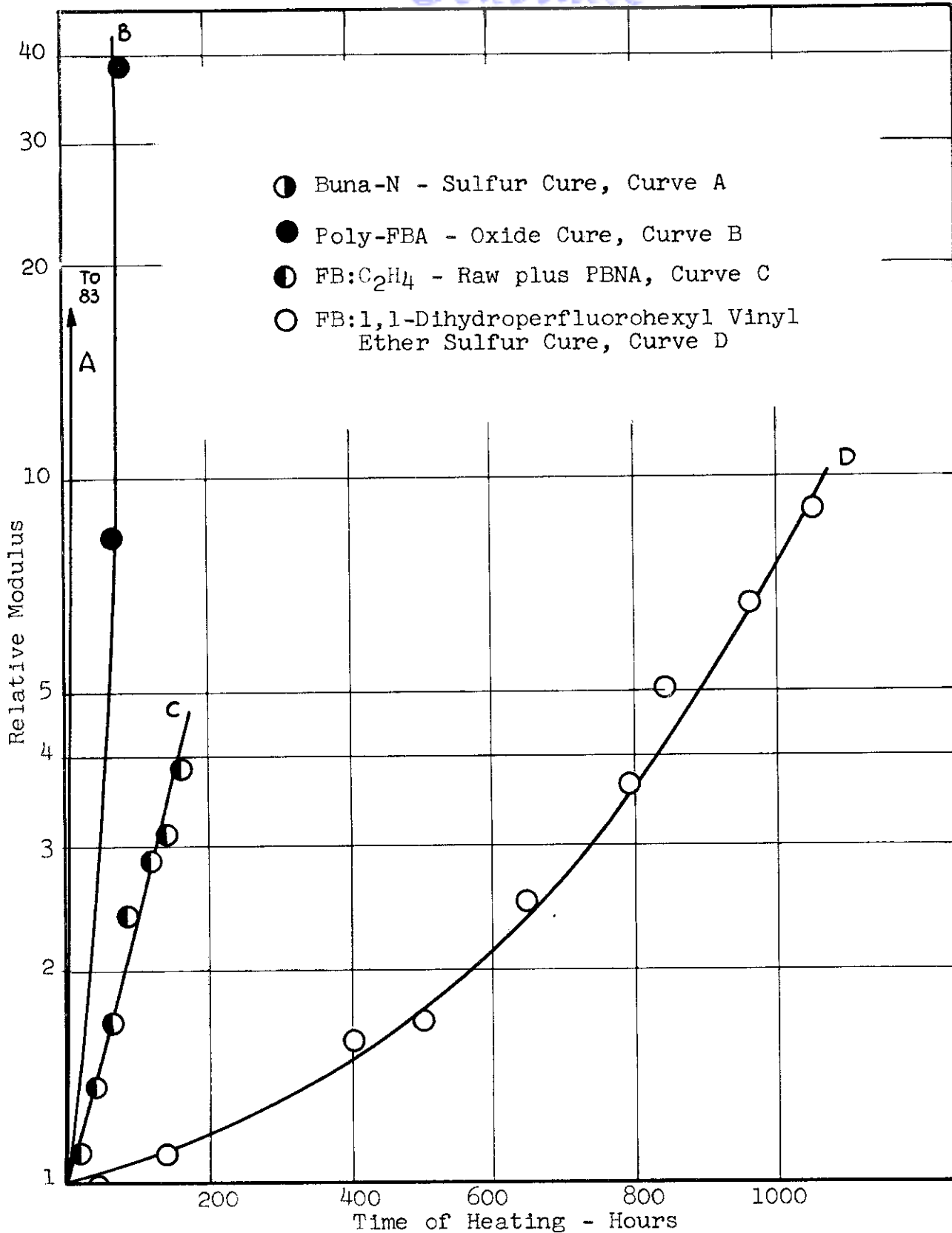


FIGURE 3

RATE OF STIFFENING OF PERFLUOROBUTADIENE COPOLYMERS AT 200°C.

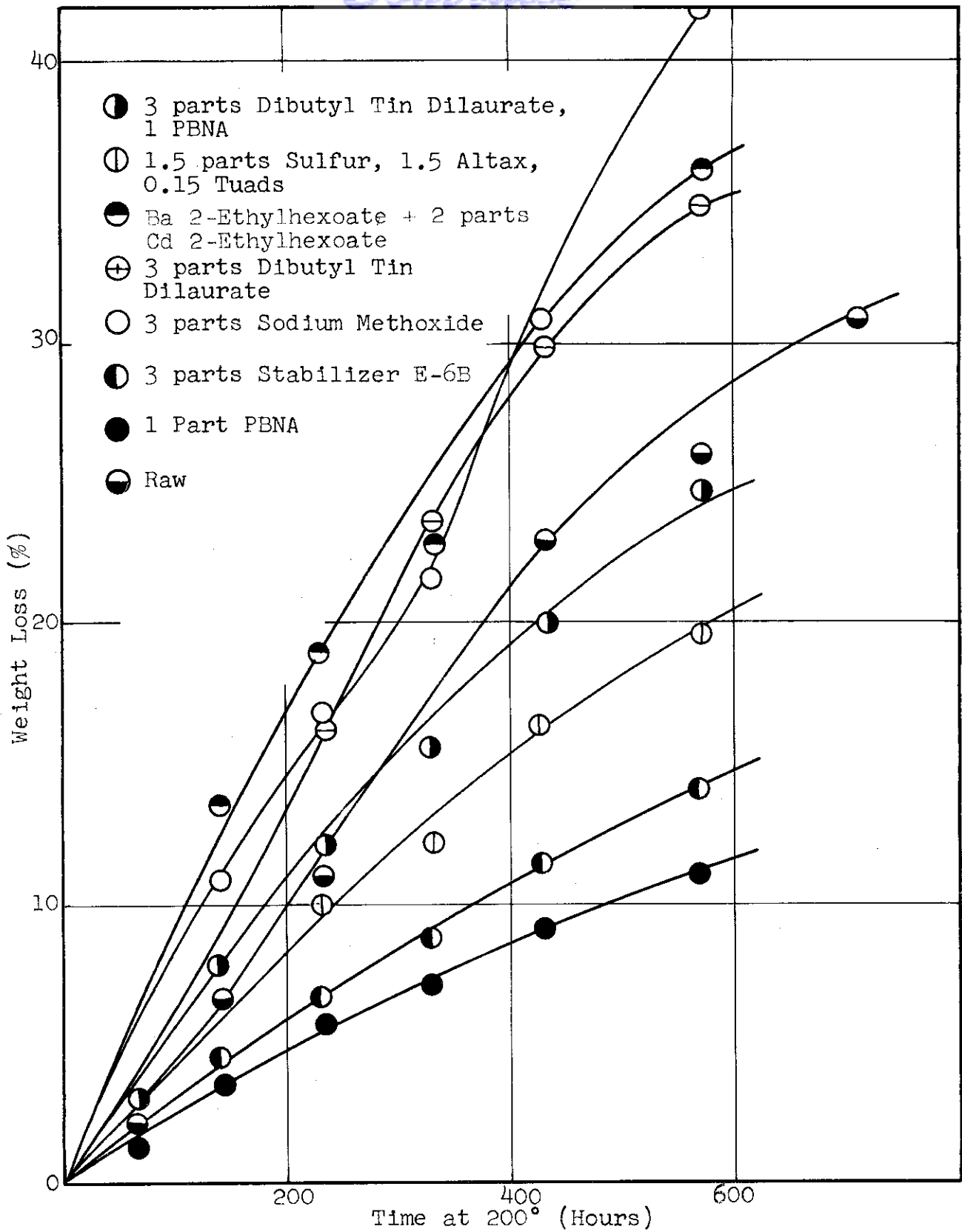


FIGURE 4

RATE OF WEIGHT LOSS OF 3:1 FB:VFHE COPOLYMER AT 200°C.

Controls

a 1:1 perfluorobutadiene:ethylene copolymer as controls. The results indicate that the VFHE copolymer is greatly superior to any of the control samples in resistance to stiffening at high temperature

Pyrolysis experiments (discussed below) showed that some HF is formed on heating these polymers. This suggested that stabilizers of the type used for polyvinyl chloride (where HCl is liberated) might prove beneficial. The materials tested included dibasic lead phosphite, sodium silicate, sodium methoxide, barium and cadmium salts of 2-ethyl hexoic acid, epoxidized soybean oil (Paraplex G-60), dibutyl tin dilaurate and Advance's Stabilizers E-6B and #52. In addition, phenyl- β -naphthylamine, methyl phenyl polysiloxane (an effective material for retarding oxidation in lubricating oils), a number of hydroxy- and amino-substituted anthraquinone dyes, a combination of dibutyl tin dilaurate and phenyl- β -naphthylamine, and a combination of sulfur, Altax and Tuads were evaluated as stabilizers. The results of many of

Conclusions

these tests are presented in Figure 4. The polyvinyl chloride stabilizers all proved very disappointing, with the possible exception of Advance's Stabilizer E-6B (a material of undisclosed composition). Phenyl- β -naphthylamine was found to be the most effective stabilizer.

Although it is not shown in Figure 4, it was found that increasing the concentration of phenyl- β -naphthylamine in the sample from one part to either two or three parts resulted in small, but significant accelerations of the weight loss rates. Although it was the best of the substituted anthraquinones studied, the 1,4-diamino derivative (which is effective in preventing the depolymerization of polymethyl methacrylate) was considerably inferior to phenyl- β -naphthylamine.

Another heat aging study involved testing the 3:2 copolymer at 200° with a number of the stabilizers mentioned above. Once again phenyl- β -naphthylamine proved far superior to any other tested. In Figure 5, the weight loss rate for the phenyl- β -naphthylamine-stabilized 3:2 copolymer is compared with that for similarly stabilized samples of the 1:1 and 3:1 copolymers, as well as

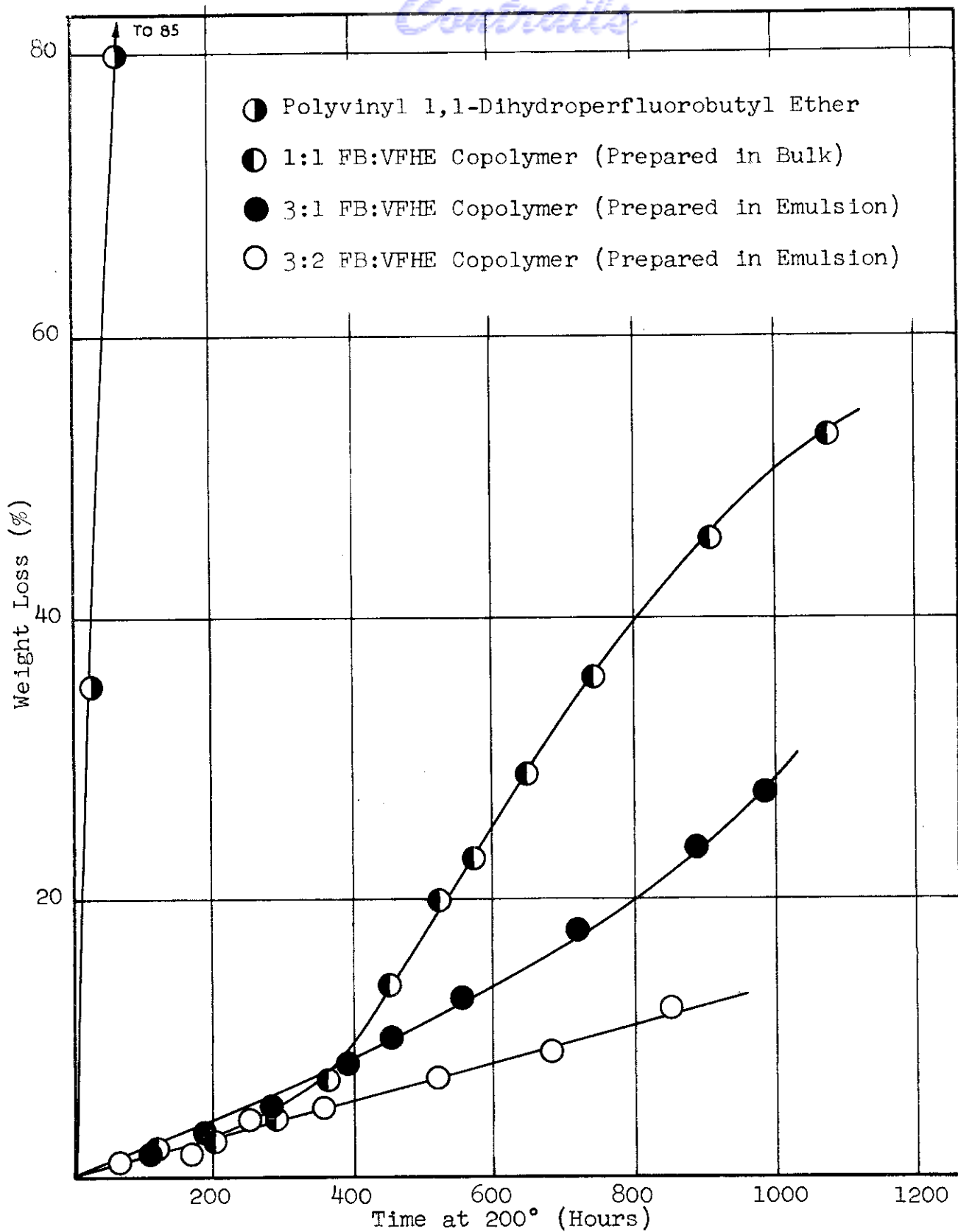


FIGURE 5

RATE OF WEIGHT LOSS AT 200°C. OF POLYMERS STABILIZED WITH ONE PART PBNA

Contrails

with that for the homopolymer of vinyl 1,1-dihydroperfluorobutyl ether. Up to about 300 hours there is no great difference among the three copolymers. After about 300-400 hours, the 3:2 copolymer begins to show markedly superior behavior. The relatively high weight loss of the bulk-prepared 1:1 product is probably a result of the method of preparation, and may perhaps be due to residual peroxides. The greater stability of the copolymer containing the larger proportion of VFHE is surprising in view of the enormously greater weight loss of the VFHE homopolymer itself. These facts will be discussed further in connection with the description of the pyrolysis experiments.

3. Pyrolysis of Perfluorobutadiene:VFHE Copolymers

Some experiments have been carried out in which unstabilized perfluorobutadiene:VFHE copolymers were heated at the same temperature as in the above aging studies, but under conditions such that the volatile products evolved during the process of losing weight could be trapped and examined. The apparatus consisted of a pyrolysis

Conclusions

vessel attached to dry ice and liquid air cold traps, the system being held at about 8 mm. pressure. The method was essentially the same as used in pyrolyzing the VFBE homopolymer, described earlier. A sample of 3:1 perfluorobutadiene:VFBE copolymer, prepared in emulsion, was found by infrared analysis to yield a very appreciable quantity of HF (not determined exactly). In addition, a small amount of a branched olefin, possibly iso-C₄F₈, and a number of unidentifiable substances were found in the liquid air trap. It is possible, and in fact probable in view of the results with the VFBE homopolymer, that some 1,1-dihydroperfluorohexyl alcohol was likewise evolved, but the presence of a considerable quantity of water among the pyrolysis products prevented the positive infrared identification of this substance.

The pyrolysis of the copolymer was attended by a decrease in the fluorine:carbon ratio in the residue from 2.11 to 1.58. This high fluorine loss suggests an appreciable splitting out of the C₅F₁₁ group of the copolymer (as in the homopolymer), in addition to the loss of HF.

Contrails

In a number of other aging tests run on the 3:1 copolymer, it has been noted that relatively well stabilized samples suffer a F:C ratio decrease to about 1.95; whereas the ratio drops to about 1.6 for poorly stabilized samples.

The conclusion from the present studies is that these copolymers degrade chiefly by:

(a) Loss of HF, presumably from $-\text{CF}_2\text{CH}_2-$ groups, probably those in the main chain.

(b) Loss of alcohol from the side chain. This would leave double bonds in the main chain, which may contribute to the accompanying stiffening.

(c) Chain scission. Simple depolymerization, or loss of monomer, does not seem to play a part.

All these processes are evidently initiated by free radicals, probably arising from peroxides present initially and/or formed during aging.

Work is planned to determine whether exclusion of oxygen by immersion of the rubber in liquids, such as dioctyl sebacate, results in

Contrails

greater heat stability of the perfluorobutadiene:VFHE copolymers.

4. Use of Other Emulsion Recipes

Although the copolymers of perfluorobutadiene and VFHE have shown good resistance to solvents and high temperatures, their strength and elasticity have been relatively poor. Consequently, some effort has been devoted to obtaining polymers with better mechanical properties. First, a study was made of the effect of modifier concentration and conversion of the polymer. The usual Duponol-persulfate-bisulfite emulsion system was used with a 60:40 perfluorobutadiene:VFHE charge ratio. The amount of mercaptan was varied from 0 to 0.2% and conversion was varied from 47 to 78%. In no case was there a significant improvement in the polymer.

Next it was thought that polymerization at lower temperatures might produce better polymer. Three different reductive activation ("redox") emulsion recipes, Table IX, were tested using a 3:2 molar charge ratio. Recipe 1 did not give polymerization at 5°C. or 25°C.

Contrails

At 50°C, this system gave a low yield of rather weak polymer. Recipe 2 was also ineffective at the lower temperatures. At 25°C., Recipe 3 gave a strong, elastic copolymer. The yield, however, was only 17%. At 50°C., Recipe 2 gave a polymer that was somewhat too soft, and Recipe 3 gave a polymer of good elasticity but poor strength.

TABLE IX

REDOX RECIPES USED IN THE PREPARATION OF
PERFLUOROBUTADIENE:VFHE COPOLYMERS

<u>Recipe #1</u>	<u>Parts</u>
Perfluorobutadiene	43 (60:40
VFHE	57 mole ratio)
Water	200
Duconol ME	4
Cumeme Hydroperoxide	0.36
$\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	0.05
$\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$	0.50
Fructose	0.50
n-C ₁₂ Mercaptan	0 or 0.2

<u>Recipe #2</u>	
Perfluorobutadiene	43 (60:40
VFHE	57 mole ratio)
Water	200
Ammonium Perfluoro-octanoate	5
Cumeme Hydroperoxide	0.36
$\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	0.50
$\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$	0 or 0.50
Fructose	0.50
n-C ₁₂ Mercaptan	0.2

- 57 -

WADC TR 52-197 Pt 3

Contracts

TABLE IX (Cont'd.)

REDOX RECIPES USED IN THE PREPARATION OF
PERFLUOROBUTADIENE:VFHE COPOLYMERS

<u>Recipe #3</u>	<u>Parts</u>
FBd	43 (60:40
VFHE	57 mole ratio)
Water	200
SF Flakes	5
Cumene Hydroperoxide	0.36
$\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	0.5
$\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$	0.50
Fructose	0.50
n-C ₁₂ Mercaptan	0 or 0.2

Recipe #4 Polyamine Recipe

FBd	43 (60:40
VFHE	57 mole ratio)
H ₂ O	200
SF Flakes	5.0
KCl	0.8
KOH	0.1
Tetraethylene Pentamine	0.3
Cumene Hydroperoxide	0.5

Recipe #5 - Veroxasulfide Recipe

FBd	43 (60:40
VFHE	57 mole ratio)
H ₂ O	200
SF Flakes	5
KCl	0.5
$\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$	0.12
$\text{Fe}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$	0.014
Versene	0.012
Diisopropylbenzene Hydroperoxide	0.5
n-C ₁₂ Mercaptan	0 or 0.2

Recipe #6

Same as Recipe #4, but 5 parts ammonium perfluoro-octanoate instead of SF Flakes.

Contrails

Recipe 4 did not give polymer at 25°C. At 50°C., it gave an elastic polymer of fair strength. Recipe 5 did not give polymer at either temperature. Recipe 6 gave polymer of good strength and elasticity at 50°C.

In most cases the latex formed was of very poor stability, and nearly complete precoagulation occurred. The addition of Daxad 11 as stabilizer did not remedy this difficulty.

None of these recipes gave a polymer showing sufficient improvement in physical properties to justify further study of such systems. It was further found that the polymers prepared in systems containing iron degraded much faster on heating than those prepared in iron-free systems.

5. Compounding and Vulcanization of Perfluorobutadiene:VFHE Copolymers

The vulcanization of the perfluorobutadiene: vinyl 1,1-dihydroperfluorohexyl ether copolymers has been studied. Chief study has been given to a 60:40 molar compound prepared in the emulsion recipe given above, with 0.2 parts of mercaptan. The double-bond between fluorine-bearing carbons

Contrails

does not seem to react readily with sulfur, but apparently vulcanization of the copolymer is possible with p-dinitrosobenzene (Polyac) and p-quinone dioxime (GMF), both activated by red lead. The recipes used are given below:

60:40 perfluorobutadiene: VFHE Copolymer	100	100	100
Phenyl β -naphthylamine	--	1	1
Stearic Acid	2	2	2
Zinc Oxide	5	5	5
Red Lead	10	10	10
GMF	3	--	--
Polyac	--	5	5
EPC Black	--	--	35

Two parts of sulfur can be included for improved heat stability.

Table X represents the properties of the best samples of the perfluorobutadiene copolymer. The merit of these curing systems cannot be judged reliably because of poor mechanical strength of the base polymer, probably due to low molecular weight.

In the balance of solvent and low temperature resistance, the perfluorobutadiene

Contrails

TABLE X
PROPERTIES OF PERFLUOROBUTADIENE:VFHE COPOLYMERS

	<u>60:40 Perfluoro- butadiene:VFHE, Raw Polymer</u>	<u>60:40 Perfluoro- butadiene:VFHE, Polyac Cure, Gum</u>	<u>60:40 Perfluoro- butadiene:VFHE, Polyac Cure With Carbon Black</u>
Tensile Strength, psi.	--	160	600
Elongation, %	--	140	100
Set at Break, %	--	0	6
Gehman T ₁₀ , °C.	-7	-5	-6
Swelling % (48 hrs.) in:			
70:30 iso-octane:toluene	15	20	24
Benzene	17	26	32
Iso-octane	8	--	13
Toluene	20	--	33
MIBK	21	--	53
Methyl perfluorobutyrate	Disintegrates	740	260
70 hrs. at 100°C. in:			
ASTM oil #3	10	--	11
"Skydrol"	9	--	35
Petroleum base hydraulic fluid (AN-O-366) syn- thetic lubricant	7	--	12
Diethyl sebacate (MIL-L-7808)	8	--	11
White fuming nitric acid resistance	No effect in 7 days at 25°C.	No effect in 7 days at 25°C.	No effect in 7 days at 25°C.
Weight loss after 400 hrs. at 200°C., %	64	12	11
Relative modulus after 400 hrs. at 200°C.	--	2.3	23

Contrails

copolymers are equal to poly-FBA. Although it appears that they must be unsaturated, they seem to be fully immune to ozone attack even under stress. They are also resistant to fuming nitric acid for a period of at least three weeks. The raw polymer hardens and decomposes rapidly at 200°C, but when vulcanized with Polyac its high temperature stability is greatly improved. Further decrease in weight loss can be achieved by addition of phenyl-β-naphthylamine or of elemental sulfur. This does not necessarily retard the stiffening rate, however. On the other hand, in the 60:40 copolymer, carbon black greatly accelerates the stiffening, although the weight loss is not affected. The heat aging data shown in Table X are not corrected for a rapid initial stiffening, which may be due to further advancement of the cure.

Some study has also been given to the vulcanization of a 75:25 molar perfluorobutadiene:VFHE copolymer. This rubber becomes extremely plastic on the mill and flows freely when placed in a hot mold. Sulfur, GMF, and Polyac

Contrails

recipes all cause severe blowing and only moderate cross-linking. A fairly satisfactory sample was prepared using benzoyl peroxide. Reaction with poly-functional amines, isocyanates, and thiols gave extremely weak and friable products. The best specimens have been prepared using litharge and magnesia in the following recipe:

Polymer	100.0
Stearic acid	1.0
Litharge	5.0
Calcined magnesia	25.0
Ethyl zimate	0 - 0.5
Polyac	0.- 5.0

Additional cross-linking seems to take place on adding a dithiocarbamate accelerator, Polyac, or both.

C. Copolymers of Perfluorobutadiene with Hydrocarbon Vinyl Ethers

Some experiments have been carried out with the aim of preparing copolymers of perfluorobutadiene with vinyl n-butyl ether (VNBE) and vinyl isobutyl ether (VIBE). The conditions and results of these experiments are detailed in Table IX.

Contrails

Table XI.

The usual persulfate-bisulfite emulsion recipe was used. The 1:1 copolymers had excellent rubbery characteristics, better than those of the perfluorobutadiene:vinyl 1,1-dihydroperfluoroalkyl ether copolymers. However, the copolymers containing higher ratios of perfluorobutadiene were very soft and showed poor elasticity.

A quantity of polymer prepared using a 1:1 molar charge of perfluorobutadiene and vinyl n-butyl ether in a separate experiment gave a 45% yield of a strong, highly elastic copolymer containing 42.5% F. (48 mole % perfluorobutadiene). The polymer can be cured using the Polyac recipe discussed above in connection with the perfluorobutadiene:VFHE copolymer. The results for the cured polymer are as follows:

a. $T_{10} = -25^{\circ}\text{C}.$

b. Heat aging at $200^{\circ}\text{C}.$

21 hrs. - 3% wt. loss

68 hrs. - 10% wt. loss

Polymer hard and brittle

c. Swelling volumes

benzene - 470%

acetone - 680%

Contrails

TABLE XI

PERFLUOROBUTADIENE (FB):HYDROCARBON VINYL ETHER (VE) COPOLYMERS

<u>Tube No.</u>	<u>Amt. FB</u>	<u>Amt. VE</u>	<u>FB:VE</u>	<u>Yield %**</u>	<u>Nature of Polymer</u>	<u>% F</u>	<u>Mol % Perfluoro-butadiene</u>
1	0.25 g.	VNBE 0.15 g.	1:1	25	Good rubber	45.1	52
2	0.25 g.	VNBE 0.15 g.	1:1	20	Good rubber	--	--
3	0.25 g.	VIBE 0.15 g.	1:1	32	Good rubber	44.3	51
4	Error in filling	VIBE 0.15 g.	1:1	--	Good rubber	49.6	59
5	0.8 g.	VIBE 0.15 g.	3:1	25	Soft, weak, slightly elastic	--	--
6	1.0 g.	VIBE 0.15 g.	4:1	23	Soft, weak, slightly elastic	59.2	76
7	1.0 g.*	VIBE 0.15 g.	4:1	57**	Soft, weak, almost no elasticity	61.1	80
8	1.0 g.*	VIBE 0.15 g.	4:1	24	Soft, weak, almost no elasticity	57.7	72

* Contained 0.2% n-C₁₂ mercaptan

** Tube 7 was reacted 144 hours at 50°C., the rest reacted 42 hours.

Contrails

Swelling in organic solvents is large and resistance to high temperatures is not outstanding. No further work on this copolymer system is contemplated.

Polymerization of perfluorobutadiene and VNBE in a 4:1 molar charge ratio was also attempted. Both tubes gave boardy, inelastic polymers.

D. Copolymers of Perfluorobutadiene and 1,1-Dihydroperfluorobutyl Acrylate (FBA)

Emulsion copolymerization of perfluorobutadiene and 1,1-dihydroperfluorobutyl acrylate was accomplished in a Duponol ME:ammonium persulfate system. Molar ratios of perfluorobutadiene to FBA of 1:1 and 2:1 were used, with and without mercaptan. Although polymerization proceeded well at 15° to rubbery polymers, the product of both charging ratios indicated only 15 mole percent perfluorobutadiene in the copolymer. Thus, this system is not as favorable for copolymerization as a perfluorobutadiene:vinyl 1,1-dihydroperfluoroalkyl ether system. One could presumably accomplish introduction of enough perfluorobutadiene into the FBA chain to serve as a point of cross-linking without

Contrails

the sacrifice of solvent resistance which accompanies the use of hydrocarbon butadiene.

E. Miscellaneous Copolymerizations of Perfluorobutadiene

Investigations of the copolymerization of perfluorobutadiene with equimolar amounts of several monomers other than those discussed above are summarized in Table XII. These reactions were made on an 0.5 gram scale with ultraviolet light as an initiator and 1% benzoyl peroxide as sensitizer. The results of the experiments are summarized in Table XII.

Of this group, only the copolymers with fluoroprene and iso-butylene appeared to show any promise. Further work on the isobutylene system is under consideration.

F. Homopolymer of Perfluorobutadiene

The preparation of copolymers of perfluorobutadiene with 1,1-dihydroperfluoroalkyl vinyl ethers, discussed above, yielded some products which, on the basis of the charge and the yield (analysis being very difficult) appeared to contain substantially more than 50 mole % perfluorobutadiene. This

Contrails

TABLE XII
PERFLUOROBUTADIENE COPOLYMERS

<u>Comonomer</u>	<u>Reaction Time (Days)</u>	<u>Nature of Product</u>	<u>% F</u>	<u>Composition (Mol %)</u>	<u>Comments</u>
Vinyl 8-hydro-perfluoro-propyl ether	19	White Powder	58.5	100% Vinyl Ether	Obtained in good yield.
Tetrafluoro-ethylene	52	Brown Powder	--	---	Insufficient amounts for analysis.
Fluoroprene	8	Rather soft, non-tacky rubber	41	18 FB: 82 FP	Good yield. Polymer degraded to powder on milling
Isobutylene	14	Very soft rubber	48	42 FB: 58 IB	Apparently of extremely low molecular wt.
Vinyl Chloride	52	White Powder	unavail-able	--	Fair yield
Vinylidene Chloride	1	White Powder	15	20 FB: 80 VCl ₂	Fair yield. Polymer pptd. during reaction.
Vinylidene Fluoride	56	Brown Powder	--	--	Insufficient amount for analysis.

seemed to indicate that homopolymerization of perfluorobutadiene should be possible, and it was indeed found that yields of homopolymer ranging from trace amounts to 15-20% can be prepared in the following recipe:

Contrails

	<u>Parts</u>
Perfluorobutadiene	100
Water	180
Ammonium Perfluoro-octanoate	6
Na ₂ S ₂ O ₈	1
NaHSO ₃	0.5
Borax	0.5
n-C ₁₂ Mercaptan	1

Reaction times were 10-15 days
at 50°C.

The products were white, resinous materials which did not possess rubbery characteristics. One sample was analyzed and proved to be rather impure: 64.0% F, 32.1% C; theo.: 70.5% F, 29.5% C.

By bulk polymerization in a quartz ampoule under ultraviolet light with 3% benzoyl peroxide as sensitizer, a 20% yield of the homopolymer was obtained after 55 days. Prepared in this way, it was a soft, greasy solid, apparently of lower molecular weight than the product from emulsion. In both cases, the polymer may contain considerable dimer. An infrared curve showed unsaturation at 5.57 μ and 5.78 μ .

Contrails

Exposure of perfluorobutadiene sealed under vacuum in a Pyrex ampoule to 200 megarepresents of gamma radiation from the Co 60 source at the Brookhaven Laboratory gave 5.3 g. (55% yield) of a soft, greasy material. This material was insoluble in all hydrocarbon and fluorocarbon solvents tested (including xylene hexafluoride, methyl perfluorobutyrate, C_6F_{14} , $(C_4F_9)_2O$ and $(C_4F_9)_3N$). At elevated temperatures, the polymer becomes softer until at 115-125°C. it becomes a liquid, and is then soluble in these solvents. This behavior suggests crystallinity in the polymer. The infrared curve was quite similar to that of the product obtained when perfluorobutadiene in a quartz ampoule was subject to ultraviolet light. Analysis shows 29.6% C, 69.2% F.

The emulsion method appears to give the product with the highest molecular weight, as would be anticipated. None of the products prepared so far appear attractive as rubbers, but the study of polymer is nevertheless of considerable interest in connection with that of the copolymers of perfluorobutadiene.

Contrails

On heating at 200° C., the polymer from the emulsion polymerization underwent a weight loss of 11% in the first 6 hours. The total weight loss after 200 hours was 22%. No evidence was found of any deep-seated degradation. The F:C ratio remained unchanged. Infrared analysis detected the presence of unsaturated fluorocarbons in the dry ice trap. Presumably these were extremely low molecular weight polymers, chiefly dimer, present in the initial sample. (The monomer is volatile at the temperature of dry ice.)

VI. FLUORINE-CONTAINING ACRYLATES

A. New Monomers and Their Polymers

A number of fluorine-containing acrylate monomers have been prepared and studied during this contract year. The acrylates that have received chief study in earlier work have been those of the series: $R_fCH_2OCOCH=CH_2$, where R_f denotes a perfluoroalkyl group. The newer ones belong to other homologous series. Particular attention has been given to those containing an ether oxygen atom in the alcohol side-chain, for by this means one may hope to increase the low temperature flexibility of the polymers.

The more important properties of the homo-polymers of these newer acrylates are all summarized in Table XIII, in which members of the $R_fCH_2OCOCH:CH_2$ series have been included for comparison. Glass temperatures, T_g , have been determined refractometrically, as described in earlier reports. The T_{10} values are, as before, determined on the Genman Torsional modulus apparatus. Likewise in Table XIII have been included the properties of certain non-fluorinated

Contrails

alkoxy acrylates having structures analogous to our fluorine-containing monomers. Individual comments on the acrylates of Table XIII are given in paragraphs below:

1. 1,1-Dihydroperfluoroamyl Acrylate (FAA)

The preparation of this monomer fills in one of the gaps in the $R_FCH_2OCOCH:CH_2$ series. The Gehman T_{10} of $-7^\circ C$. for the homopolymer is the same as that for the other rubbery members of this series, and the other properties are about what would be expected from its position in the series.

2. 1,1,5-Trihydroperfluoroamyl Acrylate (FAH₃A)

The glass temperature for this homopolymer, $-35^\circ C$., is similar to that for poly-FAA, $-37^\circ C$., but the T_{10} is about 10° lower. This is rather surprising, since a hydrogen on a fluorine-bearing carbon atom usually confers considerable polarity, and would not be expected to increase the flexibility.

An experiment was undertaken to see if the terminal hydrogen in this polymer makes it possible to obtain reinforcement with carbon black. A sample of the homopolymer was cured in the silicate recipe for 2 hours at $310^\circ F$. with 35 parts of Spheron #9 black.

Contrails

The quantity of polymer on hand was not sufficient for a control gum stock, but the carbon black sample showed tensiles in the neighborhood of 1000 psi. Since this strength can be obtained with poly-FBA, this experiment provides no evidence that the trihydro acrylate polymer is reinforceable. Further study in sulfur recipes may be desirable.

3. 1,1,3-Trihydroperfluorobutyl Acrylate (FBH₃A)

FBH₃A was polymerized in Duponol Me and Aerosol OT recipes. High conversions and good latexes and polymers were produced with both recipes. The inherent viscosities of the polymers in 2:1 acetone:MFB were 3.59 using the Duponol recipe and 4.68 with an Aerosol OT recipe.

Using the Duponol recipe 83 grams of polymer was prepared and coagulated with a solution of Al₂(SO₄)₃·18H₂O at -20°C (see p. 97). This polymer had a conversion of 97% and an inherent viscosity of 4.22. The vulcanization of this polymer will be studied.

4. β-(1,1-Dihydroperfluoroethoxy)Ethyl Acrylate (FEH₂EA)

The profound effect of only three fluorine atoms, -- and these in a terminal position on the

side-chain --, on the low temperature properties is seen by comparing the T_{10} of the homopolymer with that of poly-EEA, whose T_{10} is 30° lower. The terminal perfluoromethyl group confers some resistance to aliphatic solvents, but the swelling in benzene is high.

5. β -Hydroperfluoroethoxyethyl Acrylate (FEHEA)

The behavior of this polymer is similar to that of poly-FEH₂EA, just discussed. In neither case is the low temperature flexibility improved by the presence of the ether oxygen atom.

6. β -Hydroperfluoroethyl Diethylene Glycol Acrylate (FEHE₂A)

This is similar to FEHEA, but with two -OCH₂CH₂- groups in the side-chain. The additional ethylene-oxy group improves the low temperature flexibility somewhat but the balance of T_{10} and swelling in aromatic solvents is unfavorable.

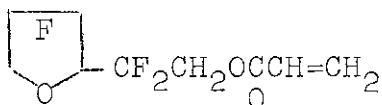
7. (1,1-Dihydroperfluorobutoxy)Ethyl Acrylate, (FBEA)

This structure, a higher homolog of FEH₂EA, is superior to it in both low temperature flexibility

and solvent resistance. The preparation of butadiene copolymers of this monomer was described in the previous annual report (May 15, 1951 to May 15, 1952). It was shown that the balance of low temperature properties and swelling for the butadiene copolymer is somewhat better than for FBA:butadiene copolymers, but not greatly so.

8. β -(2-Perfluorofuryl)-1,1-Dihydroperfluoroethyl Acrylate (HFEA)

This monomer has the following structure:



The polymer was prepared in the standard Duponol:per-sulfate emulsion recipe. As might be expected for a polymer containing cyclic groups in the side chains, the T_{10} for this material is rather high, 2°C. The nearest equivalent in a straight chain acrylate is poly- γ -(perfluoroethoxy)-1,1-dihydroperfluoropropyl acrylate (FEFPA), which has a T_{10} of -24°C.

The swelling of a vulcanizate prepared in the standard silicate recipe was tested in four solvents and found to be as follows:

Contrails

Benzene	6%
70:30 iso-octane:toluene	5%
Methyl ethyl ketone	33%
Ethyl acetate	35%

This polymer swells considerably less in both hydrocarbons and oxygenated solvents than poly-FBA.

9. γ -(Perfluoroalkoxy)-1,1-Dihydroperfluoropropyl Acrylates, $R_fOCF_2CF_2CH_2OCOCH:CH_2$

This series of acrylates has been found to have the best balance of solvent resistance and low temperature flexibility of any rubbers studied so far in this program. The data for the homopolymers (Table XIII) of the methoxy (FMFPA), ethoxy (FEFPA), propoxy (FPFPA), and butoxy (FBFPA) acrylates shows that, with the possible exception of poly-FEFPA, the T_{10} 's of samples cured in the standard silicate cure are all in the range -31° to $-35^\circ C.$, i.e. about 25° lower than the polymers having the R_fCH_2 side chain. The poly-FMFPA and -FEFPA were good rubbers, but the poly-FPFPA and -FBFPA were rather soft. The trend in T_g with length of side chain is not regular; a maximum occurs at FEFPA. Particularly striking is

Table XIII

PROPERTIES OF FLUOROACRYLATE HOMOPOLYMERS


Structure	Abbreviation	% F.	T _g , °C.	T ₁₀ , °C.	% Swell	
					70:30 iso-oct. Toluene	Benzene
CF ₃ CH ₂ COOCH = CH ₂	FFA	37.0	-10	---	---	---
CF ₃ CF ₂ CH ₂ COOCH = CH ₂	FPA	46.6	-26	-7	20-30	---
CF ₃ (CF ₂) ₂ CF ₂ CH ₂ COOCH = CH ₂	FBA	52.3	-30	-7	10-15	---
CF ₃ CFHCF ₂ CH ₂ COOCH = CH ₂	FBH ₃ A	48.3	---	-5	10-15	---
CF ₃ (CF ₂) ₃ CH ₂ COOCH = CH ₂	FAA	56.2	-37	-7	5-10	---
CF ₂ H(CF ₂) ₃ CH ₂ COOCH = CH ₂	FAH ₃ A	53.1	-35	-17	5-10	---
CF ₃ (CF ₂) ₄ CH ₂ COOCH = CH ₂	FHA	59.0	-39	-7	0-5	---
CF ₃ (CF ₂) ₆ CH ₂ COOCH = CH ₂	FOA	62.7	+37*	---	0	---
CF ₃ (CF ₂) ₈ CH ₂ COOCH = CH ₂	FOA	65.1	---	---	0	---
CF ₃ CH ₂ OCH ₂ CH ₂ COOCH = CH ₂	FH ₂ FA	28.8	---	-5	15	210
CF ₂ HCF ₂ OCH ₂ CH ₂ COOCH = CH ₂	FH ₂ FA	35.2	-22	-9	20	---
CF ₂ HCF ₂ (OCH ₂ CH ₂) ₂ COOCH = CH ₂	FH ₂ FA	29.2	-40	-15	10	100
CF ₃ CF ₂ CF ₂ OCH ₂ CH ₂ COOCH = CH ₂	FBEA	44.6	-45	-20	20	50
	FFEA	60.2	---	+2	0-5	0-5

Table XIII (Cont'd)

PROPERTIES OF FLUOROACRYLATE HOMOPOLYMERS

Structure	Abbreviation	% F.	T _g , °C.	T ₁₀ , °C.	% Swell	
					70:30 Toluene	iso-oct. Benzene
CF ₃ OCF ₂ CF ₂ CH ₂ COCH = CH ₂	FMEFA	49.2	-55	-32	10	16
CF ₃ CF ₂ OCF ₂ CF ₂ CH ₂ COCH = CH ₂	FEFPA	53.4	-49	(-23**)	10-15	7-12
CF ₃ (CF ₂) ₂ OCF ₂ CF ₂ CH ₂ COCH = CH ₂	FFFPA	56.4	-68	-35	12	13
CF ₃ (CF ₂) ₃ OCF ₂ CF ₂ CH ₂ COCH = CH ₂	FBFPA	58.8	-68	-31	2	29
<u>Hydrocarbon Acrylates</u>						
CH ₃ OCH ₂ CH ₂ COCH = CH ₂	MEA		-50	-20	30	660
CH ₃ CH ₂ OCH ₂ CH ₂ COCH = CH ₂	EEA		-50	-35	50	very high
CH ₃ CH ₂ OCH ₂ CH ₂ CH ₂ COCH = CH ₂	EPA		-65			

* Probably 1st order transition

** Silicate cure; -34° in oxide cure

Contrails

the contrast between poly-FOA and poly-FBFPA; these differ only in the replacement of a $-CF_2-$ group by an oxygen atom. The poly-FOA is a hard, crystalline plastic, whereas the poly-FBFPA is a soft rubber. It is likewise instructive to compare poly-FMFPA with poly-FEH₂EA; both have the same number of atoms in the side-chain, but the T_{10} of the poly-FMFPA is 27° lower than that of the poly-FEH₂EA, (despite the substantially higher fluorine content of FMFPA), and is about the same as that of poly-EEA, which contains no fluorine.

Two differences between this series of acrylates and the earlier, less successful alkoxy types are:

- a) CF_2 groups present on both sides of the ether oxygen.
- b) The ether oxygen atom is separated from the ester oxygen by three carbon atoms, rather than two.

It appears at present that (b) is the chief cause of the favorable properties found. Apparently, in the earlier compounds, the ether "swivel joint" is too

Conclusions

close to the root of the side-chain to have a large effect on the flexibility. This explanation needs to be checked by measurement of the low temperature properties of the $R-O-CH_2CH_2CH_2-OCOCH=CH_2$ (non-fluorinated) acrylate polymers, as well as by that of the $R_FOCF_2CH_2OCOCH:CH_2$ series.

The preparation of butadiene copolymers of FMFPA, FEFPA, FPFPA, and FBFPA was carried out, using the standard Duponol-persulfate recipe. In Table XIV the conditions and results of these experiments are shown. At 50°C. reaction times were 2-7 hours for the FMFPA and FEFPA systems, but tended to be somewhat longer for the FPFPA and FBFPA systems. In copolymerizing with butadiene, FBFPA, and to some extent FPFPA, showed a tendency to form sticky, syrupy, low molecular weight precoagulum. This was removed before the latex was coagulated.

Cures of these copolymers were carried out in the standard silicate recipe for 1 hour at 310°F. and 900 psi. The copolymers prepared from charges containing 75 mole % acrylate or more were soft, tacky, and short. They were difficult to mill and in the case of the higher members of the series could not be molded.

TABLE XIV
 FLUORINATED ALKOXY-ACRYLATE-BUTADIENE POLYMERS

Series	Charge Ratios		Reaction Time (Hrs.)	Approx. % Conversion	Analytical Ratios		% Swelling			Gelman T ₁₀ °C.	
	Molar Acrylate:B	Wt. Acrylate:B			Molar Acrylate:B	Wt. Acrylate:B	70:30 Iso-octane toluene	Iso-octane	Ben-zene		
FMFFA	100:0	100:0	2	100	---	---	Good	10	7	16	-32
	90:10	98:2	2-1/2 3	75	65:35	90:10	Soft, tacky, short	22	10	24	-35
	80:20	95:5	2-1/2 3	60	---	---	"	54	22	48	-42
	75:25	94:6	3-1/2	80	---	---	"	63	24	63	-45.5
	60:40	88:12	2-1/2 3	50	36.5:63.5	74:26	Good rubber	168	57	131	-36.5
	50:50	83:17	5-7	60	---	---	"	227	63	174	-52
	25:75	62.5:37.5	"	40	---	---	"	945	348	846	-53

WADC TR 52-197 Pt 3

100
2

TABLE XIV (continued)
 FLUORINATED ALKOXY-ACRYLATE: BUTADIENE POLYMERS

Series	Charge Ratios		Reaction Time (Hrs.)	Approx. % Conversion	Analytical Ratios		Appear. of raw polymer	% Swelling		Gelman T ₁₀ °C.	
	Molar Acrylate:B	Wt. Acrylate:B			Molar Acrylate:B	Wt. Acrylate:B		70:30 toluene	Iso-octane		Ben-zene
FEFPA	100:0	100:0	--	100	--	--	Good rubber	10-15	--	7-12	-23
	80:20	96:4	--	80	60:40	90:10	Fair rubber	10	5	8	-27
	75:25	94:6	5-1/2	80	70:30	93:7	Soft, tacky, short		Couldn't mold		
	70:30	93:7	--	80	44:56	83:17	Fair rubber	48	26	38	-37
	50:50	83:17	5-1/2	80	39:61	79:21	Good rubber	115	55	70	-44
	25:75	65.5:34.5	"	60	22:78	64:36	"	325	160	215	-50

1 83 1

TABLE XIV (continued)

FLUORINATED ALKOXY-ACRYLATE: BUTADIENE POLYMERS

Series	Charge Ratios		Reaction Time (Hrs.)	Approx. % Conversion	Analytical Ratios		Appear. of raw polymer	% Swelling			Gelman T ₁₀ °C.
	Molar Acrylate:B	Wt. Acrylate:B			Molar Acrylate:B	Wt. Acrylate:B		70:30 Iso-octane toluene	Iso-octane	Ben-zene	
FFFFA	100:0	100:0	3-5	100	--	--	Soft, tacky	12	7	13	-35
	90:10	98:2	5 - 7-1/2	50	40:60	82:18	Soft, tacky, short	71	42	42	-42
	80:20	96.5:3.5	"	50	48:52	86.5:13.5	"	Couldn't mold, crumbled			
	75:25	95:5	6-8	60	46:54	85.5:14.5	"	30	18	22	-44
	60:40	91:9	6	50	37:63	80:20	Good rubber	80	43	47	-46
	50:50	87:13	6-8	60	34:66	78:22	"	136	66	64	-50
	25:75	69.5:30.5	6-8	40	21:79	64:36	"	693	413	360	-55.5

TABLE XIV (continued)

FLUORINATED ALKOXY-ACRYLATE-BUTADIENE POLYMERS

Series	Charge Ratios		Reaction Time (Hrs.)	Approx. % Conversion	Analytical Ratios		Appear. of raw polymer	% Swelling		Gelman T ₁₀ °C.	
	Molar Acrylate:B	Wt. Acrylate:B			Molar Acrylate:B	Wt. Acrylate:B		70:30 Iso-octane toluene	Iso-octane zene		
FBFPA	100:0	100:0	6-1/2	100			Soft, tacky	2	13	29	-31
	90:10	99:1	4-1/2	60	63:37	93:7	Soft, tacky, short				Couldn't mold, crumbled
	80:20	97:3	7	60	60:40	92:8	"				Couldn't mold, crumbled
	75:25	96:4	6-1/2	50	--	--	"				Couldn't mold, crumbled
	60:40	92:8	5-8	60	39:61	83:17	Fair rubber	86	48	46	-44
	50:50	89:11	24	60	29:71	76:24	Good rubber	185	99	76	-53
	25:75	72:28	24	60	18.5:81.5	64:36	"	535	326	288	-59

WADC TR 52-197 Pt 3

- 85 -

Contrails

They crumbled on removal from the mold, even after a 1/2 hour cure.

Figure 6 shows the swelling volumes in 30% aromatic fuel vs. the T_{10} curves of the alkoxy acrylate:butadiene copolymers as compared with Buna-N, FBA:butadiene, and FHA:butadiene. These are the data of Table XIV. From the graph, it can be seen that the curves of the four series (FMFPA, FEFPA, FPFPA, FBFPA) are very close together, the FMFPA being perhaps slightly superior to FEFPA. The FMFPA series seems to offer the best balance of properties, and it is also fortunately the case that the alkoxy acid from which this monomer is synthesized can be produced in the cell in better yields than the acids required for any of the other three monomers.

Samples of poly-FMFPA and poly-FEFPA were studied further. In Table XV, the properties of vulcanizates prepared in the standard oxide and polyamine recipes are shown. The polyamine recipe is discussed more fully in a later section. The poly-FMFPA appears considerably superior in most physical properties to the poly-FEFPA, by these tests, but a comparison using the same cure is not yet available. It will be noted

Contrails

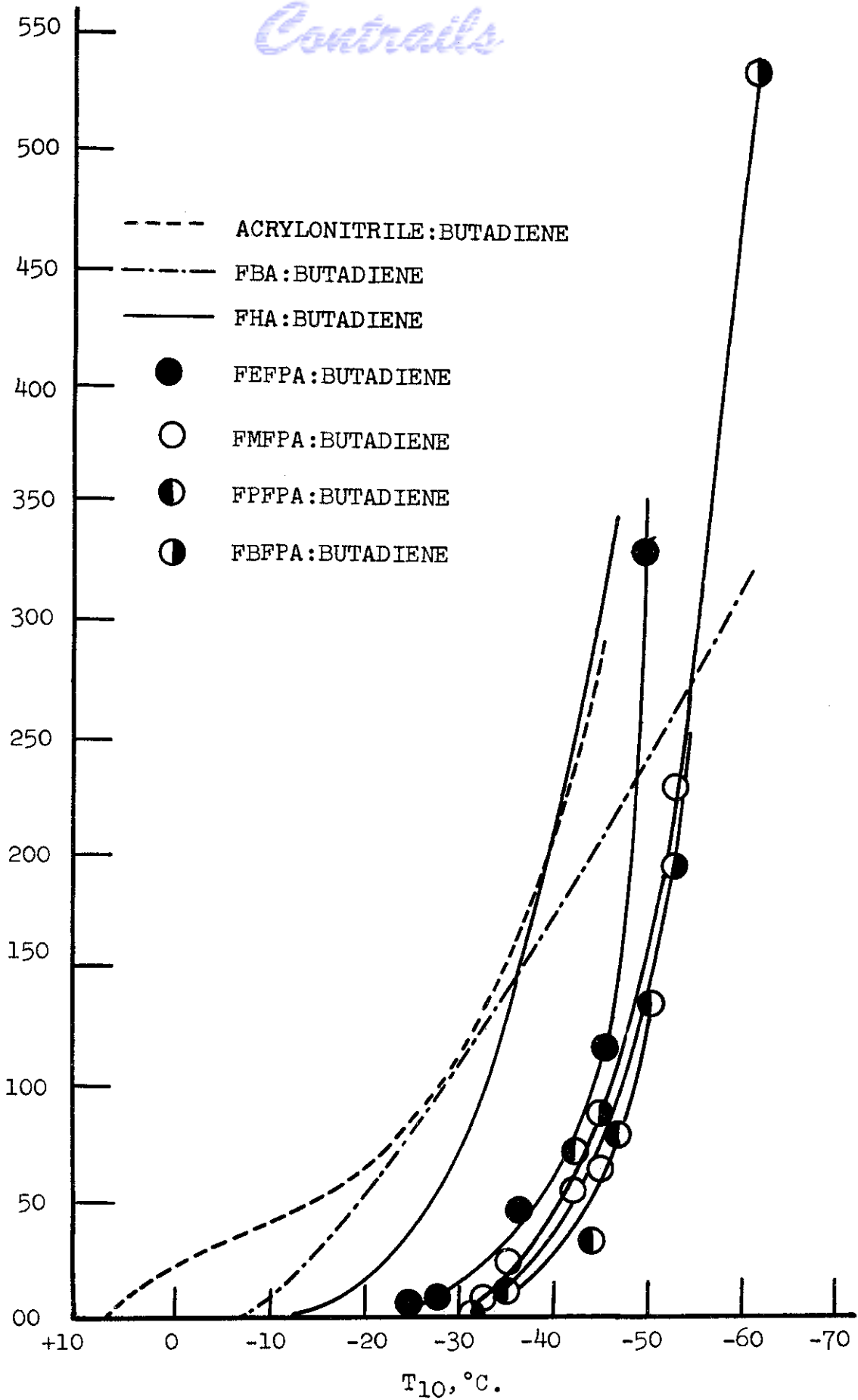


FIGURE 6

GEHMAN T_{10} VS. PERCENT SWELLING IN 70:30 ISO-OCTANE TOLUENE
WADC TR 52-197 Pt 3 - 87 -
Approved for Public Release

TABLE XV

PROPERTIES OF VULCANIZED FMFPA AND FEPPA HOMOPOLYMERS,
COMPARED TO POLY-FBA AND POLY-FHA

	Poly-FBA		Poly-FHA		Poly-FEPPA		Poly-FMFPA	
	Polyamine Cure	Standard Oxide Cure	Polyamine Cure	Standard Oxide Cure	Polyamine Cure	Standard Oxide Cure	Polyamine Cure	Standard Oxide Cure
Tensile Strength, psi.	1150	900	500	500	540	540	1060	1060
Ultimate Elongation, %	360	500	600	600	380	380	270	270
Set at Break, %	9				34	34	8	8
Compression Set, Method B (70 hrs. at 212°F.)	69				54	54	61	61
Gehman T ₁₀ , °C.	-11	-6	-8	-8	-34	-34	-27	-27
ASTM Brittle Point, °C.	-13	-12	-13	-13	-38	-38	-35	-35
Per cent Swelling, 48 hours at 25°C. in								
70:30 iso-octane:toluene	17	15	16	16	23	23	21	21
Benzene	26	17	15	15	22	22	25	25
Methyl isobutyl ketone	42	40-100	27	27	29	29	--	--
Iso-octane	--	6	13	13	--	--	--	--
Toluene	--	14	17	17	--	--	--	--
Ethyl acetate	100	120	46	46	51	51	70	70
Acetone	91	--	--	--	--	--	59	59
Fuming HNO ₃	In good condition	--	--	--	--	--	In good condition	In good condition

TABLE XVI (continued)

PROPERTIES OF VULCANIZED FMFPA AND FEFA HOMOPOLYMERS,
COMPARED TO POLY-FBA AND POLY-FHA

	Poly-FBA Polyamine Cure		Poly-FBA Standard Oxide Cure		Poly-FHA Standard Oxide Cure		Poly-FEFA Standard Oxide Cure		Poly-FMFFA Polyamine Cure	
Per Cent Swelling, 70 hours at 100°C. in										
ASTM oil #3			7				5			
Skydrol			15				14			
Petroleum base hydraulic fluid			9				8			
DOS base hydraulic fluid			10				3			
% Weight loss,										
150 hours at 300°F. in air		3.9	12				8.3			4.2
150 hours at 350°F. in air		5.9	--				--			4.6

Contrails

that the poly-FMFPA shows low temperature behavior somewhat inferior to that of the poly-FEFPA; the T_{10} of the latter in the oxide cure seems to be substantially lower than that of the silicate cure (Tables XIII and XIV).

The resistance of the poly-FMFPA and poly-FEFPA to oxygenated solvents is comparable to that of poly-FHA and better than that of poly-FBA. The superior properties produced by the amine cure with poly-FBA seem to carry over to poly-FMFPA, at least so far as weight loss is concerned. The behavior in hydraulic fluids at elevated temperatures is now being studied.

We have shown above that copolymers of these alkoxy acrylate monomers with butadiene give vulcanizates in the silicate recipe which represent a considerable improvement over the FBA:butadiene and FHA:butadiene family of copolymers. Sulfur vulcanization seemed worth studying in view of the fact that the FHA:butadiene sulfur vulcanizates showed T_{10} 's considerably higher than those of the silicate vulcanizates (discussed below). It was felt that some difficulty might be experienced with the sulfur vulcanizates of the FEFPA:butadiene series.

Contrails

Two copolymers containing 20 and 48 mole % of FEFPA were prepared in the standard Duponol persulfate emulsion recipe. The details of these preparations are shown in Table XVI.

TABLE XVI
PREPARATION OF BUTADIENE:FEFPA COPOLYMERS

FEFPA	Charge Ratio		Approx. % Con.	Analytical Results		Quantity Prepared
	Wt. % Euta.	Mol. % FEFPA Buta.		Wt. % FEFPA Buta.	Mol. % FEFPA Buta.	
65	35	24 76	69	60 40	20 80	13.4g.
90	10	60 40	75	84 16	48 52	6.5g.

Both copolymers were compounded in the sulfur recipe shown in Appendix A for FBA:butadiene copolymer, except that the Methyl Tuads and phenyl β -naphthylamine were not used. Cure was 45 min. at 300°F. They were both readily vulcanized but only the copolymer having the higher proportion of butadiene had acceptable physical properties. The properties of the vulcanizates are shown in Table XVII. The balance of properties of these products is significantly superior to that of either FBA or FHA copolymers with butadiene, and confirms the previous results obtained in the silicate recipe. Thus, the difficulties experienced with the FHA:butadiene system, in which higher T_{10} 's were

obtained in the sulfur vulcanizate than in the silicate vulcanizate, are not observed with the FEFPA:butadiene copolymer.

TABLE XVII

PROPERTIES OF BUTADIENE:FEFPA COPOLYMERS

	<u>20:80</u> <u>FEFPA:Bd.</u>	<u>48:52</u> <u>FEFPA:Bd.</u>
Gehman T ₁₀ , °C.	-56	-41
Brittle Point, °C.	-67	appr. -41
Percent Swelling		
48 hrs. at 25°C. in 70:30		
iso-octane:toluene	130	53
benzene	130	50
toluene	130	46
MIBK	87	44
70 hrs. at 100°C. in ASTM oil		
#3	50	14
Petrol. base		
hydr. fluid	74	12
DOS base		
hydr. fluid	79	16
"Skydrol"	67	22

The butadiene copolymers of FMFPA and FEFPA represent the closest approach to satisfying the Air Force's original low temperature and solvent resistance requirements of any materials so far prepared in this program. However, as indicated above, improvement in the strength of these copolymers is needed.

B. Copolymers of Fluoroprene (FP) with FHA and γ -(Perfluoromethoxy)-1,1-Dihydroperfluoropropyl Acrylate (FEFPA)

Copolymers of FHA and FEFPA with fluoroprene have been prepared in the standard Duponol recipe with the object of obtaining products superior to the corresponding butadiene copolymers of these acrylates in the balance of low temperature and solvent resistance. The conditions and results of these experiments are shown in Table XVIII in which the swelling and low temperature properties are given for vulcanizates prepared in the standard silicate recipe.

It can be seen that fluoroprene tends to enter the copolymer rather rapidly. The samples were fairly good rubbers and although not high in strength they were quite readily molded. When the T_{10} values and swelling volumes in 70:30 iso-octane:toluene and in benzene are compared, it is apparent that these copolymers are not quite so good in balance of properties as the series of copolymers with butadiene and FEFPA

TABLE XVIII

COPOLYMERS OF FLUOROPRENE (FP) WITH 1,1-DIHYDROPERFLUOROCHEXYL
ACRYLATE (FHA) AND (FERFLUOROETHOXY)
1,1-DIHYDROPERFLUOROPROPYL ACRYLATE (FEFPA)

Comonomers	Charge Ratio Acrylate:FP Weight Moles	Approx. Conversion	% Fluorine in Copolymer	Monomer Ratio in Copolymer Acrylate:FP Weight Moles	T ₁₀	Swelling Volumes*			
						Benzene	Toluene	Iso-octane	
FHA & FP	5:1	60 to 75%	51%	75:25	38:62	-21°C.	45	45	15
FEFPA & FP	4:1	65 to 80%	41%	54:46	21:79	-39°C.	149	100	37

Contrails

C. Poly-1,1-Dihydroperfluorobutyl Acrylate (Poly-FBA)

1. Preparation of Poly-FBA: Six homopolymerizations of FBA have been carried out on a 5-gallon scale within this contract period. The compounding and vulcanization of poly-FBA is discussed in more detail in a later section (p.112). The polymers from Runs 1, 2, and 5 were believed to be somewhat lower in molecular weight than the others. Runs 3, 4, and 6 were combined into one 15-lb. batch. Samples of this material vulcanized in the standard oxide recipe exhibit an unusual amount of bubbling and very high elongation. Though set at break was not abnormal, the polymer appeared to be poorly cured. The anti-oxidant, the method of coagulation, and the presence of impurities were eliminated as possible sources of these difficulties. Only Runs 3 and 6 exhibited bubbling, but the high elongation was exhibited by all lots. The cause of these unusual properties is not yet entirely clear.

The polymerization of FBA in the presence of 15 parts of Spheron 9 carbon black was mentioned in Quarterly Report #14. More recently, larger amounts of black, 25, 35, and 50 parts, have been used and it

Contrails

has been found that polymerization can be successfully carried out. After 19 hours at 50°C., the reactions had reached completion in all cases except the one containing 50 parts black, which reached 42% conversion. Analytical results show that the polymers containing 16, 24 and 50 parts of black respectively. When vulcanization was attempted, it was found that the products thus prepared did not cure properly in the standard magnesium oxide recipe (Appendix A). Therefore, it is not yet possible to state whether or not carbon black has any reinforcing effect when incorporated under these conditions.

Emulsifiers other than Duponol ME (used in the above runs) have been tested for the emulsion polymerization of FBA. With Daxad 11, the reaction was slow and the yield poor. Hercules Emulsifier No. 52, a non-ionic reagent, permitted high conversions but also caused almost complete preccagulation. With two parts of Aerosol OT good conversions were obtained, giving a polymer having an inherent viscosity of 2.9 in 60:40 methyl perfluorobutyrate:acetone. With four parts of the emulsifier, a polymer having an inherent viscosity of 3.2 was found. The latter represents a higher

Contrails

molecular weight than previously observed for any emulsion product. Rosin Amine D acetate (Hercules) was also tried as an emulsifier but most of the polymer coagulated as formed.

The high molecular weight polymer made in the Aerosol OT emulsion has been compounded and vulcanized, but difficulties in processing and molding were encountered. So far, it appears that the optimum inherent viscosity is 1.5-2.0 in 60:40 methyl perfluorobutyrate: acetone. The products of lower molecular weight are weak, while those of higher molecular weight are difficult to mold. With other curing recipes, higher molecular weight material may be desirable. The preparation and evaluation of polymers of still higher molecular weight than the above is now in progress. It is believed to be particularly important to test these materials in the new polyamine recipe (see below).

It was found necessary to develop a revised method of coagulation for these larger quantities of latex. Coagulation by freezing, which is satisfactory for small quantities, is not suitable for larger scale work because large lumps of polymer are formed which are

Contrails

difficult to wash. The method developed for further work involves addition of the latex with vigorous stirring to a 1:1 water-methanol solution containing aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$) at 0° to -20°C . The low temperature prevents agglomeration to large lumps, and a fine crumb is obtained which is readily washed to a product of low ash content. Polymer prepared in this way has been found to age as well at 150°C . as polymer prepared by coagulation with barium chloride or by freezing.

2. Copolymerization of FBA and FHA

a. Copolymers with Chloroprene

We have previously reported that attempts to copolymerize FBA with very small amounts of hydrocarbon butadiene have been disappointing because of the low molecular weight copolymers obtained. A similar series of copolymers of FBA and chloroprene (2-chlorobutadiene-1,3) has now been made. The standard Duponol-persulfate emulsion recipe was employed. As shown in Table XVIX, the inherent viscosity of the copolymers was low even when no mercaptan was present during polymerization. Further work with this system is not planned, since the same difficulties are encountered as with butadiene itself.

- 98 -

WADC TR 52-197 Pt 3

Contrails

TABLE XVIX

FBA:2-CHLOROBUTADIENE COPOLYMERS

<u>Sample No.</u>	<u>Charge, Parts by Wt.</u>			<u>% Conversion</u>	<u>$\langle \eta \rangle$ *</u>
	<u>FBA</u>	<u>2-chloro-butadiene</u>	<u>t-C₁₂ Mercaptan</u>		
1	99	1	--	86.2	0.81
2	99	1	--	90.9	0.63
3	98	2	--	89.8	0.63
4	98	2	--	95.5	0.65
5	95	5	--	81.2	--
6	95	5	--	89.6	0.64
7	95	5	0.10	86.0	0.50
8	95	5	0.10	87.3	0.53
9	95	5	0.25	86.7	0.41
10	95	5	0.25	Broke	--
11	95	5	0.50	84.6	0.35
12	95	5	0.50	83.2	0.36

* 0.9 g. per 100 ml. in methyl perfluorobutyrate

b. Copolymerization of FBA with Non-Fluorinated Alkoxyalkyl Acrylates

Earlier work with 90:10 ratios of FBA and ethoxypropyl acrylate was directed to obtaining copolymers which might permit vulcanization through the alkoxyalkyl side chain. It was found that this copolymer did not vulcanize in typical sulfur recipes even after six hours at 310°F. Tests with other curing recipes have also been disappointing.

Another interest in copolymers of FBA with alkoxyalkyl acrylates is the solubility or swelling characteristics of such copolymers. It will be recalled that FBA homopolymers swell very little in either aliphatic or aromatic hydrocarbons, and polyethoxyethyl acrylate showed surprisingly low swell in 70:30 iso-octane:toluene.

Copolymers containing 25 and 50 parts of ethoxyethyl acrylate and methoxypropyl acrylate have now been made. These polymers were cured in the following accelerated sulfur recipe:

Contrails

	<u>Parts</u>
Polymer	100
HAF Black (Philblack O)	35
Zinc Oxide	10
Sulfur	5
Tetramethyl Thiuram Disulfide	2

Cure - 6 hrs. at 310°F.

The results of these tests are shown in Table XX. Poor physical properties should be disregarded, since no attempt was made to develop optimum cures. The swelling values can be regarded, however, as conclusive. In one case, a copolymer of the fluorine-containing acrylate with the hydrocarbon alkoxyalkyl acrylates swelled much more greatly than either homopolymer. This result appears logical if one considers the probable cohesive energy densities of these copolymers.

No further work is anticipated with this type of system.

- 101 -

WADC TR 52-197 Pt 3

TABLE XX
 COPOLYMERS OF FEA AND ALKOXYALKYL ACRYLATES

Sample Number	Alkoxyalkyl* Acrylate Wt. %	Tensile Test		Swelling %			Gehman T ₁₀
		Elongation %	psi. at break	70:30 Toluene	Benzene	Iso-octane	
2	FEA 50	750	211	110	853	6	-17.5
4	MPA 50	800	308	44	979	6	-17.5
6	FEA 25	350	472	33	110	9	-5.5
8	MPA 25	350	477	33	82	12	-9.5
--	FEA 100	--	--	50	--	--	-35.0

*FEA = ethoxyethyl acrylate
 MPA = methoxypropyl acrylate

c. Copolymers of FBA with Vinyl Triethoxysilane

FBA was copolymerized with vinyl triethoxysilane in solution and emulsion. By incorporating vinyl triethoxysilane it was hoped to introduce groups capable of a new type of cross-linking, i.e. by hydrolysis of ethoxysilyl groups with the formation of Si-O-Si cross-links. This might be accomplished, for example, by the use of hydrated salts, such as $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, which would yield water on heating.

Details of the polymerizations are shown in Table XXI. Some gelation occurred during all the copolymerizations. The polymers molded poorly, but could be cured when compounded with $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$. The products were quite weak, however. The precoagulum obtained in the emulsion systems appeared to be highly cross-linked, probably due to hydrolysis of the silane. The silane was shown to hydrolyze rapidly, even at the relatively low polymerization temperature used. Vistex viscosities indicated the copolymers probably had low molecular weights.

TABLE XXI

COPOLYMERS OF FBA AND VINYL TRIETHOXY-SILANE

Tube No.	Weight % Vinyl Silane Charged	System	Reaction Conditions	Yield %	$\langle \eta \rangle^*$	Weight % Vinyl Silane in Copolymer	Remarks (Samples milled with 10% Na ₂ CO ₃ ·10H ₂ O)
3-2	5	Emulsion**	1.5 hr. at 30°C.	74	--	1.55	Flows poorly in mold; very little cure.
3-3	10	"	"	76	--	1.77	"
4-1	0	"	"	92	2.03	--	No cure.
4-2	15	"	"	51	0.21	4.25	Flows poorly in mold; mild cure.
4-3	25	"	"	67	0.10	4.6	Flows poorly in mold; fairly good cure.
4-4	100	"	"	--	--	--	50% of monomer hydrolyzed.
4-5	10	Solution***	18 hr. at 50°C.	74	--	6.7	Molds and cures quite well, but is weak.
4-6	0	"	"	83	1.05	--	--

* In 0.1% solution in 2:1 acetone:MFB.

** Water - 180, monomers - 100, DuPont ME - 3, sodium bisulfite - 0.4, potassium persulfate - 0.2.

*** 50% solution in xylene hexafluoride.

d. Copolymers of FHA and Acrylic Acid

FHA was copolymerized with 5 and 10 parts of acrylic acid using emulsion systems with dodecylamine hydrochloride. Since the polymer pre-coagulates, 1 part of Triton K-60 (cetyl dimethyl benzyl ammonium chloride) was added as a stabilizer in half of the reaction tubes, but it seemed to have little effect. Analytical results showed both polymers to have about the same amount of acrylic acid, 6.5 wt. % (25.5 mole %). The polymer was insoluble in methyl perfluorobutyrate, ethyl acetate, and a 1:1 mixture of the two. Since only about two grams of each copolymer was made, no further solubility studies were carried out.

These polymers and samples of FBA and FHA were cured at 310°F. for three hours, using the standard silicate recipe. Swelling volumes of the acrylic acid copolymers in 30% aromatic fuel, iso-octane, toluene, acetone, Skydrol, and a synthetic lubricant having a di-(2-ethylhexyl)sebacate base were measured. The values obtained exhibited no reduction in swelling volume compared to poly-FHA. The T_{10} 's were also about the same for the four samples. However, acrylic acid did improve the high temperature properties. At 150°C., 10% weight

loss for FBA was reached after 6 hours and for FHA after 14 hours, while the AcAc copolymers did not reach 10% weight loss until after about 36 hours. These results are shown in Table XXII.

3. Fundamental Copolymerization Studies

The copolymerization ratios of FBA with butadiene, methyl methacrylate, and styrene have been determined in the usual way. The method involves analyses of very low conversion copolymers from charges of different initial monomer ratios. Polymers were isolated by freezing and careful washing, followed by purification through repeated solution in xylene hexafluoride:benzene mixtures and reprecipitation with methanol. The data obtained are tabulated in Tables XXIII, XXIV, and XXV. The results are probably most clearly illustrated by the monomer-polymer composition curves in Figure 7. The curve for FBA:butadiene is that of a typical "cross-over" system similar to that for butadiene:acrylonitrile. The strong tendency toward alternation is illustrated by the reactivity ratios, r_1 and r_2 , calculated from the curves for the FBA:butadiene system (Table XXVI). Butadiene radicals

TABLE XXII
 COPOLYMERS OF 1,1-DIHYDROPERFLUOROHEXYL ACRYLATE (FHA) AND ACRYLIC ACID (AcAc)

Sample	% Swelling Volumes, 48 hours at Room Temperature					Synthetic Lubricant Di-(2-Ethylhexyl) Sebacate Base	T ₁₀ °C	Hours at 150°C. to reach 10% Wt. Loss
	Iso-octane: Toluene	Iso-octane:	Benzene	Acetone	Skydrol			
A-FHA:AcAc, 10 wt. % (35 mol %) AcAc charged, 6.3 wt. % (25 mol %) AcAc Found	70:30 9-12	7-10	10-21	27-33	Lost weight	Lost weight	-9.5	37
B-FHA:AcAc, 5 wt. % (21 mol %) AcAc charged, 6.6 wt. % (26 mol %) AcAc Found	8-11	3-4	8-9	24-28	Lost weight	Lost weight	-11	34
C-FHA	0-4	0-3	0-6	15-23	Lost weight	Lost weight	-9.5	14
D-FBA	9-10	1-4	13-14	72-73	Lost weight	Lost weight	-13.5	6

Contrails

TABLE XXIII

COPOLYMERIZATION OF FBA WITH BUTADIENE*

Tube No.	Charge Composition Mol %		Reaction Time at 50°C., Min.	% Conversion	% C Found	Copolymer Composition Mol %	
	Bd	FBA				Bd	FBA
2-1	4	96	30	5.8	35.2	15.5	84.5
2-2	10	90	30	3.3	38.7	35.3	64.7
2-3	20	80	35	3.6	41.9	46.8	53.2
2-4	35	65	45	6.8	43.3	51.3	48.7
2-5	50	50	55	6.5	45.2	56.6	43.4
2-6	65	35	60	3.1	47.5	62.0	38.0
2-7	79	21	65	3.6	50.6	68.3	31.7
2-8	90	10	65	3.8	52.7	71.9	28.1
2-9	95	5	65	4.2	56.6	77.5	22.5

* In standard emulsion: monomers -100, water -180, Duponol ME -3, borax -2, potassium persulfate -1.

TABLE XXIV

COPOLYMERIZATION OF FBA WITH METHYL METHACRYLATE*

Tube No.	Charge Composition Mol %		Reaction Time at 50°C., Hr.	% Conversion	% C Found	Copolymer Composition Mol %	
	MMA	FBA				MMA	FBA
4-3	90	10	2.7	3.7	55.1	91.9	8.1
4-1	80	20	1.75	5.4	52.4	86.6	13.4
4-0	70	30	2.5	4.5	49.4	79.6	20.4
4-4	60	40	2.7	4.6	48.2	76.4	23.6
4-5	50	50	2.7	5.2	44.7	65.8	34.2
4-6	40	60	2.25	4.1	43.7	62.3	37.7
4-7	30	70	3.0	5.3	41.1	51.7-	48.3
4-2	20	80	3.0	4.9	39.2	42.6	57.4
4-9	10	90	3.5	6.1	36.4	26.3	73.7

* In bulk system, using 0.5% benzoyl peroxide initiator.

TABLE XXV

COPOLYMERIZATION OF FBA WITH STYRENE*

Tube No.	Charge Composition Mol %		Reaction Time at 50°C., Hr.	% Conversion	% C Found	Copolymer Composition Mol %	
	Styrene	FBA				Styrene	FBA
5-1	90	10	3.75	6.4	68.9	78.9	21.1
5-2	80	20	3.0	6.5	61.4	69.1	30.9
5-3	70	30	3.25	7.6	57.6	63.3	36.7
5-4	60	40	2.75	7.6	56.5	61.5	38.5
5-5	50	50	3.0	8.4	54.5	58.0	42.0
5-6	40	60	2.75	7.7	52.0	53.4	46.6
5-7	30	70	1.75	5.2	50.5	50.4	49.6
5-8	20	80	1.5	5.7	49.0	47.2	52.8
5-9	10	90	1.5	5.6	45.4	39.0	61.0

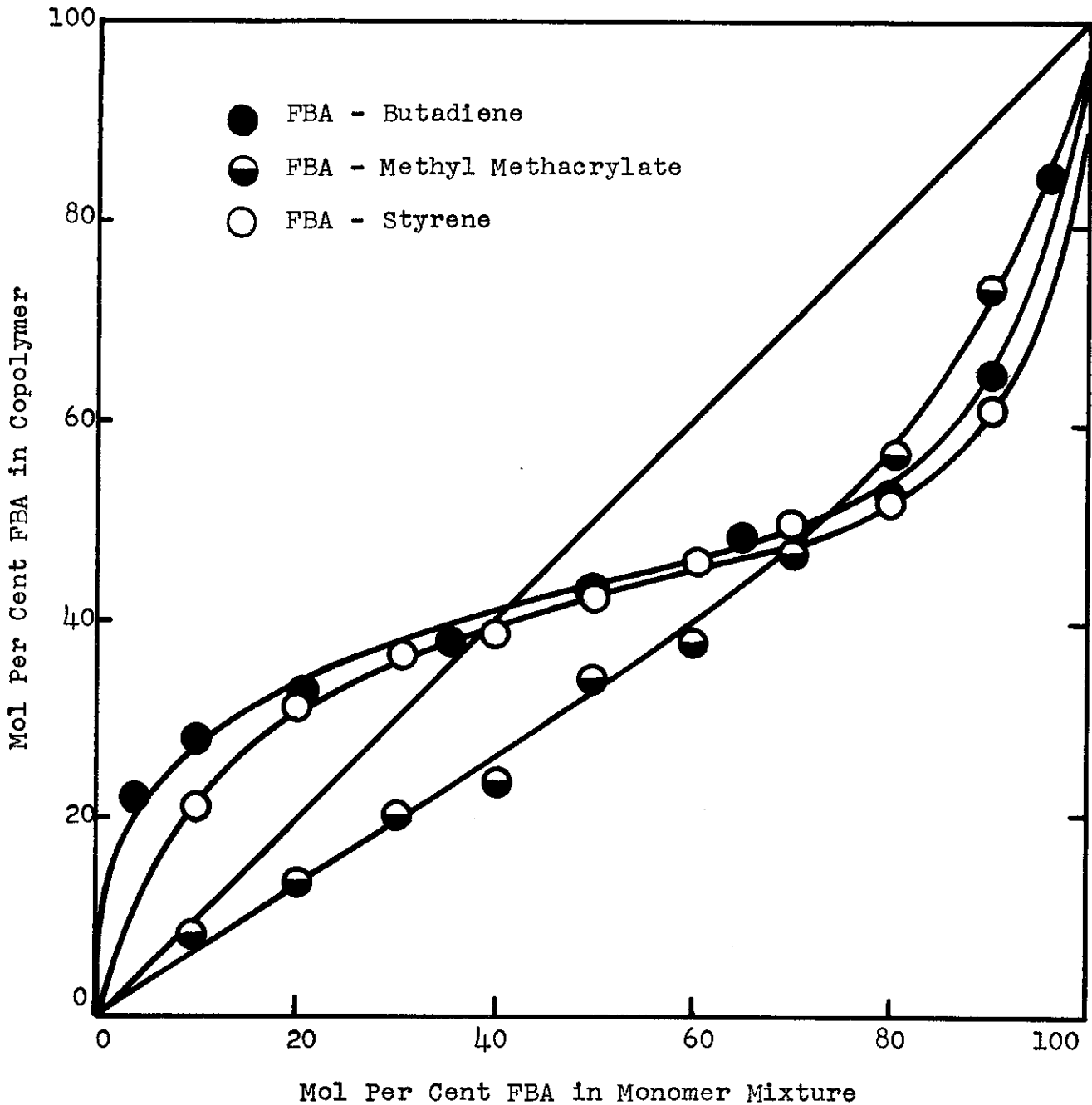
* In bulk system, using 0.5% benzoyl peroxide initiator.

TABLE XXVI

REACTIVITY RATIOS AND Q - e VALUES FOR FBA

M ₁	M ₂	r ₁	r ₂	e ₂	Q ₂
Butadiene	FBA	0.35	0.07	1.1	0.82
Methyl methacrylate	FBA	1.4	0.25	1.4	0.78
Styrene	FBA	0.33	0.07	1.1	0.64

FIGURE 7 - COPOLYMERIZATION CURVES
FOR FBA WITH BUTADIENE,
METHYL METHACRYLATE, AND STYRENE



Contrails

add three times as fast to FBA as to butadiene, and FBA radicals have a fourteen-fold preference for butadiene.

In Table XXVI these reactivity ratios are shown for the three copolymer systems studied. In the case of styrene:FBA, the values are similar to those of butadiene:FBA.

Methyl methacrylate, on the other hand, shows less tendency toward alternation in combination with FBA. In the same table, the Price-Alfrey Q and e values, calculated from our data, are shown. Fairly concordant values are obtained from the three systems studied. The average values of Q and e for FBA are 0.75 and 1.2, respectively. These values place FBA very close to acrylonitrile on the Q - e chart, quite distant from the point for methyl methacrylate ($Q=0.42$ and $e=0.6$). The strong electronegative influence of the C_3F_7 group is illustrated by these data. One practical consequence of these kinetic studies is confirmation of the observation that it is difficult to prepare homogeneous high conversion copolymers of FBA:butadiene from a charge containing small amounts of butadiene.

4. Compounding and Vulcanization of Poly-FBA and Poly-FHA

a. Vulcanization in Silicate and Oxide Recipes: Effect of State of Cure

During the current period a careful study of the effect of state of cure upon some physical properties of vulcanizates of poly-FBA and of FBA:butadiene copolymers was made. In this case the FBA:butadiene copolymer contained approximately 35 mole % of FBA.

Before describing the results of the quantitative tests, it may be well to summarize the qualitative observations made to date on the maximum tensile strength observed for poly-FBA and FBA:butadiene copolymers in various types of compounds. The polyamine cure is discussed later, and is not considered here.

(1) Tensile strengths of approximately 1000 psi. appear maximum for either oxide or silicate vulcanizates with or without carbon black. Thus, no carbon black reinforcement is observed for the homopolymers or butadiene copolymers with either of these two curing systems.

(2) As expected, sulfur does not vulcanize the homopolymer of FBA.

Contrails

(3) As reported earlier, sulfur readily vulcanizes FBA:butadiene copolymers to tensile strengths of 2000 to 2500 psi. in the presence of an optimum loading of channel black. Very weak compounds (i.e., tensile strengths 300 psi.) are obtained, however, by sulfur curing in the absence of a reinforcing agent.

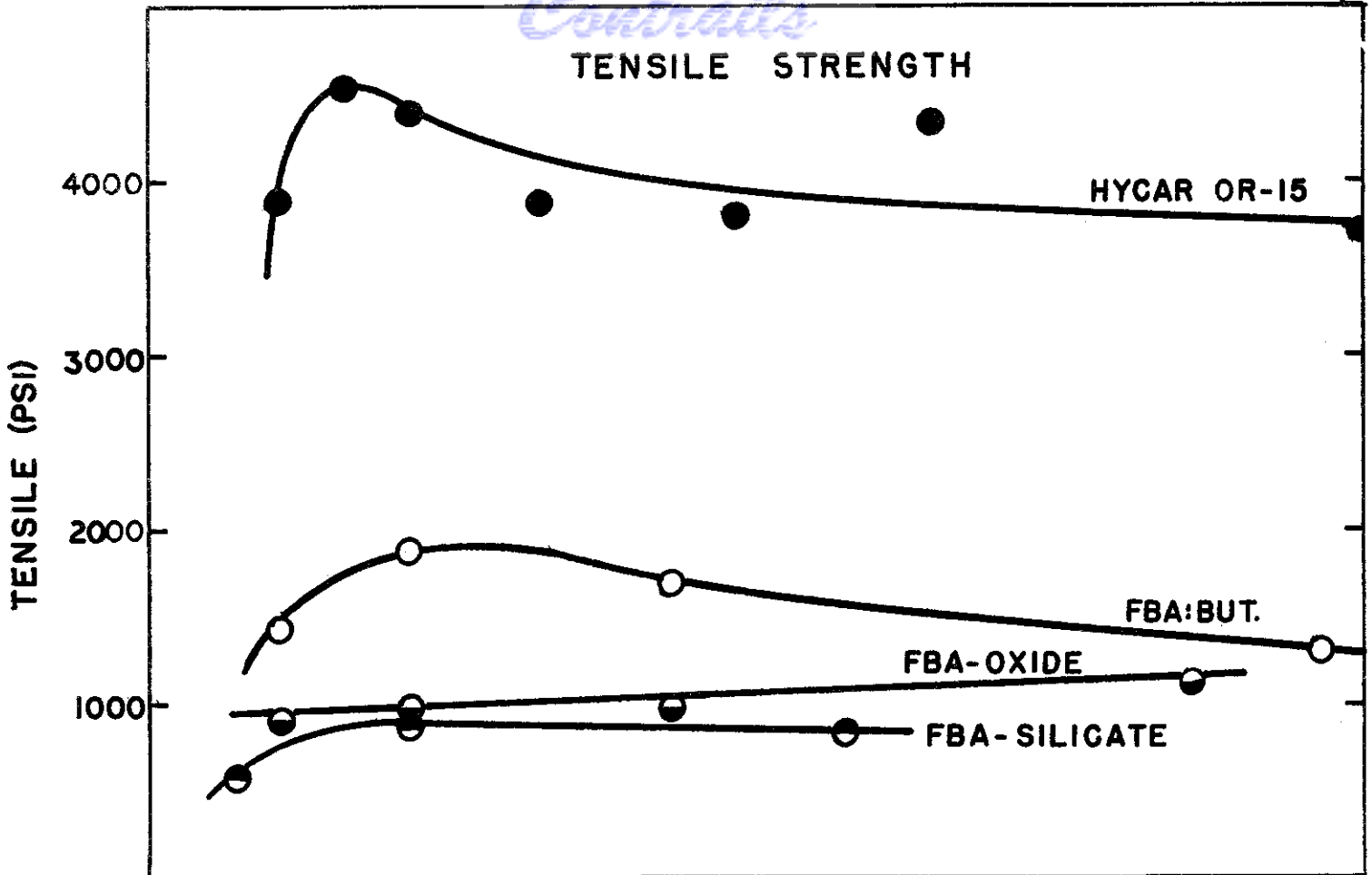
For tests of the effect of state of cure, four compounds were chosen: the homopolymer with the silicate and oxide cures, the FBA:butadiene copolymer with carbon reinforcement and sulfur vulcanization, and Hycar OR-15, sulfur-cured with black. The formulae are shown in Appendix A of this report. Samples were cured to four or more curing times with the longest being greatly in excess of that used in our screening work. For purposes of convenient graphing, an arbitrary abscissa scale was chosen to represent the state of cure.

Each division mark on the abscissas of Figures 8, 9, and 10 represents:

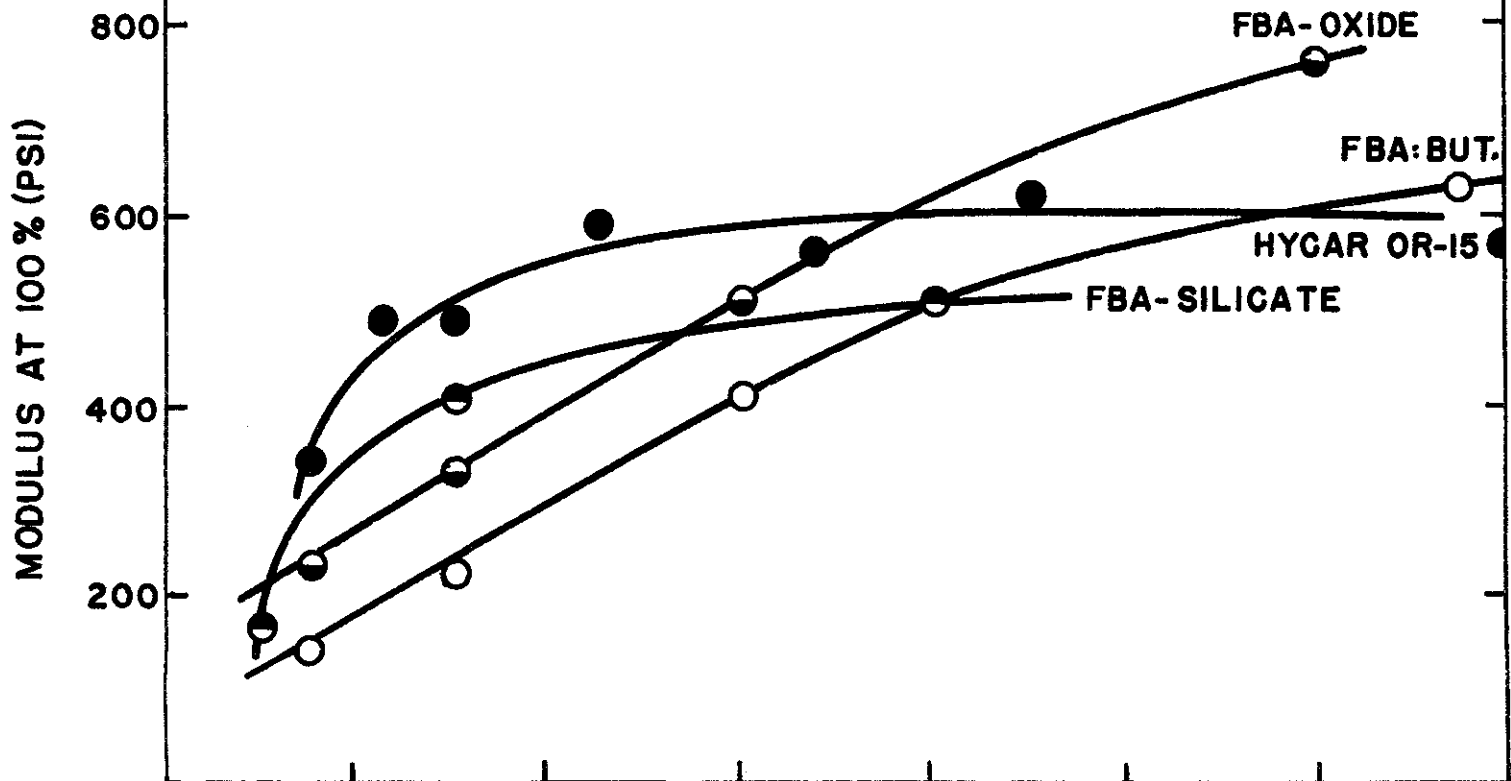
FIGURE 8

Controls

TENSILE STRENGTH



MODULUS AT 100 % ELONGATION



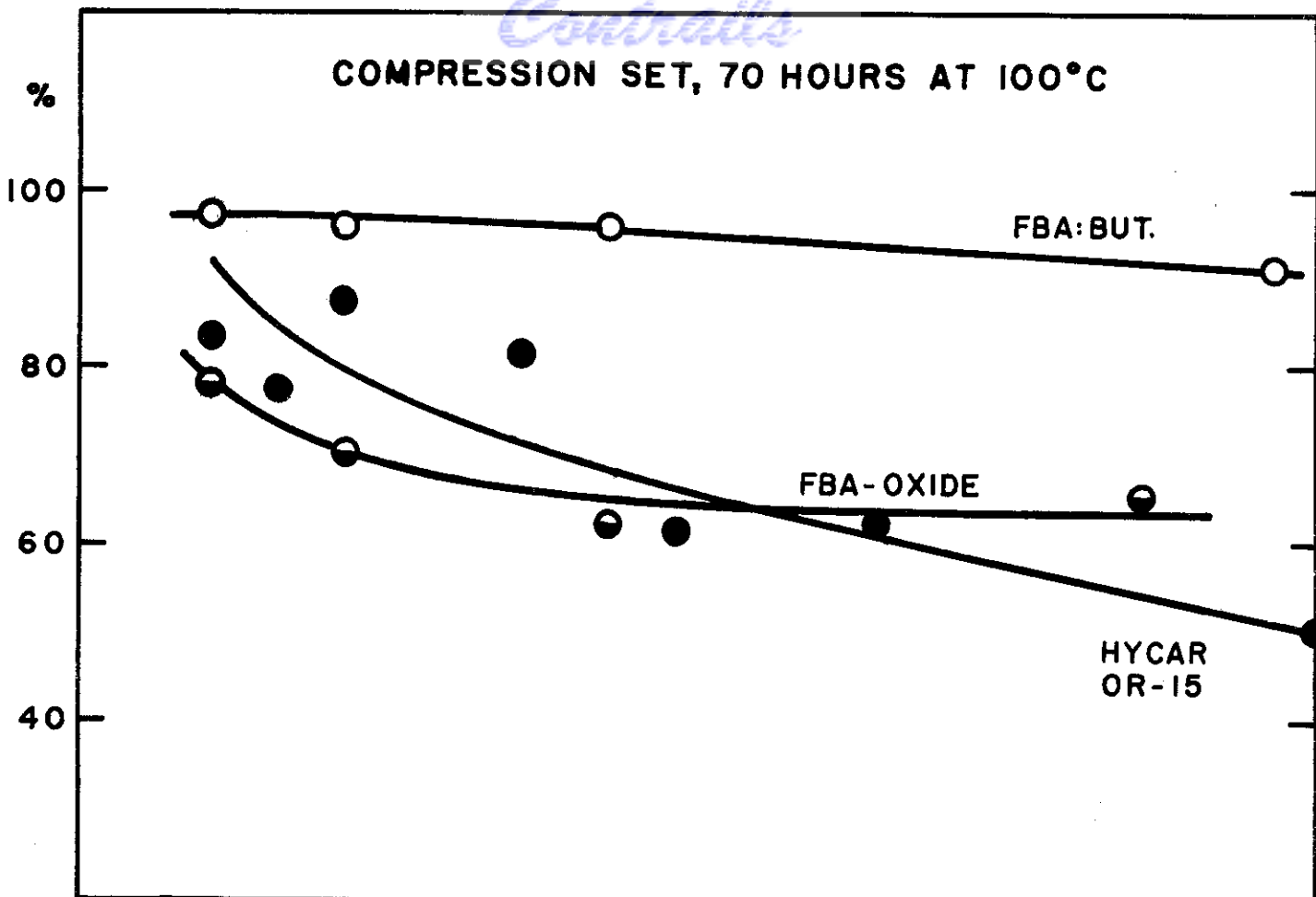
INCREASING CURE →

(See Text P.117)

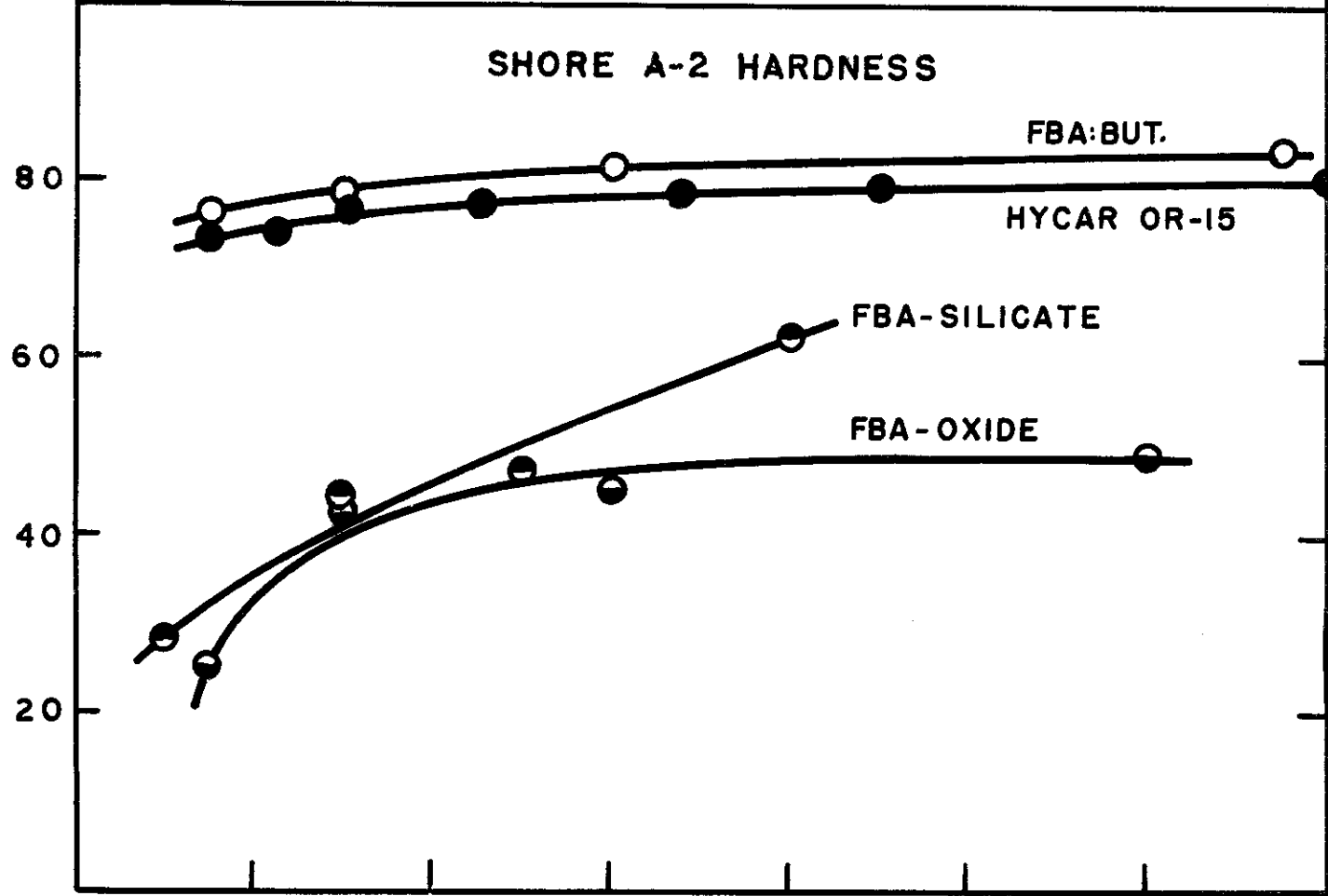
FIGURE 9

Contrails

COMPRESSION SET, 70 HOURS AT 100°C



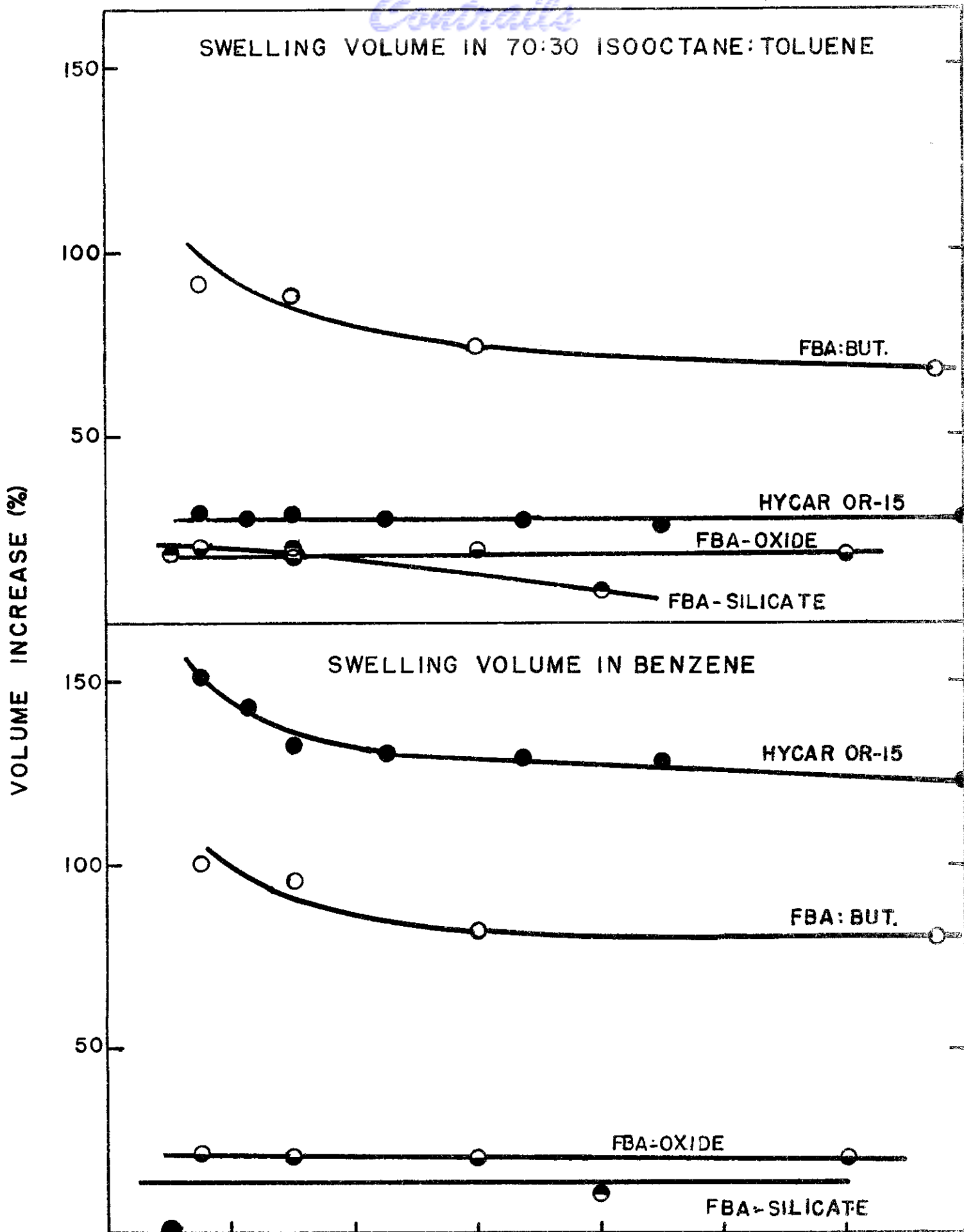
SHORE A-2 HARDNESS



INCREASING CURE →

(See Text P. 117)

FIGURE 10



Contrails

Hycar OR-15	13-1/3 min at 300°F.
FBA:Butadiene (35 mole %)	6-2/3 min at 300°F.
Poly-FBA, silicate cure	120 min at 310°F.
Poly-FBA, oxide cure	40 min at 310°F.

In Figure 8, the tensile strength and 100% modulus of these four compounds are shown. Advancing cures are observed for the oxide cured poly-FBA and the sulfur-cured FBA:butadiene copolymer. In general, however, it appears that the times arbitrarily chosen for single cures in earlier work did not result in misleading conclusions.

In Figure 9, compression set values and Shore A-2 Hardness values of the samples are shown at the various degrees of cure. Poly-FBA has not been cured to low compression set in the silicate or oxide recipes and to hardness values greater than 60 for a gum compound. Further work is needed. The FBA:butadiene copolymers were in a more acceptable hardness range, but still high in compression set. The set values for the Buna-N compound probably reflect the absence of plasticizer as well as the lack of enough curative for a tighter cure.

Contrails

In Figure 10, the swelling values in 70:30 iso-octane:toluene and in pure benzene for these same compounds are shown. After a short initial curing period, further cure has little influence upon volume swelling in these solvents. These graphs again illustrate the relative insensitivity of FBA-containing polymers to the aromatic content of an aliphatic-aromatic hydrocarbon mixture. Thus, in the 70:30 blend, the FBA:butadiene copolymer swells approximately three times as much as Hycar OR-15. In benzene, however, the order is reversed. Again the swelling of the homopolymer of FBA is not changed with the change in fuel.

b. Vulcanization with Polyamine Recipes

We have known for some time that polyfunctional amines readily crosslink poly-FBA, but the product has always been extremely weak and friable. It has now been found that polyfunctional amine vulcanizates of good physical properties can be prepared. Two recipes have so far been developed that give good results. These are:

Contrails

	Recipes	
	<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 O)	35.0	35.0
Triethylene tetramine	1.0	--
Trimene Base	--	1.0
Cure, Minutes at 300°F.	60.0	60.0

Properties of these compounds are shown in detail in Table XXVII.

As anticipated, solvent swelling and low temperature properties are substantially the same as with silicate or oxide curatives. However, the amine vulcanizates resist attack by fuming nitric acid and by dilute alkali, whereas oxide compounds are quickly disintegrated by these reagents. No visible change takes place in amine-cured samples immersed for 5 days in fuming HNO_3 , and they appear to remain tough and flexible. The vulcanizates do not disperse in 10% NaOH , though they do swell greatly. Retention of tensile strength at elevated temperatures is very much

Contrails

TABLE XXVII

PROPERTIES OF POLYAMINE VULCANIZATES OF POLY-FBA

<u>Recipe No.</u>	<u>A</u>	<u>B</u>
Modulus at 300% Elongation, psi.	1020	--
Tensile Strength, psi.	1150	1230
Ultimate Elongation, %	360	300
Set at Break, %	9	20
Hardness (Shore Duro A)	56	61
Resilience (Bashore), %	6	7
Compression Set, ASTM Method B (70 hrs. at 212°F.)		
as molded	69	53
tempered 48 hrs. at 300°F. in air	23	33
Gehman Freeze Test, T ₁₀ , °F.	12	12
ASTM Brittle Point, °F.	9	7
Ozone Test	Inert	Inert
Tensile Strength at 212°F., psi.	600	580
Ultimate Elongation at 212°F., %	180	150
Tensile Strength at 250°F., psi.	470	425
Ultimate Elongation at 250°F., %	155	130
Per cent Swelling, 48 hrs. at 77°F. in		
70:30 iso-octane:toluene	17	16
Iso-octane	8	8
Benzene	26	23
Acetone	91	86
Methyl ethyl ketone	86	84
Methyl isobutyl ketone	42	39
Ethyl alcohol	9	9
Ethyl acetate	100	95
10% H ₂ SO ₄	0	3
10% NaOH	225	186
Fuming HNO ₃	In good	In good
	condition.	condition.
Per cent Swelling, 70 hrs. at 212°F. in		
Water	30	21
ASTM Oil No. 3	3	0
Petroleum base hydraulic fluid	3	3
Skydrol	9	9
Per cent Swelling, 70 hrs. at 350°F. in		
Di-(2-ethylhexyl) sebacate fluid	2	-3
Di-(2-ethylhexyl) adipate fluid	3	3
Blended silicate ester	-3	3
Polyglycol base engine oil	3	13

superior to all diene rubbers, though it is not as good as in fluorine-free polyacrylates with the recipes developed thus far.

The stearic acid in these recipes is a processing aid and also activates the cure. Sulfur is probably not a cross-linking agent here, but serves as a retarder. It reduces scorching and improves heat stability (see below). Metallic oxides seriously interfere with the cure, the dithiocarbamate accelerators have been found to be ineffective.

The effect of black loading was studied in a separate series of cures, all carried out in Recipe A, but with variable black and a cure time of 45 min.

TABLE XXVIII

Effect of Black Loading in Recipe A, 45 Min. Cure

<u>HAF Black, Parts</u>	<u>0</u>	<u>20</u>	<u>30</u>	<u>40</u>	<u>50</u>
Modulus at 100% elongation, psi.	30	75	190	440	530
Tensile strength, psi.	80	390	630	920	710
Ultimate elongation, %	230	450	310	310	180
Set at break, %	0	13	0	25	38
appearance	porous	some bubbles	OK	OK	OK

The improvement in compression set, achieved by tempering the samples at 300°F. after molding, is highly encouraging and indicates the possible elimination of a major defect.

The chief beneficial effect produced by these amine cures is improvement in retention of properties on heat aging. This will be discussed in the next section.

5. Heat Stability of Poly-FBA and Poly-FHA

Preliminary data were reported in the third annual progress report of this contract, describing the change in weight and physical appearance of vulcanized poly-FBA and FBA:butadiene copolymers during oven aging. Poly-FBA vulcanized with mixture of lead and magnesium oxides ("oxide cure") appeared most stable at temperatures of 150° to 200°C. Qualitatively, this compound retained flexibility much better than silicate vulcanized poly-FBA or the copolymers of FBA with butadiene.

Quantitative determinations of the heat stability of oxide vulcanized poly-FBA have now been made in comparison with a non-heat-advancing commercial

Contrails

Buna-N compound:

Hycar OR-15	- 100
Phenyl β -naphthylamine (Neozone D)	- 1
Zinc oxide (Kadox 15)	- 5
Tetramethyl thiuram disulfide (Methyl Tuads)	- 2.5
Zinc dibutyl dithiocarbamate (Sharples 77-0)	- 2.5
Litharge	- 2.5
SRF carbon black (Furnex)	- 40

Cure: 45 minutes at 310°F.

Modulus, tensile, and ultimate elongation values for these specimens after various times of heating at 150-200°C. are plotted in Figure 11. In the case of the Buna-N compound, the discontinuation of the tensile and elongation curves indicates that the samples had become too brittle for measurement in the stress-strain tester. It is apparent that after two to three days at 150° or about three hours at 200°C., the poly-FBA compound was more flexible and stronger than the Buna-N compound. It is of interest that the tensile strength of the FBA compound, although relatively low, does not change during the heating periods involved. At the temperatures in this range, poly-FBA offers an advantage over rubbers containing substantial amounts

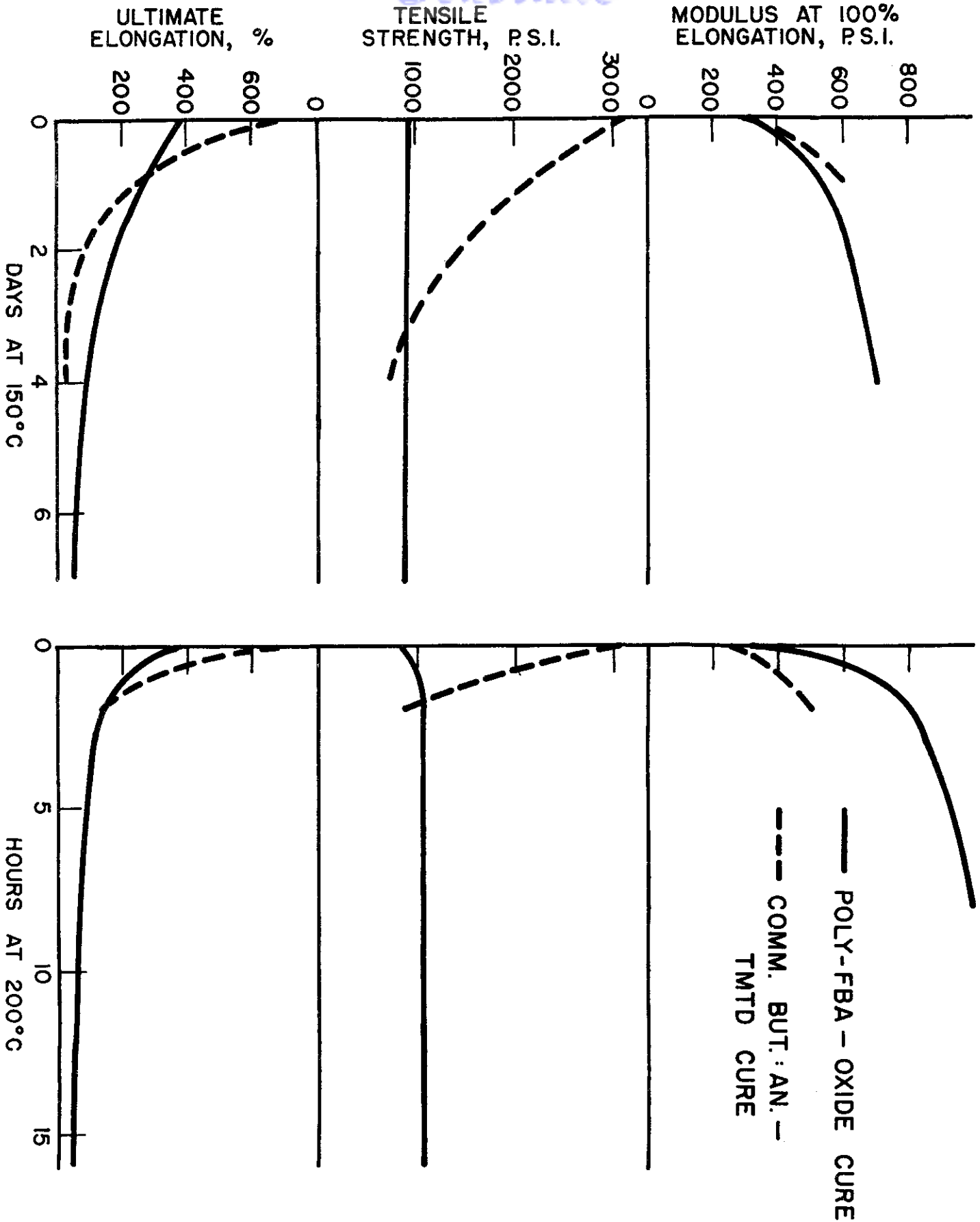


FIGURE 11 HEAT AGING OF POLY-FBA

Contrails

of butadiene.

Further heating tests with FBA copolymers containing relatively small amounts of butadiene show that a sulfur vulcanizate of a copolymer containing 5 mole % of butadiene was still soft and flexible after 30 hours at 200°C. Oxide vulcanizates appeared comparable but silicate vulcanizates embrittled much more rapidly. Polymers of substantially higher diene content embrittle still more rapidly.

For the purpose of identification of volatile products from FBA samples heated to high temperatures, the silicate vulcanized materials were selected. This permitted volatilization and collection of much larger amounts of material. Pyrolysis products at 270°C. of the silicate vulcanized poly-FBA were shown to be mostly $C_3F_7CH_2OH$. Also present were water, carbon dioxide, and small quantities of carbon-fluorine compounds. The total weight loss at this temperature was 29%. Unvulcanized poly-FBA heated to 300°C. evolved small amounts of volatiles shown by infrared spectroscopy to be composed of carbon-fluorine compounds. As before, the unvulcanized material degraded and became soft during heating whereas the vulcanizate became brittle.

- 125 -

WADC TR 52-197 Pt 3

Contrails

In these experiments samples were heated in vacuum with 30 minutes at each temperature level, the temperature being raised in 25° steps, successively with the same sample. The data are shown in Tables XXIX and XXX.

At the present time there is not sufficient quantitative information from pyrolysis or other tests to establish any mechanism of degradation or vulcanization. However, two possible mechanisms for elimination of $C_3F_7CH_2OH$ are hydrolysis by the alkaline vulcanization ingredients, or a Claisen reaction between adjacent chains. Studies on the vulcanization and structure of polyacrylic rubbers by S. T. Semegen and J. H. Wakelin (Rubber Age, Vol. 71, No. 1, April 1952), indicate that the latter type is responsible in hydrocarbon polyacrylates and that it is catalyzed by the alkaline materials. For this reason, it might be anticipated that if inorganic oxides and other alkaline substances could be eliminated from the curing recipe, greater heat stability might result.

Heat aging results for poly-FBA and poly-FHA cured in the oxide and "A" polyamine recipe are presented in Tables XXXI and XXXII. Table XXXI gives

Contrails

TABLE XXIX

PYROLYSIS OF POLY-FBA - PO 227, LOT 3

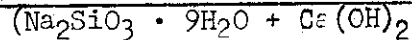
Original weight poly-FBA = 1.3338 grams

Original # 3.12

<u>Immersion Time, mm.</u>	<u>Temperature °C.</u>	<u>Pressure mm.</u>	<u>Noncumulative Weight Loss g's per 1/2 Hr.</u>	<u>Color of Residue</u>
30	70	4	0.0090	White
30	100	4	0.0085	White
30	125	4	0.0077	White
30	150	4	0.0062	White
30	175	4	0.0029	White
30	200	4	0.0014	Slight yellow
90	221	4	0.0010	Yellow
60	243	4	0.0016	Brown
75	310	4	0.0468	Brown

TABLE XXX

PYROLYSIS OF POLY-FBA VULCANIZATE - PO 227, LOT 3



Original weight of poly-FBA = 1.0354 grams

<u>Immersion Time, mm.</u>	<u>Temperature °C.</u>	<u>Pressure mm.</u>	<u>Noncumulative Weight Loss g's per 1/2 Hr.</u>	<u>Color of Residue</u>
30	70	1	0.0142	White
30	100	4	0.0068	White
30	125	4	0.0030	White
30	150	1	0.0040	White
30	175	5	0.0067	White
30	200	1	0.0062	White
90	220	1	0.0095	Slight yellow
60	240	4	0.0103	Slight yellow
30	270	5	0.0352	Brown

Contrails

TABLE XXXI

AIR OVEN AGING

	Poly-FBA		Poly-FHA
	Oxide (Best sample)	Amine (Recipe A)	Oxide (Best sample)
500 hrs. at 300°F. wt. loss, % 180° bend	8.3 OK	5.6 OK	7.2 OK
1000 hrs. at 300°F. wt. loss, % 180° bend	14.0 OK	8.8 OK	13.7 OK
1200 hrs. at 300°F. wt. loss, % 180° bend	16.0 Fails	10.5 OK	17.4 Fails
250 hrs. at 350°F. wt. loss, % 180° bend	14.0 OK	5.9 OK	13.9 OK
500 hrs. at 350°F. wt. loss, % 180° bend	29.6 Fails	14.6 OK	24.7 Fails
750 hrs. at 350°F. wt. loss, % 180° bend	42.5 Fails	24.6 Fails	33.2 Fails

RETENTION OF PROPERTIES AT 350°F.

	Poly- FBA		Hycar 4021	
	Recipe A	Recipe B	Recipe A	Recipe B
	<u>Pg.119</u>	<u>Pg.119</u>	<u>Pg.119</u>	<u>Pg.119</u>
<u>Original Properties</u>				
Modulus at 300% Elongation, psi.	1020	---	1560	1730
Tensile Strength, psi	1150	1230	2490	1930
Ultimate Elongation, %	360	300	450	330
Hardness, (Shore Duro A)	56	67	59	61
<u>Aged in Air at 350°F. - 100 hrs.</u>				
Weight loss, %	3.7	6.3	7.2	3.3
Modulus at 300% Elongation, psi	350	---	---	---
Tensile Strength, psi.	380	540	Very low; degraded.	1720
Ultimate Elongation, %	(-67%) 430	(-56%) 155		(-11%) 250
Hardness (Shore Duro A)	(+19%) 73	(-48%) 88	65	(-24%)
180° bend	(+17) OK	(+21) OK	(+6) OK	OK
<u>Aged in Air at 350°F. - 250 hrs.</u>				
Weight loss, %	5.9	8.9	13.5	10.5
Modulus at 300% Elongation, psi.	--	--	--	--
Tensile Strength, psi.	Very low; degraded.	230	brittle	310
Ultimate Elongation, %		(-81%) 25	--	(-84%) 150
Hardness (Shore Duro A)	(+16) 72	(+20) 87	(+9) 68	(+20) 81
180° bend	OK	OK	FAILS	OK
<u>Aged in Sebacate * at 350°F. - 100 hrs.</u>				
Volume Change, %	0	-3	+64	+40
Modulus at 300% Elongation, psi.	--	--	495	--
Tensile Strength, psi.	1070	1050	630	430
Ultimate Elongation, %	(-7%) 195	(-15%) 50	(-75%) 330	(-78%) 110
Hardness (Shore Duro A)	(+11) 67	(+23) 90	(-27%) 31	(-67%) 56
180° bend	OK	OK	OK	OK
<u>Aged in Sebacate * at 350°F - 250 hrs.</u>				
Volume Change, %	-2	-6	+85	+52
Modulus at 300% Elongation, psi	--	--	210	--
Tensile Strength, psi.	930	1150	270	390
Ultimate Elongation, %	(-19%) 230	(-6%) 30	(-89%) 360	(-80%) 80
Hardness (Shore Duro A)	(+6) 62	(+28) 95	(-31) 28	(-1) 60
180° bend	OK	OK	OK	OK

* di-(2-ethylhexyl)sebacate
Esso Turbo Oil

Contrails

results of weight loss and qualitative stiffening tests under dry heat. Table XXXII shows the results of more complete tests, both in air and in di-(2-ethylhexyl) sebacate; Hycar 4021 (ethyl acrylate: chloroethyl vinyl ether copolymer, formerly called Hycar PA 21) was tested as a control.

The oxide-cured poly-FBA and poly-FHA show about equal resistance to dry heat. Their stability in these tests seems to be considerably superior to that of polymers prepared earlier in this program (1-2 years ago). The reason for this is not clear. Amine vulcanizates show less weight loss, and the retention of flexibility extends to more than 500 hrs. at 350°F. After 1200 hrs. at 300°F. the samples can yet be bent 180° without cracking. (The raw polymers still darken and degrade rapidly at 300°F., however).

The quantitative data in Table XXXII show that retention of physical properties by polyamine vulcanizates at 350°F. in air is poor. Compound A seems to degrade excessively whereas Compound B hardens too

Contrails

much. We feel confident that a better polyamine recipe can be developed for this application. On the other hand, Compound A performs very well in contact with di-(2-ethylhexyl) sebacate at 350°F., and properties after immersion are thus far well within tentative requirements described by Wright Air Development Center. Aging properties of Hycar 4021 also show the importance of selecting and balancing the amine curative and sulfur properly. This polymer is less satisfactory in the synthetic lubricant because of greater swelling.

6. Copolymers of FBA and FHA with Butadiene

We have indicated in earlier reports that it is desirable to prepare copolymers of the 1,1-dihydroperfluoroalkyl acrylates with butadiene in order to improve the low temperature flexibility and to permit curing in conventional sulfur recipes. There is also interest in preparing copolymers having very low butadiene content which would allow sulfur curing without great sacrifice of ozone and solvent resistance. Copolymers containing from 0.4 to 1.0 weight percent of butadiene, with conversions from 44-87% have been prepared and cured in silicate, oxide, and

Contrails

strongly accelerated sulfur recipes. Regardless of the type of vulcanizing agent used, none of the products showed tensile strengths in excess of 800 psi. even in the presence of reinforcing carbon blacks. Furthermore, the gum compounds cured in the silicate recipe were very weak. The raw polymers appear to be of a relatively low degree of polymerization. Interest in this type of copolymer has diminished considerably with the development of the polyamine cure, discussed just above.

Interest in copolymers with larger amounts of butadiene persists, since this furnishes a way of reaching lower service temperatures, particularly with the alkoxy acrylates. Properties of the sulfur vulcanizates of the first two pilot plant lots of FBA:butadiene copolymer are shown in Table XXXVIII. The first lot exhibited poor physical properties due to high conversion. The second is typical in strength of laboratory preparations but somewhat poorer than expected in balance of solvent resistance and low temperature flexibility. In Table XXXVIII are shown test values for three lots of FHA:butadiene copolymers. Again one lot is inferior because of high conversion;

Continued

TABLE XXXIII
FBA AND FHA COPOLYMERS OF BUTADIENE

Sample Number	Mol % FHA or FBA	Charged Polymer	Found in	Con- ver- sion %	Tensile Strength psi.	Ultimate Elon- gation %	Swelling %		Gelman T ₁₀ °C.	Brittle Point °C.	Conclusion
							70:30 Iso:Tol.	Ben- zene			
PP-68, Lot 1 (FBA)	55	50		79	750	180	80	85	-21	-27	Poor physical prop- erties due to high conversions.
PP 68, Lots 2 & 3 (FBA)	55	38		61	2100	370	105	125	-25	-36	Somewhat poor balance of solvent resistance and low temperature properties.
PP 67, Lot 1 (FHA)	35	27		69	1900	310	115	90	-32	-49	Representative rubber
PP 67, Lot 2 (FHA)	55	49		82	480	100	42	41	-16	-22	Poor physical prop- erties due to high conversion.
PP 67, Lots 3 & 4 (FHA)	55	40		60	1700	350	65	60	-26	-36	Representative rubber

Contrails

the other two lots are satisfactory and a sample has been furnished to Wright Air Development Center (see Appendix C).

In Table XXXIV are the swelling values for vulcanizates of FBA and FHA copolymers in "Skydrol". In general, swelling values were less than 40% after seven days at 75°C. Swell seems to decrease with increase in acrylate content. All vulcanizates swelled less than 25% in No. 3 oil at the same time and temperature.

Results of a thorough testing of laboratory prepared copolymers are shown in Table XXXV. Vulcanizates were compounded in the sulfur cure shown in Appendix B of this report. Swelling of both of these compounds in a series of iso-octane:toluene mixtures shows maximum swelling in the range of 20 to 50% of iso-octane. The FHA copolymers appear to be slightly more sensitive to the aliphatic fraction of the mixture than the FBA copolymer of similar acrylate content.

TABLE XXXIV

SWELLING OF VULCANIZATES IN "SKYDROL"

<u>Polymer</u>	<u>Type of Cure</u>	<u>Carbon Black</u>	<u>Swell (%)</u> <u>(7 days at 75°C.)</u>
Poly-FBA	silicate	none	13
Poly-FBA	oxide	none	14
32:68 FBA:Butadiene	sulfur	35 pts.	32
40:60 FBA:Butadiene	sulfur	35 pts.	40
17:83 FHA:Butadiene	sulfur	35 pts.	48
25:75 FHA:Butadiene	sulfur	35 pts.	34
31:69 FHA:Butadiene	sulfur	35 pts.	28
40:60 FHA:Butadiene	sulfur	35 pts.	21
Hycar OR-15	sulfur	50 pts.	180

TABLE XXXV

EVALUATION OF FBA AND FHA COPOLYMERS OF BUTADIENE

<u>Polymer</u>	<u>PO-268, Lot 2 31:69 FHA:But.</u>	<u>PO-213, Lot 2 32:68 FBA:But.</u>
Curing system	Sulfur-Altax	Sulfur-Altax
Parts of EPC black	35	35
Cure at 300°F., min.	30	45
Processing characteristics	Very good	Very good
 <u>Original Properties</u>		
Modulus at 300% elongation, psi.	1420	1350
Tensile Strength, psi.	2000	2000
Ultimate Elongation, %	410	430
Set at break, %	40	60
Bashore resilience, %	21	18
Shore A-2 hardness	69	64
Compression set "B", % (70 hrs. at 100°C.)	87	91
Compression set at -10°C., %*	37	41
-20°C., %*	60	56
-40°C., %*	73	76
Ozone resistance (min. to failure in 350 ppm. ozone at 25% elongation)	5	4
Gehman T ₁₀ , °C.	-33	-33
ASTM Brittle point, °C.	-53	-36
% Volume swell after 48 hours in		
70:30 iso-octane:toluene at 25°C.	125	110
iso-octane at 25°C.	62	--
toluene at 25°C.	116	--
benzene at 25°C.	96	125
MIBK at 25°C.	66	115
10% sodium hydroxide at 25°C.	4.4	2.7
10% sulfuric acid at 25°C.	2.9	2.0
concentrated nitric acid at 25°C.	Disintegrates	Disintegrates

* 30 min. recovery at test temperature

Contrails

TABLE XXXV (continued)

<u>Polymer</u>		<u>PO-268, Lot 2</u> <u>31:69 FHA:But.</u>	<u>PO-213, Lot 2</u> <u>32:68 FBA:But.</u>
% Volume swell after 48 hours in			
distilled water	at 25°C.	2.4	3.7
distilled water	at 100°C.	5.7	14
ASTM oil #1	at 100°C.	3.5	-2.0
ASTM oil #3	at 100°C.	23	19

Properties after one week of oven aging at 100°C.

Weight loss, %		3.1	6.4
Tensile Strength, psi.		1330 (-34%)	1100 (-45%)
Ultimate Elongation, %		135 (-67%)	105 (-76%)
Set at break, %		3	3
Shore A-2 hardness		82 (+13 pts.)	84 (+20 pts.)

Properties after one week of oven aging at 150°C.

Weight loss, %		18.5	22.1
Fluorine content, %:	before aging	31.0	24.0
	after aging	22.0	18.0
Shore A-2 hardness		>100	>100

Contrails

The discrepancy between the low temperature properties of the silicate and sulfur vulcanizates of FHA and FBA copolymers with butadiene, referred to above in the discussion of FEFPA copolymers, is clarified by the data shown in Table XXXVI.

The T_{10} and brittle point of the FBA copolymers are independent of curing system and carbon black loading. On the other hand, silicate gum vulcanizates of the FHA copolymers perform appreciably better at low temperatures than compounds containing carbon black, or gum stocks vulcanized with sulfur or metal oxides. Consequently, FHA copolymers are superior to FBA copolymers in balance of cold and solvent resistance only if the comparison is made with silicate vulcanizates. The reason for this behavior is not known.

Solvent resistance is generally independent of the curing system and is improved by carbon black loading. As shown in Table XXXVII, silicate or oxide cures give higher tensile strengths than sulfur in a gum stock, but the opposite is true for reinforced stocks. However, recent experience indicates that

Contrails

TABLE XXXVI

COMPARISON OF T_{10} 's AND BRITTLE POINTS OF FHA: BUTADIENE AND
FBA: BUTADIENE VULCANIZATES IN VARIOUS CURING SYSTEMS

<u>Polymer</u>	<u>Curing System</u>	<u>EPC Carbon Black</u>	<u>T_{10}, °C.</u>	<u>B.P., °C.</u>
27:73 FHA:But. (PP-67, Lot 1)	Sulfur-Altax	None	-32 to	-50 to
	Sulfur-Altax	35 pts.	-37	-57
	Oxide	None		
	Oxide	35 pts.		
	Silicate	35 pts.		
	Silicate	None	-44	-65
40:60 FHA:But. (PP-67, Lot 4)	Sulfur-Altax	None	-24 to	-36 to
	Sulfur-Altax	35 pts.	-28	-45
	Oxide	None		
	Oxide	35 pts.		
	Silicate	35 pts.		
	Silicate	None	-37	-53
38:62 FBA:But. (PP-68, Lot 2)	Sulfur-Altax	None	-25 to	-40 to
	Sulfur-Altax	35 pts.	-30	-50
	Oxide	None		
	Oxide	35 pts.		
	Silicate	35 pts.		
	Silicate	None	-27	-47

Contrails

TABLE XXXVII

TENSILE PROPERTIES OF FHA: BUTADIENE AND FBA: BUTADIENE VULCANIZATES

<u>Polymer</u>	<u>Curing System</u>	<u>EPC Car- bon Black</u>	<u>Tensile Strength psi.</u>	<u>Ultimate Elongation %</u>	<u>Compression Set % (70 hr. at 100°C.)</u>
27:73 FHA: But. (PP-67 Lot 1)	Sulfur-Altax	None	300	360	85
	Sulfur-Altax	35 pts.	1900	310	82
	Oxide	None	400	440	52
	Oxide	35 pts.	1200	240	53
	Silicate	None	1100	260	80
	Silicate	35 pts.	1300	230	52
40:60 FHA: But. (PP-67, Lot 4)	Sulfur-Altax	None	300	450	81
	Sulfur-Altax	35 pts.	1700	410	88
	Oxide	None	400	410	63
	Oxide	35 pts.	1200	230	54
	Silicate	None	1000	90	96
	Silicate	35 pts.	1000	220	54
38:62 FBA: But. (PP-68, Lot 2)	Sulfur-Altax	None	600	440	81
	Sulfur-Altax	35 pts.	2100	370	83
	Oxide	None	1100	610	48
	Oxide	35 pts.	1600	290	72
	Silicate	None	900	100	91
	Silicate	35 pts.	1600	310	69

Contrails

reinforcement in silicate or oxide recipes is possible if care is taken to keep the polymer alkaline. Success often hinges on following the proper compounding procedure and on selecting the proper black.

Surprisingly, the best compression set values were obtained with the oxide recipe despite its high pigment loading. The reason was found to lie in an undesirable advancement of cure in the sulfur system and in poor heat stability of the silicate vulcanizate. Lower set values can probably be achieved by further improvements in compounding.

The swelling and low temperature properties of a series of copolymers of FBA and FHA with butadiene have been carefully measured. As solvents for the swelling measurements, 70:30 iso-octane:toluene and benzene have been used. All polymers were cured in the standard silicate cure. As in previous work, the Gehman T_{10} is taken as the measure of low temperature serviceability. The swelling is plotted against the T_{10} in the same way as in Figure 6. In fact, Figure 6 contains part of the same data as plotted here, but

Contrails

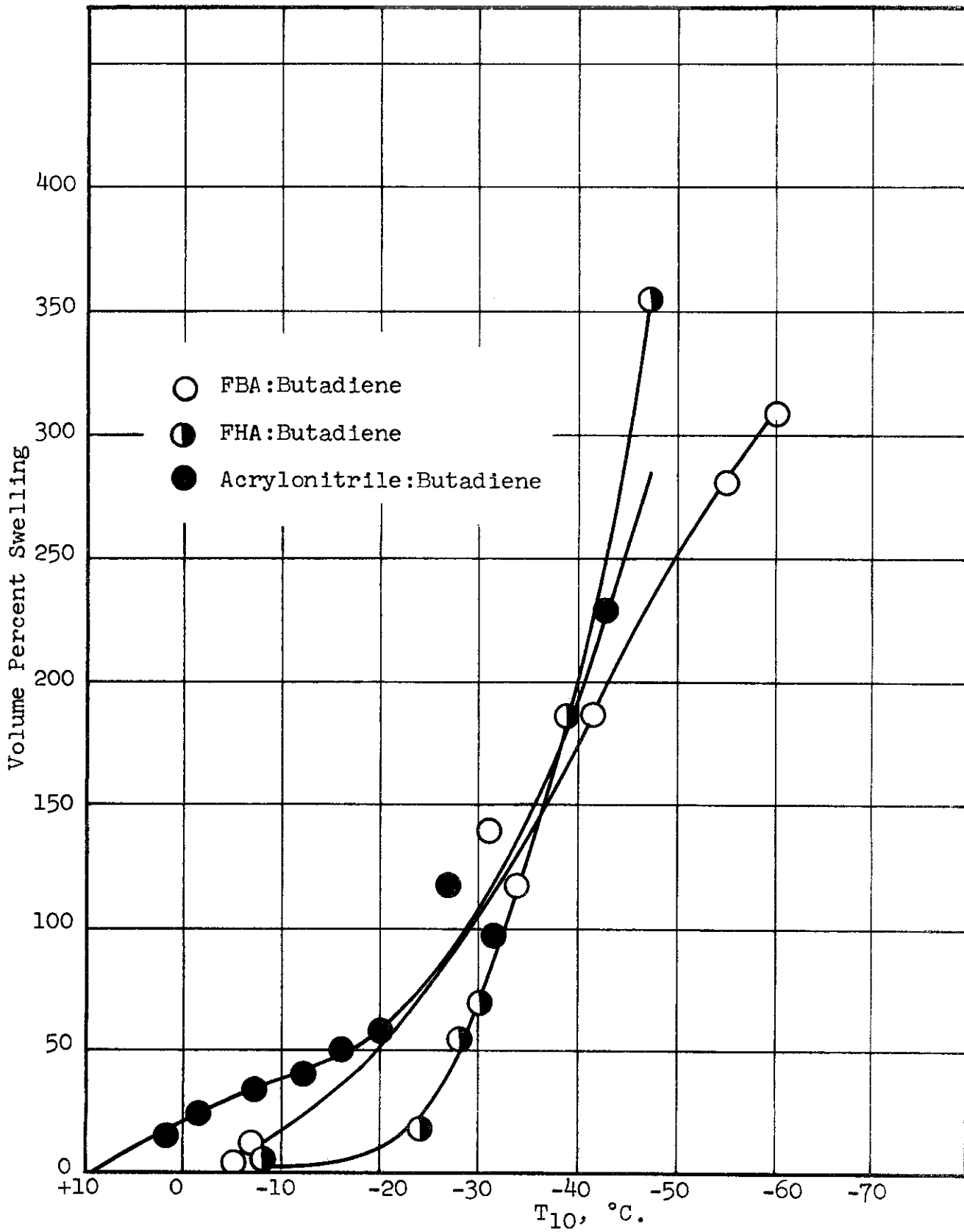


FIGURE 12

PERCENT SWELLING IN 70:30 ISO-OCTANE:TOLUENE OF COPOLYMERS OF FBA, FHA AND ACRYLONITRILE WITH BUTADIENE

Contrails

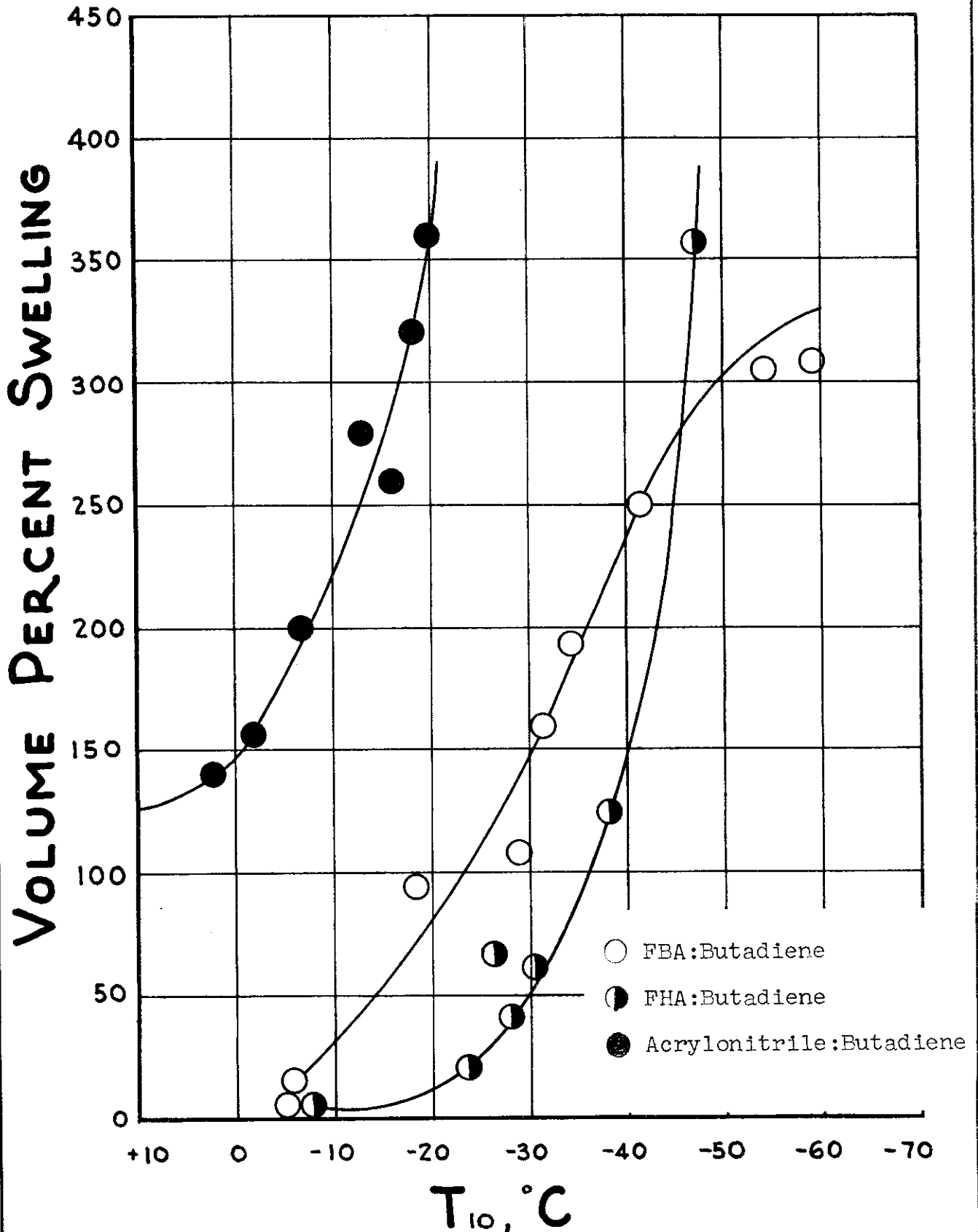


FIGURE 13

PERCENT SWELLING IN BENZENE VS. GEHMAN T_{10} OF COPOLYMERS OF FBA, FHA, AND ACRYLONITRILE WITH BUTADIENE

Conclusions

without the individual experimental points. Results are shown in Figure 12 and Figure 13, and indicate that in 70:30 iso-octane:toluene the FBA:butadiene copolymers are about equivalent in balance of properties to the butadiene:acrylonitrile family of polymers. The FHA series is somewhat superior. In benzene (and in highly aromatic solvents in general), the superiority of both the FBA and FHA series over the acrylonitrile copolymers is very marked. The anomalously higher T_{10} values obtained for FHA:butadiene copolymers cured in sulfur recipes has been discussed above. The swelling of these materials is discussed from a more fundamental viewpoint in Section 9.

In general, only swelling measurements have been made in this work for predicting the influence of solvents upon the fluorine-containing rubbers. It is, of course, equally important to know the effect of solvents upon the physical properties of the rubber compound. Hardness, tensile strength, and ultimate elongation of vulcanized poly-FBA, FBA:butadiene copolymer (35-40 mole % of FBA), and Hycar OR-15 have been measured after 48 hours immersion in 70:30

Conclusions

iso-octane:toluene. After measurements on the wet samples, the solvent was allowed to evaporate and the same measurements were repeated for the dried specimens. The results of these measurements in terms of percentage change are shown in Table XXXVIII together with the physical properties of the original vulcanizates before exposure to solvent.

It is clear that because of the higher original tensile strength of Hycar OR-15 it is stronger in the swollen condition than the fluoro rubbers tested here, although the percentage change in tensile strength is much smaller for the poly-FBA. It is interesting that after evaporation of the solvent, the properties of the fluoro rubbers are nearly the same as before immersion. In the case of this particular Hycar compound, however, evaporation of the solvent restores very little of the loss of tensile strength which accompanied the swelling with hydrocarbon.

7. Plasticizer Studies

During this period considerable attention was given to the examination of the plasticizing of

Contrails

TABLE XXXVIII

EFFECT OF SOLVENT UPON PHYSICAL PROPERTIES

<u>Rubber</u>	<u>Poly-FBA</u>	<u>Poly-FBA</u>	<u>FBA:Buta- diene</u>	<u>Hycar OR-15</u>
Cure	Silicate	Oxide	Sulfur- black	Sulfur- black
<u>Original Properties</u>				
100% modulus, psi.	410	510	410	490
Tensile, psi.	860	970	1700	4400
Ultimate Elongation	230	230	310	400
Shore Hardness (A-2)	44	45	81	76
Swelling in 70:30 Fuel (%)	20	20	74	28
<u>After 48 hours in 70:30 Iso-octane:toluene*</u>				
% Change in hardness	0	13	30	10
% Change in tensile	20	30	75	60
% Change in ultimate elong.	+17	9	60	40
<u>After Redrying</u>				
% Change in hardness	0	0	25	8
% Change in tensile	20	18	20	55
% Change in ultimate elong.	13	13	20	36

* All changes are negative unless marked +.

Contrails

poly-FBA with fluorine-containing compounds. As a preliminary testing for possible plasticizer effect, measurements were made of the extent to which various liquids lowered the Gehman T_{10} stiffening temperature and also the extent to which these liquids were extractable by either aliphatic or aromatic hydrocarbons. In general, liquids were added to the polymer either by milling or by swelling of a strip of the sample immersed in the liquid. The plasticized strips were used for Gehman torsional tests. These same specimens were later immersed in 70:30 iso-octane: toluene mixture for at least 24 hours at room temperature. After removal from the solvent, the specimens were dried to constant weight in a vacuum oven and the losses in weight assumed to be due to extraction of plasticizer. The results of these tests are tabulated in Table XXXIX.

In general, it is observed that the non-fluorine-containing polyesters, such as Paraplex G-20 and G-50, are only partially extracted but are not good plasticizers.

A wide variety of fluorine-containing compounds

Contrails

TABLE XXXIX
PLASTICIZERS FOR POLY-FBA

EXTRACTIBILITY AND LOW TEMPERATURE FLEXIBILITY

(Samples cured in silicate formula, 1 hour, 310°F.)

<u>Plasticizer</u>	<u>Plasti- cizer Added (% by Volume)</u>	<u>Gehman T₁₀ (°C.)</u>	<u>Extraction by 70:30 Iso-octane: Toluene* (% of Plasticizer Removed)</u>
None (control)	None	-5	
Tri(1,1-dihydroperfluorobutyl) phosphate	30	-45	100
Tri(1,1-dihydroperfluorohexyl) phosphate	25	-32	100
Tri(1,1-dihydroperfluoro-octyl) phosphate	25	-7	36
Di(1,1-dihydroperfluorobutyl) adipate	25	-40	100
Di(1,1-dihydroperfluorohexyl) adipate	25	-31	100
Di(1,1-dihydroperfluoro-octyl) adipate	25	-18	100
Di(1,1-dihydroperfluorodecyl) adipate	25	-7	78
F-Decyl phosphate (50%) + F-Decyl adipate (50%)	25	-7	48
F-Octyl adipate (50%) + F-Octyl phosphate (50%)	25	-7	62
Polydiethylene glycol perfluoroadipate	25	-10	--
Polydiethylene glycol perfluorosuccinic	25	-10	-- 100
FBA Monomer	30	-39	100
Low Molecular Weight Poly-FBA	25	-10	70
Low Molecular Weight Poly-FBA higher viscosity than that above	25	-15	45
Pentaerythritol perfluorobutyrate	25	--	Sample could not be evaluated.

* 24 hours at 25°C.

Contrails

TABLE XXXIX (continued)

PLASTICIZERS FOR POLY-FBA

EXTRACTIBILITY AND LOW TEMPERATURE FLEXIBILITY

(Samples cured in silicate formula, 1 hour, 310°F.)

<u>Plasticizer</u>	<u>Plasti- cizer Added (% by Volume)</u>	<u>Gehman T₁₀ (°C.)</u>	<u>Extraction by 70:30 Iso-octane: Toluene* (% of Plasticizer Removed)</u>
Perfluorotributylamine bottoms	25	-15	68
Cyclo-C ₁₀ F ₂₀ O	27	-27	B.P. -143°C. added to strip for swelling.
C ₈ F ₁₆ O ₂	26	-32	B.P. -101°C. (swelled)
C ₄ F ₉ CC ₂ F ₄ CC ₄ F ₉	26	-21	B.P. -135°C. "
C ₂ F ₅ (CC ₂ F ₄) ₂ CC ₂ F ₅	22	-27	B.P. -95°C. "
M-C ₁₄ F ₃₀	30	-1	--
Perfluoromethyl naphthalene	22	-20	Plasticized by swelling.
Perfluorodiethylcyclohexane	22	-27	"
1,1-Dihydroperfluorohexylamine	41	-20	"
Cyclo-C ₈ F ₁₃ Cl ₃ O	35	-29	
Fluorolube 600	25	-13	--
Halocarbon oil	25	-10	--
N,N-diethylperfluoro- butyramide	25	-7.5	--
Paraplex G-20	25	-11	50
Paraplex G-50	25	-6	36
G-20 + F-Octyl phosphate	25	-7	40
G-50 + F-Octyl phosphate	25	-8	40
1,1-dihydroperfluorohexyl phthalate	25	-22	65
$ \begin{array}{c} \text{CF}_2 - \text{CF}_2 \\ \quad \\ \text{CF} \quad \text{CFCF}_2\text{COOCH}_2\text{C}_7\text{F}_{10} \\ \diagdown \quad / \\ \text{O} \end{array} $	25	--	Poor samples obtained.

Contrails

were examined, including 1,1-dihydroperfluoroalkyl esters of adipic and phosphoric acids, polyesters of perfluorosuccinic and perfluoroadipic acids, perfluoro ethers, amines, amides, fluorocarbons and low molecular weight poly-FBA. The conclusion is that those materials which are effective plasticizers appear to be fairly readily removed from the vulcanized elastomer by 70:30 iso-octane:toluene, while those which are less readily removed are poor plasticizers. No further work with low molecular weight liquids for plasticization of poly-FBA is planned, but some study with the newer alkoxy acrylates of better low temperature properties may be worthwhile.

The excellent solvent resistance and low temperature flexibility of Thiokol vulcanizates have prompted a check of the compatibility of Thiokol LP-3 with poly-FBA. As high as 45 parts of Thiokol LP-3 were successfully added to 100 parts FBA on the mill. Homogeneous vulcanization of the blend appeared to take place with litharge and lead peroxide in the formulae of Table XL. No tensile strengths above 800 psi. were obtained and, surprisingly, no improvement in low temperature flexibility resulted.

Contrails

TABLE XL

COMPOUNDING OF POLY-FBA WITH THIOKOL LP-3

	<u>A</u>	<u>B</u>	<u>C</u>
Poly-FBA	100	100	100
Thiokol LP-3	--	44	44
Stearic acid	1	1	1
Litharge	5	5	5
Calcined magnesia	25	25	25
Lead peroxide	--	6.6*	6.6*
Spheron #9	--	--	35

* 15 parts based on Thiokol

Cure: 60 min. at 310°F.

Tensile Strength, psi.	870	300	820
Ultimate Elongation, %	340	280	280
Gehman T ₁₀ , °C.	-4	-4	-8
Per cent Swelling (48 hrs.)			
70:30 iso:toluene	20	22	16
Benzene	20	120	53
Per cent Extracted (48 hrs.)			
70:30 iso:toluene	0	4.4	0.8
Benzene	0	5.9	2.5

In 70:30 aviation fuel the added Thiokol did not influence swelling, but in benzene it caused swelling of approximately six times that of poly-FBA alone. Hydrocarbon extraction of the vulcanizates showed very low amounts of polymer removed. No further work is planned.

8. Compression Set and Relaxation

In the third annual report, stress relaxation measurements for vulcanized butadiene:FBA copolymers under tension at room temperature were recorded. The stress relaxation rates appeared comparable to those for other butadiene-containing synthetic rubbers. The Instron stress-strain tester has now been equipped for such measurements at elevated temperatures. We have also acquired and calibrated a Hi-Po-Log stress relaxometer, like that described by McDonald and Ushakoff (Anal. Chem. 20 713 (1948)). This instrument records the relaxation of cylindrical specimens held under compression. Information on relaxation under both compression and tension is important in predicting the effectiveness of rubbers as gaskets, O-rings, and other types of seals.

Contrails

Compression set measurements over a temperature range of -40° to $+100^{\circ}\text{C}$. were made and tabulated in Table XLI for the following compounds:

- (1) Poly-FBA, silicate cured, no reinforcing pigment.
- (2) Poly-FBA, oxide cured, no reinforcing pigment.
- (3) FBA:butadiene copolymer (approximately 35 mole % FBA), sulfur cured, no reinforcing pigment.
- (4) FBA:butadiene copolymer (approximately 35 mole % FBA), sulfur cured, carbon black.
- (5) Hycar OR-15, sulfur cured, no reinforcing pigment.
- (6) Hycar OR-15, sulfur cured, carbon black.
- (7) Paracril 18, sulfur cured, carbon black.

The exact formulae used are shown in Appendix B of this report. It should be recalled that no plasticizers are present in these compounds and hence the compression set values for the commercial Buna-N rubbers are higher than might be obtained for the conventional plasticized compounds.

TABLE XII

COMPRESSION SET OF OIL RESISTANT COMPOUNDS

Temperature °C.	COMPRESSION SET (%)*							
	Poly-FBA Silicate Gum	Poly-FBA Oxide Gum	FBA:But. Sulfur Gum	FBA:But. Sulfur Carbon Black	Hycar OR-15 Sulfur Gum	Hycar OR-15 Sulfur Carbon Black	Paracril 18 Sulfur Carbon Black	
-40	93	93	45	76	96	97	83	
-30	73	96	45	69	95	98	66	
-20	44	65	39	56	95	98	49	
-10	30	22	29	41	27	48	37	
0	27	15	14	33	12	27	28	
10	13	13	12	30	8	21	18	
25	13	15	7	27	6	10	14	
50	20	31	10	21	3	13	9	
100	60	52	63	80	44	55	33	

* Held compressed for 24 hours at test temperature; recovery for 30 minutes at the same temperature.

Contrails

In each experiment the sample was held at the test temperature under compression for 24 hours and then allowed to recover for 30 minutes at the same temperature. It is of interest to consider the results at the lower test temperatures. For example, the -20°C . values are shown separately in Table XLII together with glass temperatures of each uncured polymer. It will be noted that at this temperature, the compression set values of the extremely solvent resistant poly-FBA or FBA:butadiene copolymers are less than those for the commercial Buna-N of 37% acrylonitrile content. The values for the fluorine-containing rubbers at this temperature are similar to those for the less solvent resistant Buna-N with 18% acrylonitrile content.

Compression set values, like stress relaxation measurements, are helpful in evaluation of the suitability of rubber compounds for gasket performance. The results reported earlier for poly-FBA and its butadiene copolymers were obtained under test conditions of 70 hours at 100°C . (212°F .). In general, with the curing systems used to date compression set values lower than 50-80% have not been reached. As in the

Contrails

TABLE XLII

COMPRESSION SET AT -20°C.*

<u>Polymer</u>	<u>Type of Cure</u>	<u>Channel Black, pts. per 100 pts. Polymer</u>	<u>Compression Set, %</u>	<u>T_g of Uncured Polymer</u>
Poly-FBA	Silicate	0	44	-30
Poly-FBA	Oxide	0	64	-30
FBA:Butadiene	Sulfur	0	39	-60
FBA:Butadiene	Sulfur	35	56	-60
Butadiene:Acrylonitrile (37%)	Sulfur	0	95	-25
Butadiene:Acrylonitrile (37%)	Sulfur	50	98	-25
Butadiene:Acrylonitrile (18%)	Sulfur	50	49	-55

* Compressed 24 hours at -20°C., recovered 30 minutes at -20°C.

Contrails

case of the Buna-N rubbers, however, it may be possible at the proper tightness of cure to bring the compression set values to a lower range.

Compression set determinations at low temperatures are useful in studying possible gasket performance at these temperatures. Thus, any crystallization which may occur in a rubber specimen at a particular temperature can readily be detected by the rate and amount of compression set. In the absence of any crystallization, the increased stiffness at low temperatures as the rubber approaches its glass temperature is also reflected in compression set measurements of specimens held under the cold conditions. For a prediction of gasket performance such data are probably more significant than the more customarily used tests for low temperature flexibility such as torsional modulus, temperature-retraction curves, and impact brittle determinations.

In the case of poly-FBA, it appears that the silicate cure gives smaller compression set values at lower temperatures than the oxide cure. Carbon black is detrimental to compression set values and the

Contrails

effect is particularly severe in the copolymers of FBA with butadiene. Nevertheless, the reinforced copolymer, as indicated above, is similar to the Buna-N compound with 18% acrylonitrile content. In all cases the cold set was almost fully recovered when the sample was warmed to room temperature. It will be recalled that part of the high temperature set was permanent and irreversible.

Using the Hi-Po-Log Relaxometer, we have measured the rate of stress decay in poly-FBA and in FHA:butadiene copolymer at 25° and 100°C. As a control, we have also carried out these measurements on a Hycar OR-15 vulcanizate. These data can be interpreted in terms of gasket performance and are therefore important in evaluating our fluorine-containing rubbers. Samples can be compressed almost instantaneously, but since the recorder response is slow, the initial stress (S_0) is taken as the stress after 0.01 hours (t_0). The data obtained at 25° and at 100° are shown in Table XLIII and plotted in Figures 14 and 15.

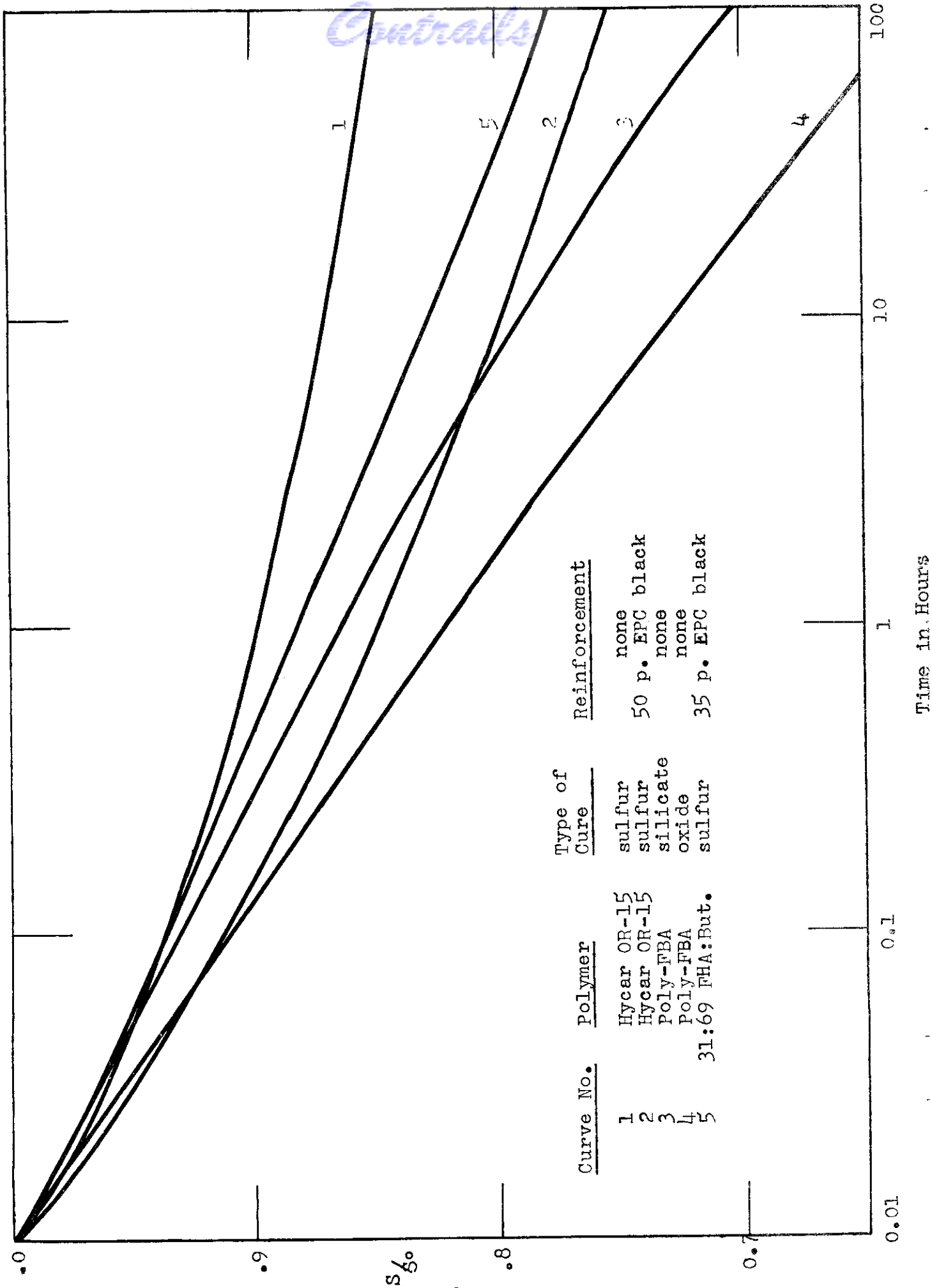
Contrails

Table XLVIII

STRESS RELAXATION DATA, Figs. 14 and 15.

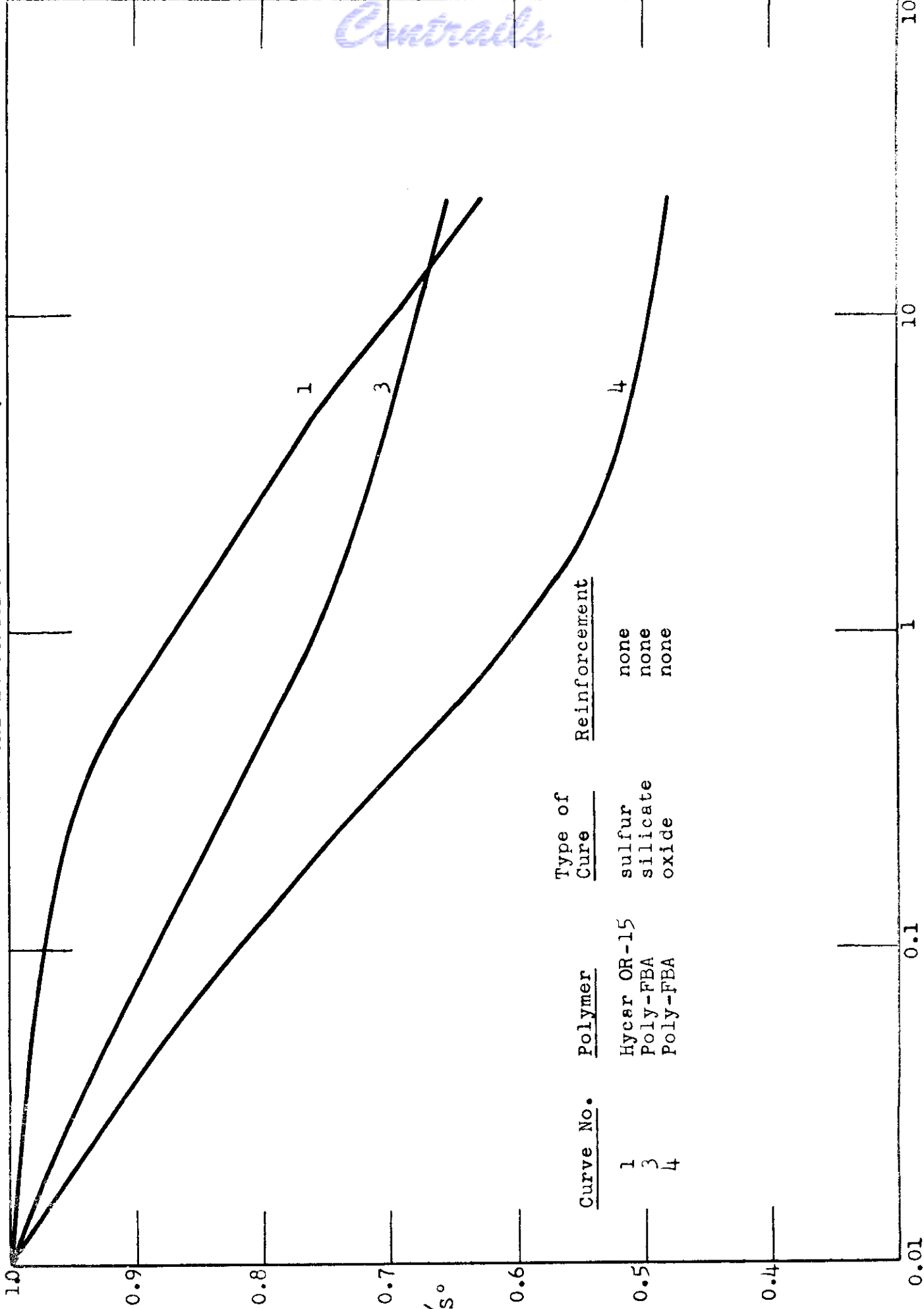
Figure 14 Curve No.	1	2	3	4	5
Approx. Deflection %	40	30	40	40	30
Max. Recorded Stress ($S_{max.}$), psi.	220.0	300.0	180.5	156.5	250.7
$S_0/S_{max.}$	0.829	0.896	0.926	0.911	0.917
Per cent Recovery:					
1/2 hr. at 25°C.	98	98	96	91	95
24 hrs. at 100°C.	100	100	100	98.5	99
Figure 15, Curve No.	1	3	4		
Approx. Deflection %	40	40	40		
Max. Recorded Stress ($S_{max.}$), psi.	227.8	146.7	147.5		
$S_0/S_{max.}$	0.952	0.881	0.849		
Per cent Recovery:					
1/2 hr. at 25°C.	87	--	80		
24 hrs. at 100°C.	92	--	86		
24 hrs. at 150°C.	--	--	96		

FIGURE 14
STRESS DECAY IN COMPRESSION AT 25°C.



Centrad's

FIGURE 15
STRESS DECAY IN COMPRESSION AT 100°C.



Contrails

The data appear to indicate that the stress decay is due nearly entirely to reversible relaxation processes in all cases. This is shown by the percent recovery, which is close to 100%. A satisfactory material should show a rapid stress relaxation during the first few seconds but after this period the change of stress with time should be relatively slow and the stress should maintain a high value even after a long period. The Hycar CR-15 vulcanizate used in these tests shows a nearer approach to this ideal behavior than the FBA:butadiene or FMA:butadiene vulcanizates so far examined. At 25°, the stress in poly-FBA decays almost linearly with the logarithm of time and does not appear to be approaching an equilibrium value. At 100°C., the Hycar CR-15 shows a very rapid attainment of equilibrium modulus, followed by a renewed fast relaxation which is probably due to chain scission. The poly-FBA curve is again approximately linear. From its structure, it would not be expected that poly-FBA would show scission, or at least not to the same degree as the Hycar CR-15, and the shape of the relaxation curve does not particularly suggest scission. The fact that it does not reach an equilibrium modulus within a reasonable length of

Contrails

time even at 100° may mean that some other process, not yet defined, may be contributing to the relaxation.

Relaxation curves at three temperatures of oven post-cured poly-FBA (oxide recipe) are shown in Figure 16. It is found that the stress appears to approach an equilibrium value at -10°C. If this is a true equilibrium modulus, it should be theoretically possible by proper curing and stabilization to eliminate the subsequent stress decay exhibited at higher temperatures.

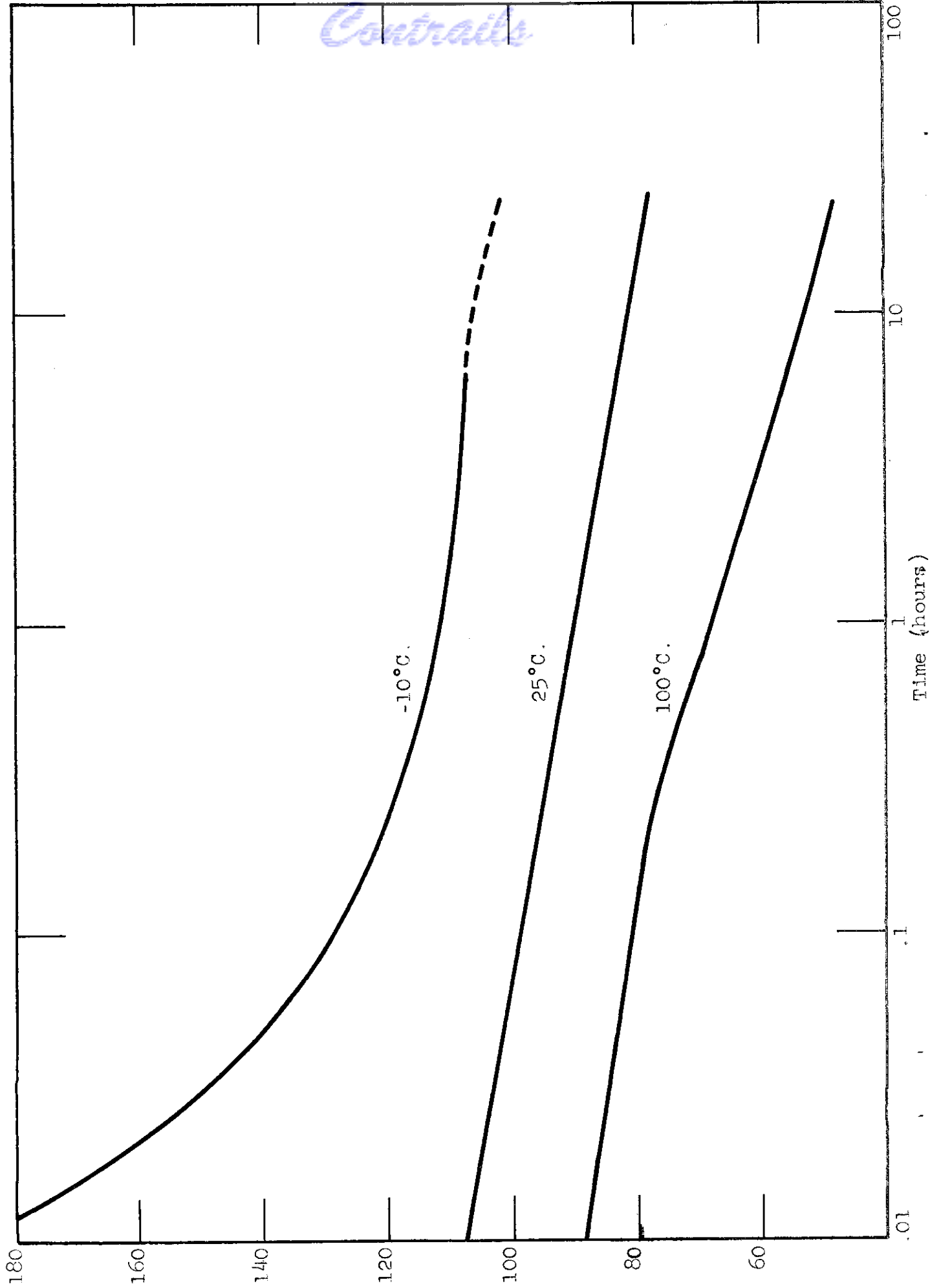
The importance of proper cross-linking on stress relaxation is illustrated in Figure 17. Amine-cured Hycar PA-21 exhibits very acceptable behavior in compression, exemplified by the fact that the 100° curve falls above the room temperature curve. This indicates that equilibrium stress is reached rapidly and that very few long-term relaxation processes remain at the elevated temperature. In contrast, oxide-cured Hycar PA shows no sign of approaching an equilibrium stress value; in fact, this compound is far inferior to poly-FBA.

Attention is again directed to the superior compression set values of the oven tempered polyamine

FIGURE 16

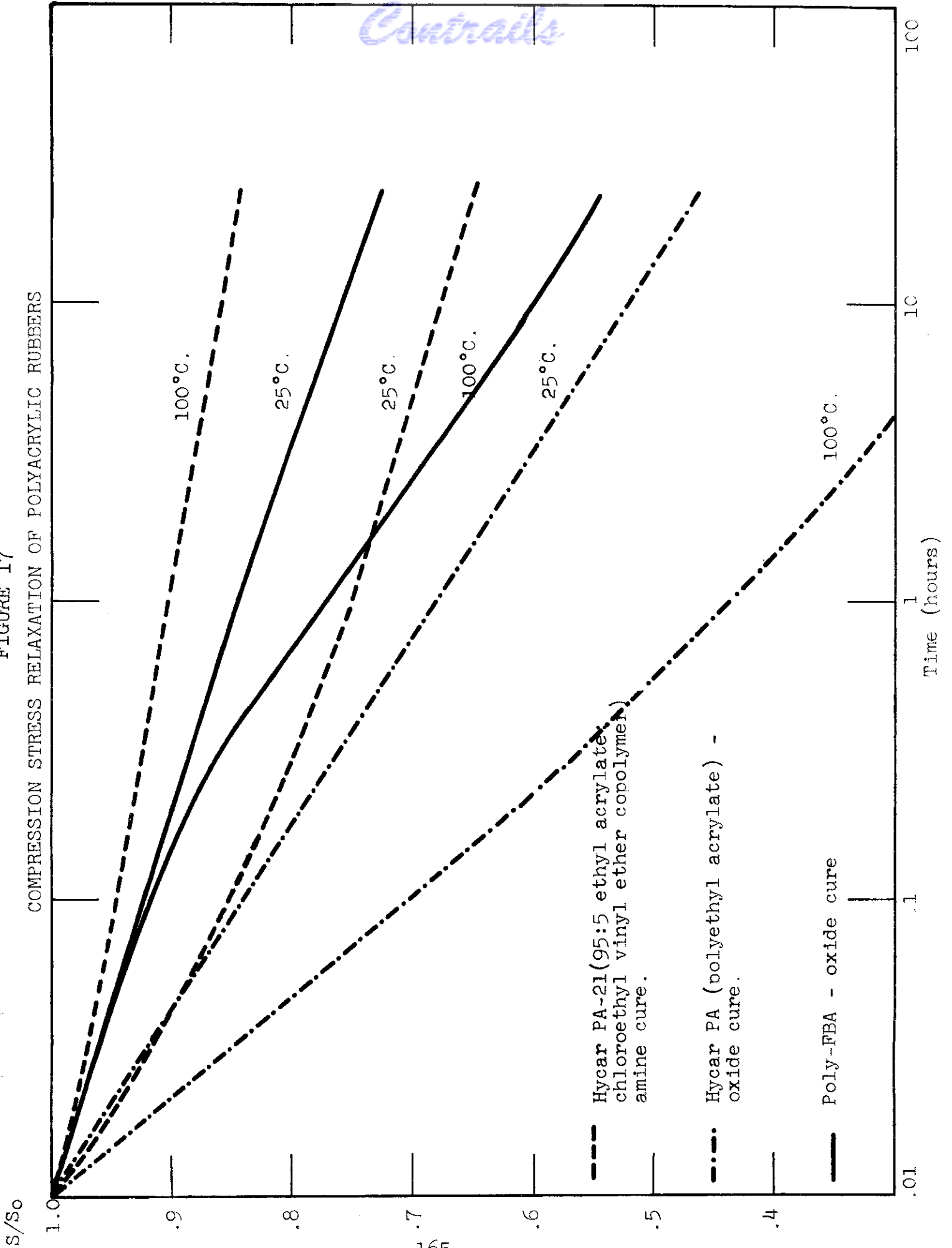
COMPRESSION STRESS RELAXATION OF POLY-FBA (OXIDE) CURE

$S_x \frac{298}{T}$ (psi)



Contrails

FIGURE 17
COMPRESSION STRESS RELAXATION OF POLYACRYLIC RUBBERS



vulcanizates, discussed in the previous section on the polyamine cure. These vulcanizates have not yet been examined for their stress relaxation characteristics as carefully as the earlier cures, but indications are promising.

9. Fundamental Swelling Studies with Poly-FBA

With the object of obtaining a better understanding of the solvent resistance of fluorine-containing acrylate polymers, careful measurements were made of the swelling of poly-FBA in 32 liquids and in seven mixed solvents. Samples used for this purpose were vulcanized with a combination of sodium metasilicate nonahydrate and calcium hydroxide according to the following formula:

	<u>Parts</u>
Polymer	100
Calcium hydroxide	2.72
Sodium metasilicate nonohydrate	6.72

Cure: 30 min. at 310°F.
(standard cure:60 min.)

The results of swelling measurements are shown in Figures 18 and 19 and in Tables XLIV and XLV. The numbers in the tables identify the points in the figures.

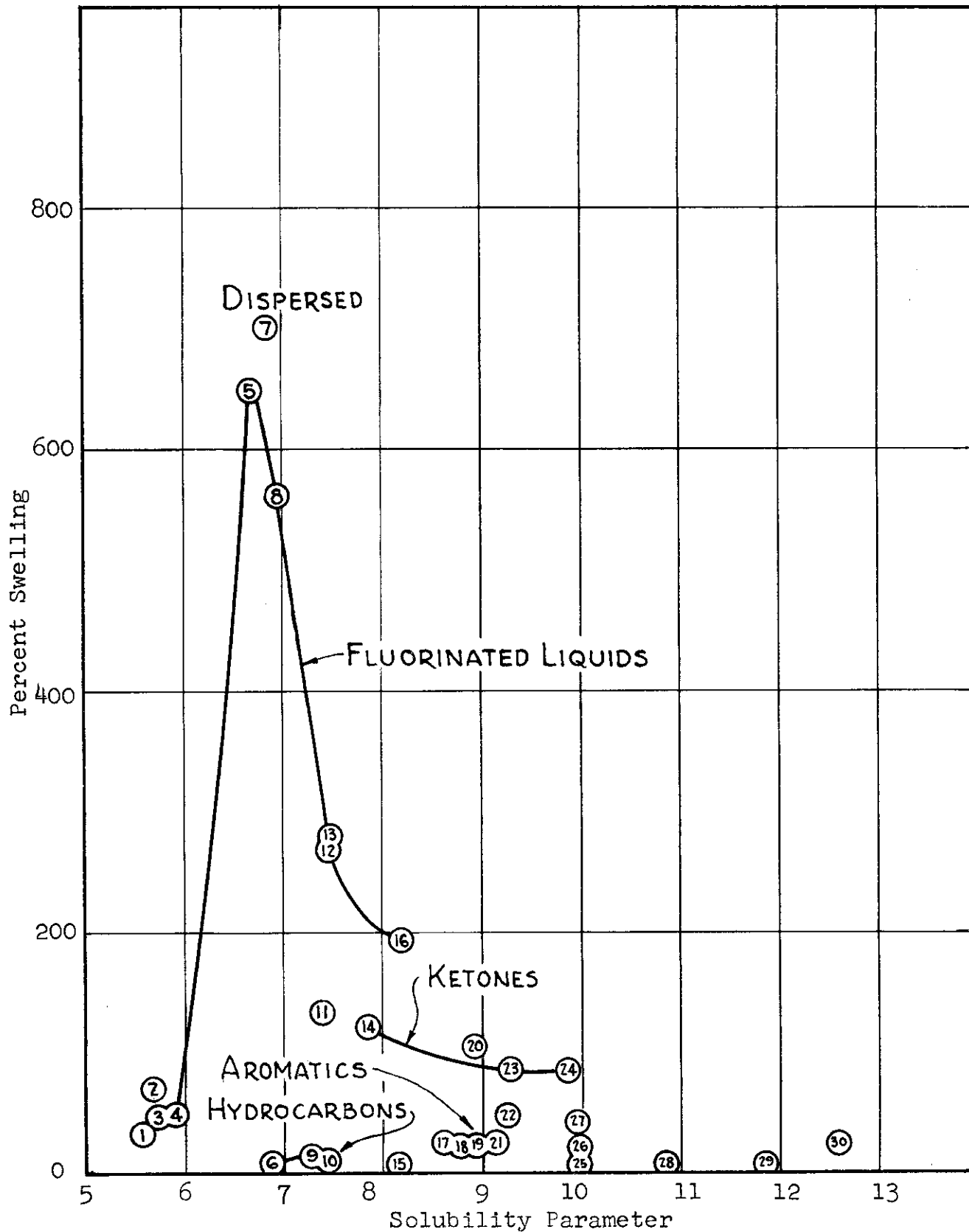


FIGURE 18

PERCENT SWELLING OF SILICATE CURED FBA VS. SOLUBILITY PARAMETER

TABLE XLIV
SWELLING OF POLY-FBA

<u>No.</u>	<u>Solvent</u>	<u>δ</u>	<u>% Swelling</u>
1	$(C_4F_9)_2O$	5.6	33
2	C_8F_{18}	5.7	70
3	$(C_3F_7)_2NC_2F_5$	5.75	47
4.	$\underline{c}-C_8F_{16}O$	5.9	48
5	$CF_3CFHCF_2OC_3H_7$	6.7	644
6	"Iso"-octane (2,2,4-trimethyl pentane)	6.85	8
7	Methyl perfluorobutyrate	7.0	700 dis- persed
8	FBA monomer	7.25	530
9	Hexane	7.3	13
10	Heptane	7.4	8
11	Ethyl ether	7.4	133
12	$CF_2HCF_2OC_4H_9$	7.5	270
13	Xylene hexafluoride	7.5	276
14	Methyl isobutyl ketone	7.9	120
15	Oleic acid	8.2	5
16	Benzotrifluoride	8.2	192
17	Carbon tetrachloride	8.6	24
18	Xylene	8.8	20
19	Toluene	8.9	23
20	Ethyl acetate	8.95	105

Table XLIV (Cont'd)

SWELLING OF POLY-FBA

<u>No.</u>	<u>Solvent</u>	<u>λ</u>	<u>% Swelling</u>
21	Benzene	9.15	24
22	Chloroform	9.3	48
23	Methyl ethyl ketone	9.3	85
24	Acetone	9.9	85
25	CS ₂	10	11
26	Nitrobenzene	10	16
27	1,4-Dioxane	10	42
28	Amyl alcohol	10.9	7
29	Propyl alcohol	11.9	7
30	Nitromethane	12.6	23
31	Methyl alcohol	14.3	61-slow
32	Dimethyl formamide	14	126-slow
33	Water	24	250-slow

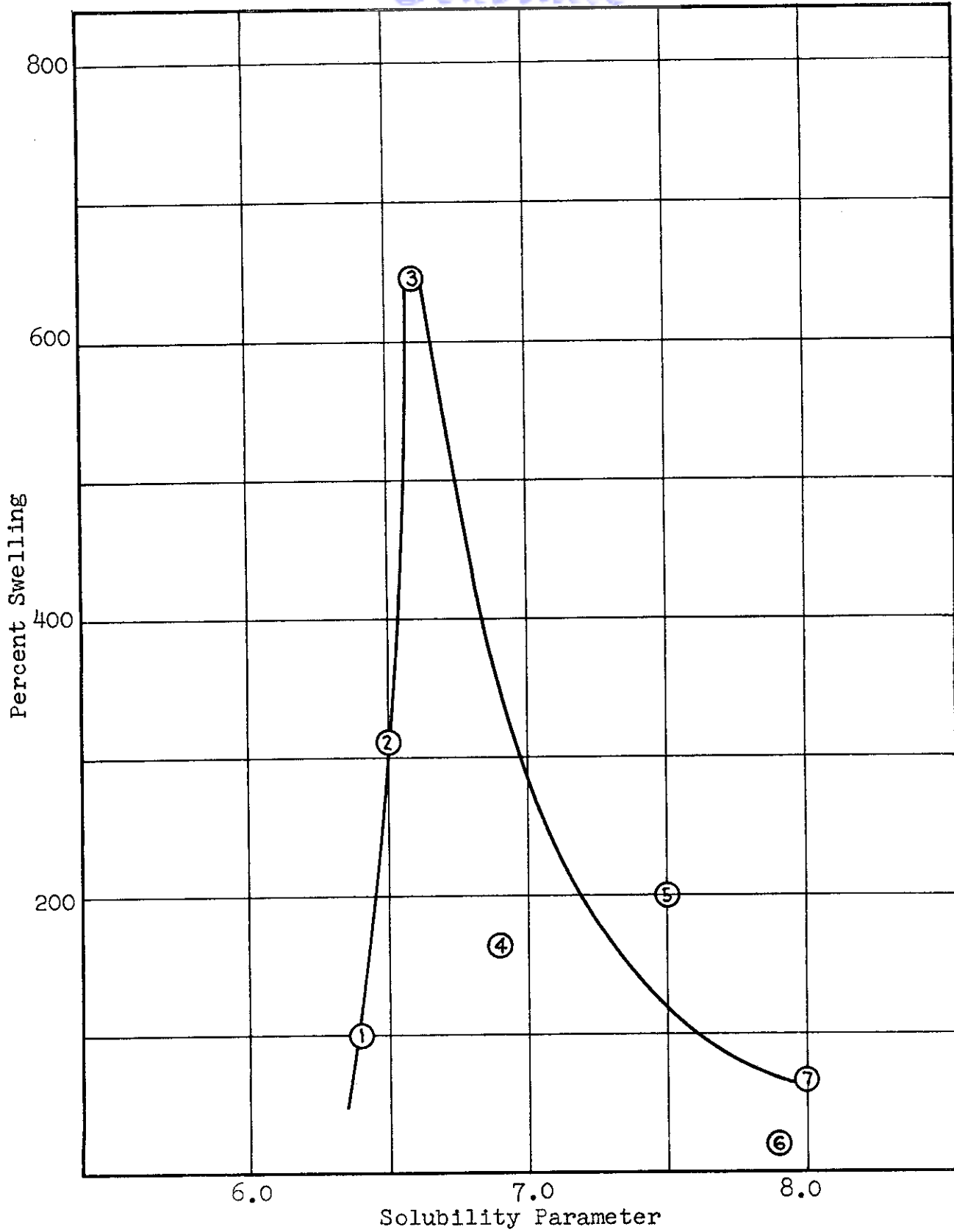


FIGURE 19

PERCENT SWELLING OF SILICATE CURED POLY-FBA VS. SOLUBILITY
PARAMETER OF MIXED SOLVENTS

Contrails

TABLE XLV

SWELLING OF POLY-FBA IN MIXED SOLVENTS*

<u>Mixture</u>	<u>Average Solu- bility Para- meter</u>	<u>Arithmetic Mean of Swelling in Pure Components</u>	<u>Swelling Volume</u>	<u>Identification Number in Figures</u>
c-C ₈ F ₁₆ O:iso-octane	6.4	28	100	1
c-C ₈ F ₁₆ O:C ₃ F ₆ HCC ₃ H ₇	6.5	344	313	2
c-C ₈ F ₁₆ O:Ethyl ether	6.6	90	644	3
(C ₄ F ₉) ₂ O:(C ₂ H ₅) ₂ O:1.4 Hexane	6.9	54	165	4
c-C ₈ F ₁₆ O:Methyl ethyl ketone:Hexane	7.5	45	200	5
Toluene:iso-octane	7.9	15	20	6
c-C ₈ F ₁₆ O:Amyl Alcohol: Hexane	8.0	22	67	7

* Equal volumes of each liquid unless marked otherwise.

Contrails

In the figures the swelling volumes are plotted against the solubility parameter δ , which is defined as the square root of the energy of vaporization per cc. This quantity is known for most of the liquids used and can be estimated with fair accuracy for the others from the densities and boiling points by use of the Hildebrand and Scott modification of the Trouton rule.

It will be recalled that the solubility parameter for a polymer cannot be determined directly but can be estimated by the assumption that a polymer has the same solubility parameter as the liquid in which it exhibits maximum swelling. Several anomalies are observed for the fluorine-containing acrylate polymer. For example, certain solvents of high cohesive energy density swell the polymer more than can be expected. It is probably, for example, that acetic acid and water are attacking the polymer chemically.

The general trend of the data indicates a δ value for the poly-FBA of about 6.7. Mixtures of liquids, as shown in Figure 19, which average to this value swell the polymer much more than either liquid alone. A

Contrails

similar large swelling was obtained in $C_3F_6HOC_3H_7$, an ether which is fluorocarbon on one side and hydrocarbon on the other.

The most interesting anomaly is that the aliphatic hydrocarbons with cohesive energy densities close to that of poly-FBA swell the polymer very little. This is a striking example of the observation that swelling is not alone a matter of cohesive energy density but must depend on other factors as well. This anomaly is indeed fortunate for the practical use of poly-FBA as a rubber having resistance to hydrocarbon fluids.

The swelling of poly-FHA and an FBA:butadiene copolymer containing 38.4 mole % FBA has likewise been measured in a number of solvents. Both polymers were also cured in the standard silicate recipe. The swelling data are plotted in Figures 20 and 21, to which Table XLVI provides the key. Table XLVI also gives the exact values of the swelling in each case. The tie-lines join liquids to the same chemical class.

Since only highly fluorinated liquids swelled FHA more than FBA, FHA must have a lower solubility parameter. The peak in Figure 20 has been drawn at a

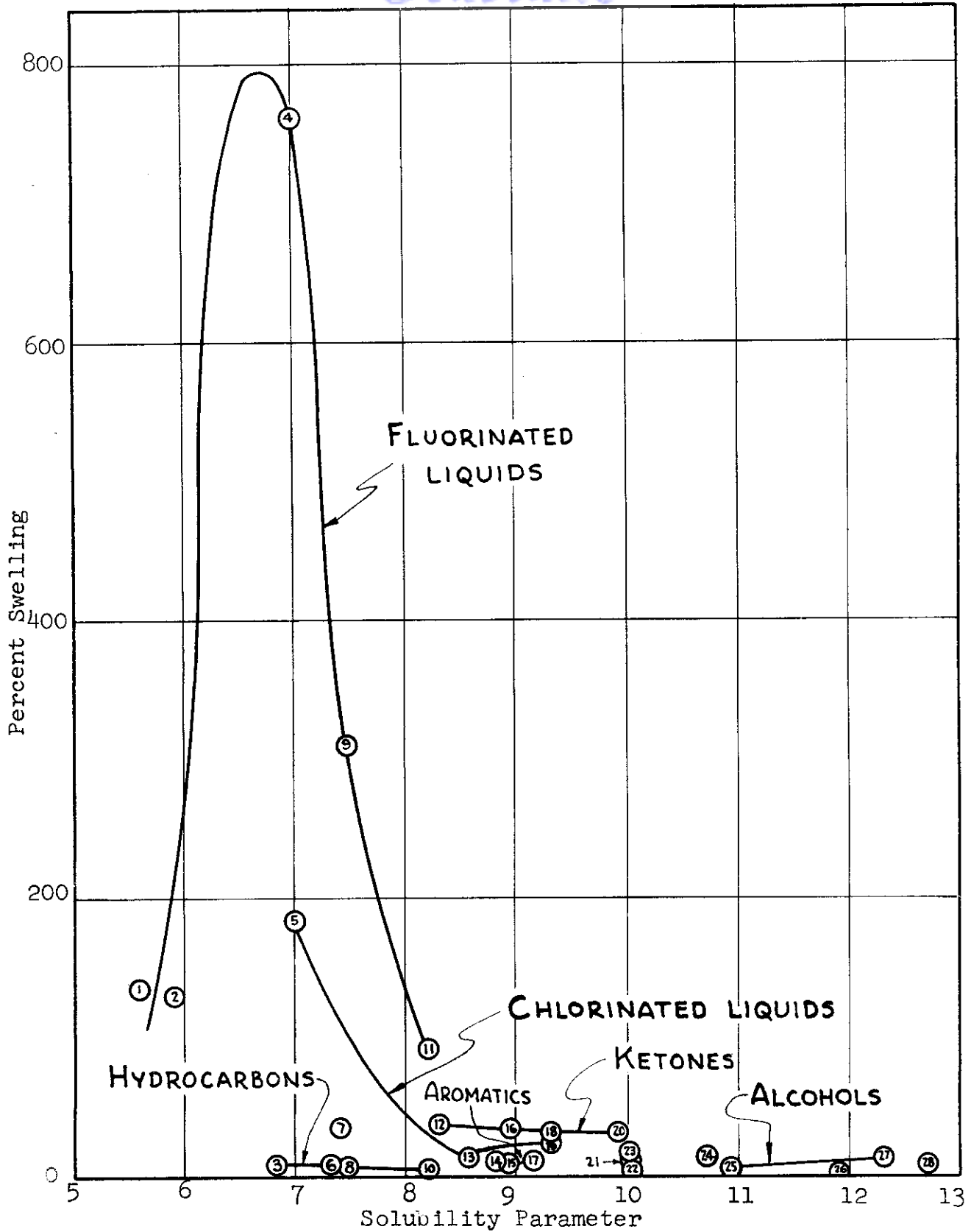


FIGURE 20

PERCENT SWELLING OF SILICATE CURED FHA VS. SOLUBILITY PARAMETER OF SOLVENT

Contrails

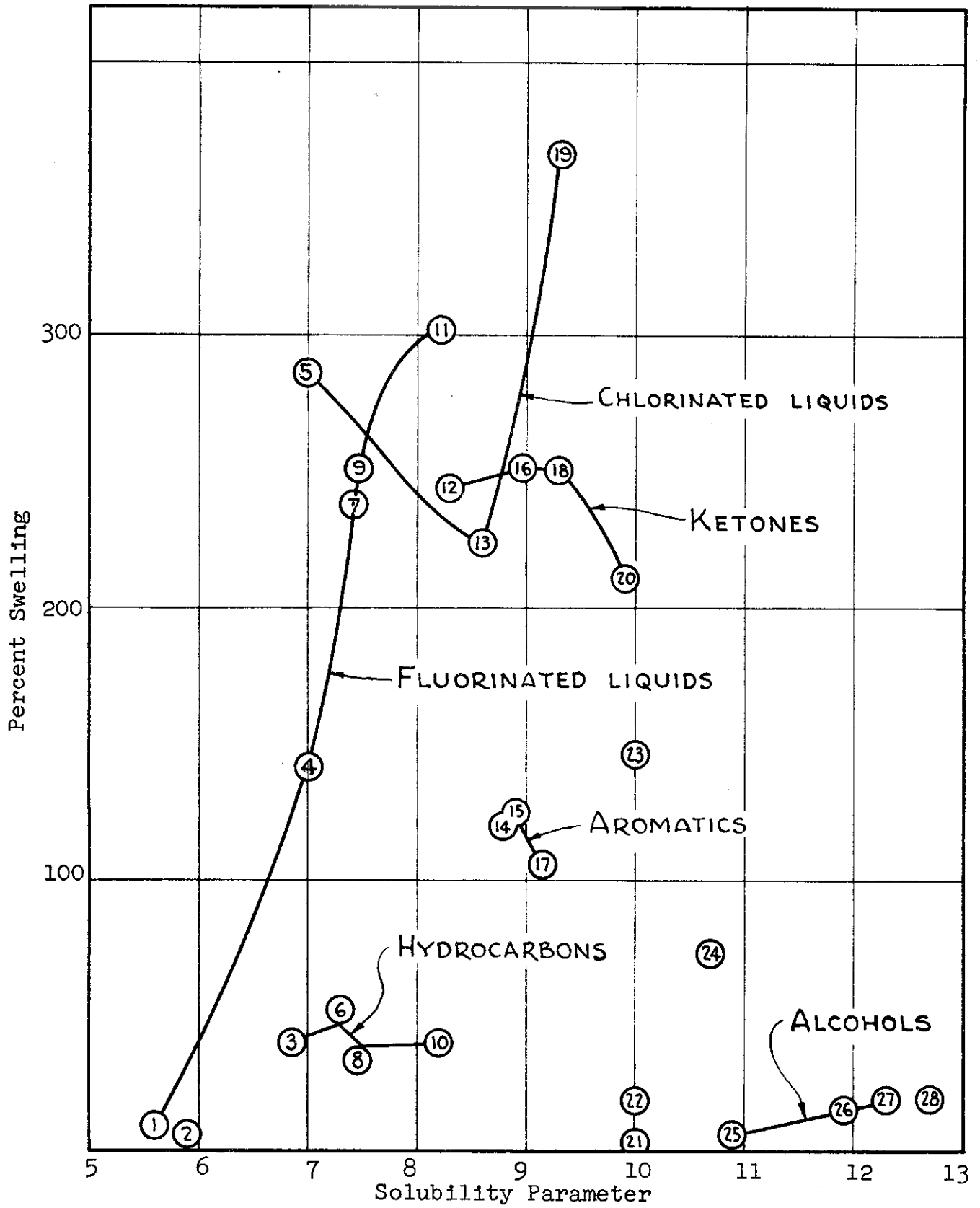


FIGURE 21
 PERCENT SWELLING OF SILICATE CURED FBA:BD COPOLYMERS VS.
 SOLUBILITY PARAMETER

Contrails

TABLE XLVI

SWELLING OF SILICATE CURED POLY-FHA AND POLY-FBA:BD SWOLLEN 160 HRS.

No.	Solvent	Per cent Swelling		6
		Poly-FHA	Poly-FBA:BD	
1	Perfluorohexane	137	9	5.6
2	Cyclo-C ₈ F ₁₆ O	130	6	5.9
3	Iso-octane	6	40	6.85
4	MFB purified	762	141	7.0
5	Freon 113	192	287	7.0
6	Hexane	6	52	7.3
7	Ethyl ether	33	238	7.4
8	n-Heptane	3	33	7.45
9	Xylene hexafluoride	310	251	7.47
10	Cyclohexane	3	40	8.20
11	Benzotrifluoride	91	302	8.20
12	MIBK	37	244	8.3
13	CCl ₄	12	224	8.6
14	Xylene	6	120	8.80
15	Toluene	9	125	8.90
16	Ethyl acetate	37	251	8.95
17	Benzene	9	105	9.15
18	MEK	30	251	9.3
19	Chloroform	23	366	9.3
20	Acetone	30	211	9.9
21	Nitrobenzene	6	3	10.0
22	CS ₂	3	19	10.0
23	1,4-Dioxane	19	146	10.0
24	Pyridine	12	73	10.7
25	n-Amyl alcohol	3	6	10.9
26	Isopropyl alcohol	3	16	11.9
27	Ethyl alcohol	12	19	12.3
28	Nitromethane	9	19	12.7
29	Dimethyl formamide	19	26	14.0
30	Methyl alcohol	58 (Init. swell) 50 (Amt. extrac.)	48 25	14.3
31	Oleic acid	1	6	7.3
32	Glacial acetic acid	95	64	10.0
33	Skydrol T-17	0	16	
34	Diocetyl sebacate	0	12	
35	Water	12	16	24.0

Contrails

value of 6.5. Although no pure liquid with a δ of 6.5 was available to substantiate the curve as drawn, the swelling of poly-FHA in mixed solvents, Figure 22, is consistent with a δ of 6.5. As was observed for FBA, the hydrocarbons are surprisingly poor swelling agents, exhibiting only 5% of the swelling observed for fluorinated liquids with comparable solubility parameters.

Most of the lines connecting the swelling volumes for similar liquids show the anticipated trends of swelling vs. solubility parameter. The swelling volumes in water and alcohols, however, increase with increasing δ . Chemical interaction, probably involving the cure, is apparently occurring here as with poly-FBA. Water eventually swelled the poly-FHA samples 565%. Methanol extracted 50% of the sample into solution, probably through an ester exchange mechanism, leaving the remainder stiff and (for some reason) apparently very highly cross-linked. A similar chemical interaction was observed with the FBA:butadiene samples. Curing with sulfur appears to eliminate the interaction completely.

"Skydrol" and dioctyl sebacate, which are of commercial interest, have little effect on either

Contrails

poly-FHA or FBA:butadiene even after heating the solutions for one week at 100°C. Although δ values are not available for these molecules, they probably are well above that of FHA. Since swelling volumes are well above that of FHA. Since swelling volumes vary inversely as the molar volume, the large molar volumes of these materials also tend to reduce swelling.

ing. Comparison of these swelling volumes for poly-FHA with values measured previously for a more highly cured sample demonstrates the expected dependence of swelling on the state of cure. A reduction in swelling from 310% to 105% is observed in xylene hexafluoride and from 137% to 73% for perfluorohexane. Where the swelling volume is already small, as in benzene, it is not reduced by further cross-linking.

The FBA:butadiene copolymer has an entirely different pattern of swelling. The δ value of polybutadiene is 8.5. As a result, many liquids with solubility parameters from 7 to 9.9 swell the copolymer more than 200%, producing a flattened swelling curve with a suggestion of two maxima. Had the force fields of the two monomers not interacted, two sharply defined maxima at 6.7 and 8.5 would have been observed. On

Contrails

the other hand, if complete averaging of the forces had occurred, a single maximum at approximately 7.6 would have been found. The observed behavior indicates that some interaction is occurring but suggests heterogeneity of force fields along the copolymer chain.

Swelling data for FHA and the FBA:butadiene copolymer in mixed solvents are plotted in Figure 22. The results determine a solubility parameter near 6.5 for poly-FHA and 8.1 for the FBA:butadiene copolymer.

For poly-FHA as with poly-FBA, if the δ values of the two solvents are both higher or lower than the optimum value, little enhancement of swelling is observed. When one value is above and one below, however, the observed swellings are substantially greater than the calculated. This fact justified characterizing these solvent systems by a single δ value in interpreting the swelling of poly-FHA in mixtures.

In contrast, the poly-FBA:Bd results have numerous exceptions. Though the points describe a reasonable curve, several mixtures are unexplainable efficient swelling agents. Apparently, the copolymer system frequently fails to comply even qualitatively with

Contrails

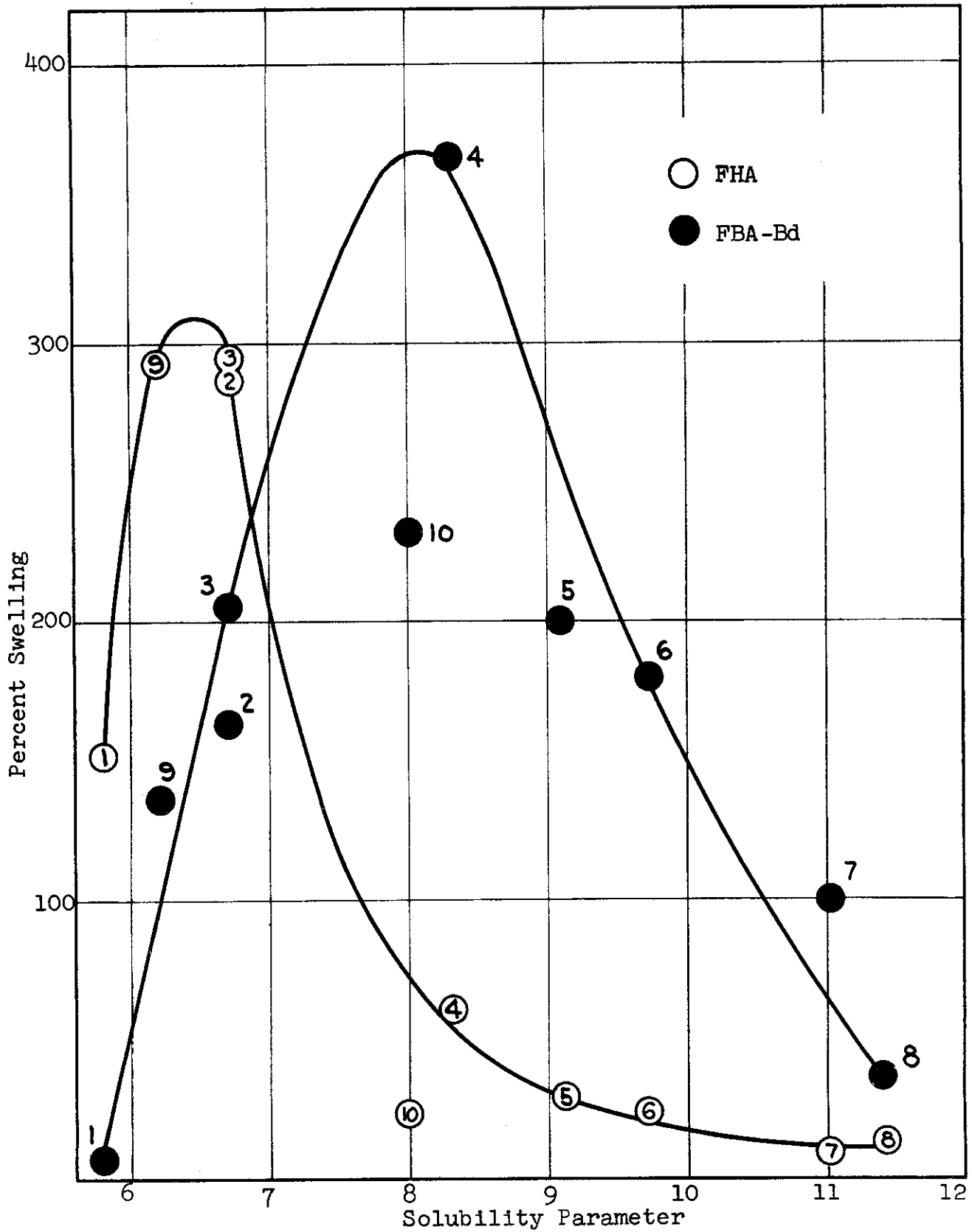


FIGURE 22

PERCENT SWELLING OF FHA AND FBA:BD VS. SOLUBILITY PARAMETER OF MIXED SOLVENTS

simple solubility theory. Though the theory serves to resolve some apparent anomalies, it must be applied cautiously to such complicated systems.

10. Determination of Molecular Weight of Poly-FBA by Light Scattering

Seven fractions of poly-FBA produced by light polymerization, each the result of at least three fractionations, have been prepared. The intrinsic viscosities of these, measured in benzotrifluoride, varied from 0.55 to 1.62. The molecular weights of these fractions dissolved in benzotrifluoride were determined by light scattering and the following relationships were found in this solvent:

$$[\eta] = 1.3 \times 10^{-4} \times M^{0.56} \text{ at } 26.6^\circ$$

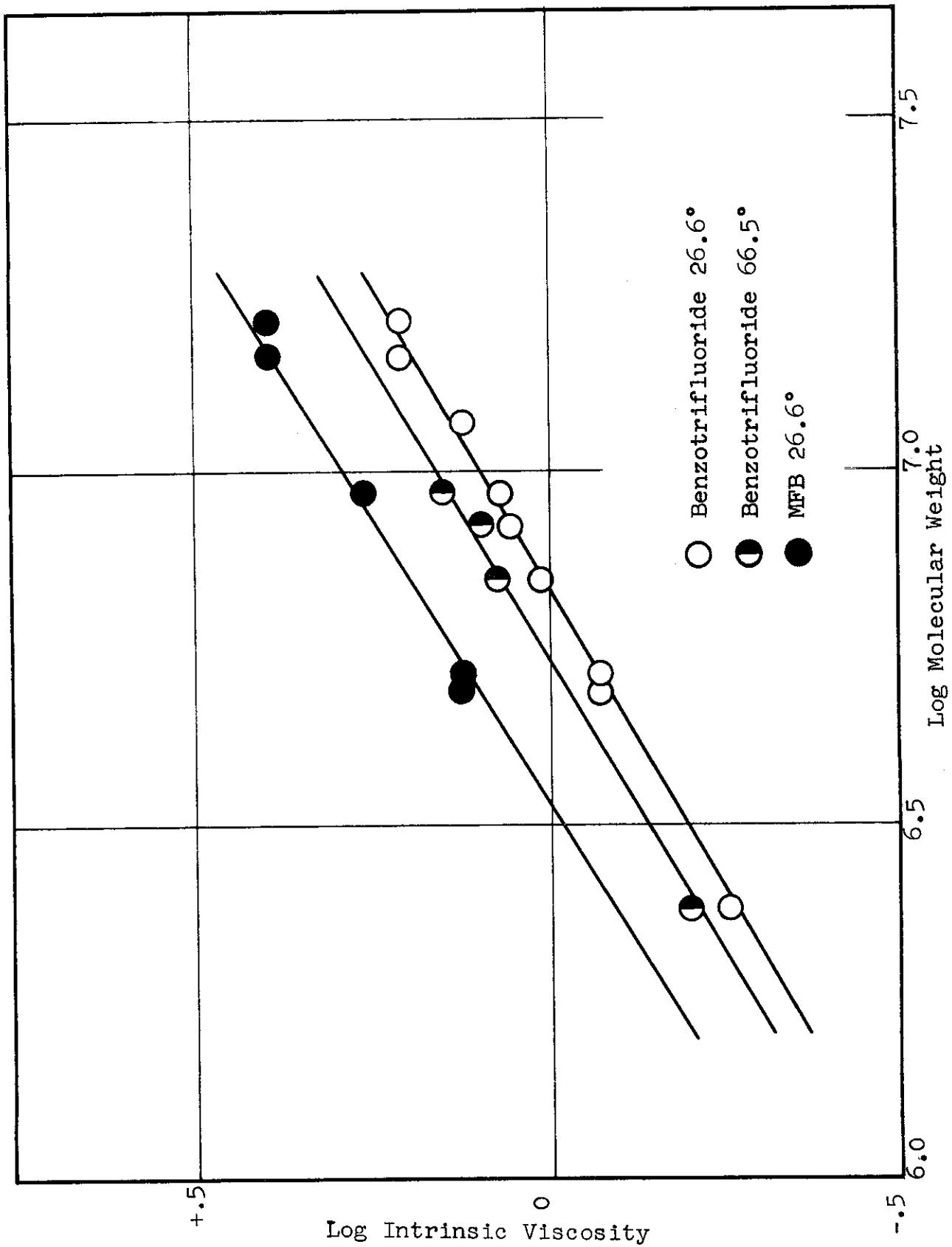
$$[\eta] = 1.4 \times 10^{-4} \times M^{0.57} \text{ at } 66.5^\circ$$

In methyl perfluorobutyrate:

$$[\eta] = 1.2 \times 10^{-4} \times M^{0.60} \text{ at } 26.6^\circ$$

The temperatures shown refer to the temperature at which the viscosity was determined. The viscosity-molecular weight relationships are plotted in Figure 23.

FIGURE 23
INTRINSIC VISCOSITY VS. MOLECULAR WEIGHT FOR FRACTIONATED FBA



Contrails

In addition to the molecular weight, the molecular size was determined for all fractions by dissymmetry measurements. The intrinsic viscosities and molecular weights are shown in Table XLVII. Likewise, the molecular size, expressed as the root mean square length of the molecule, L , is shown. The intrinsic viscosity should be proportional to L^3 . In the last column of Table XLVII the value of $L^3/[\eta]$ is shown. Except for the first value, the results are approximately constant, indicating that this relationship holds.

The values of the change of refractive index with concentration are shown in the next to last column of the table. These values are in good agreement for the three fractions measured and are likewise in quite good agreement with the calculated value of 2.85×10^{-2} . It was found to be important to dry the polymers thoroughly for this determination, since small amounts of residual solvent can introduce large errors.

The viscosity values indicate that benzotrifluoride is a considerably poorer solvent than methyl

Contrails

TABLE XLVII

MOLECULAR WEIGHTS AND INTRINSIC VISCOSITIES OF POLY-FBA FRACTIONS

benzotrifluoride 26.6°	[η] 66.5°	fluorobutyrate 26.6°	70.0°	md. wt. x 10 ⁶		Molecular length, Å, I benzotri- fluoride	benzotri- methyl per- fluorobutyrate	dn _D dc x 10 ²	$\frac{I^3}{dn}$ x 10 ¹⁷
				benzotri- fluoride	methyl per- fluorobutyrate				
0.55	0.64	--	--	2.4	--	1020	--	3.11	0.195
0.85	--	1.33	1.28	5.5	4.9	1440	1660	3.11	0.353-0.341
1.04	1.20	--	--	7.1	--	1610	--	3.05	0.401
1.12	1.25	--	--	8.4	--	1640	--	--	0.387
1.16	1.42	1.84	--	9.4	--	1640	--	--	0.380
1.32	--	--	--	11.8	--	1710	--	--	0.379
1.62	--	2.48	--	16.4	12.8	1800	2030	--	0.360-0.336

Contrails

perfluorobutyrate, but that it improves as the temperature is raised. The molecular weight values indicate, as has been previously shown, that the molecules are very large and give viscosities much lower than most polymers.

If these molecules were unbranched, the molecular weight would be proportional to L^2 . The fact that the molecular weight increases faster than L^2 indicates that the larger molecules are relatively more compact than the smaller ones, which is in turn indicative of branching.

An interesting test of Debye's prediction of a maximum turbidity for some concentration of polymer in solution was obtained for one of these fractions. According to Debye,¹

1. P. Debye, J. Chem. Phys. 18, 1423 (1950)

the polymer solution should be most turbid when

$$V_2 = \frac{1}{n^{1/2}},$$

where V_2 is the volume fraction and n is the degree of polymerization. For the fraction studied, the molecular weight was 8.4×10^6 and that calculated from the above

Contrails

equation was 7.5×10^6 . For polystyrene Debye observed a 35% discrepancy in the opposite direction, so the agreement must be regarded as only qualitative.

VII. TESTING METHODS AND EQUIPMENT

We now have the necessary equipment for measuring percent swelling of vulcanizates in accordance with Method B of ASTM D471. A new mold, die, and reading table have been made. The method involves following the linear elongation of strips of rubber 10 cm in length immersed in a test fluid, and calculating the corresponding volume increase. The procedure is very simple and rapid but somewhat more material is required for each test than was needed in our previous measurements. Reproducibility of results is poorer than when the weight method is used and the swelling volumes obtained tend to run about 10-20% lower. This method is probably more accurate than previous measurements employing Gehman strips.

The laboratory ozonizer was recalibrated with potassium iodide solution. Under the usual operating conditions, 500-600 ppm. of ozone by volume were found in the test chamber, compared to the originally reported concentration of 350 ppm. This represents extremely severe conditions, far exceeding those in standard tests.

Contrails

The acquisition of the Hi-Po-Log relaxometer has been mentioned in the discussion above. The modification of the Instron stress-strain tester for measurements at elevated temperatures has also been indicated. The capacity of the Instron tester has been increased to 1000 lbs. by the purchase of a new load cell, jaws, and appropriate accessories.

Contrails

APPENDIX

A -

CURING FORMULAE FOR STATE OF CURE STUDIES

<u>Poly-FBA - Silicate Cure</u>		<u>Poly-FBA - Oxide Cure</u>	
Poly-FBA	100	Poly-FBA	100
Calcium hydroxide	2.72	Stearic acid	1
Sodium metasilicate nonohydrate	6.72	Litharge	5
		Calcined magnesia	25

FBA:But. Copolymer - Sulfur Cure

40:60 FBA:butadiene copolymer	100
Phenyl β -naphthylamine (Neozone D)	1
Stearic acid	1
Zinc oxide (Kadox 15)	5
Benzothiazyl disulfide (Altax)	1.5
Tetramethyl thiuram disulfide (Methyl Tuads)	0.15
Sulfur	2
EPC carbon black (Spheron #9)	35

Hycar OR-15 - Sulfur Cure

Hycar OR-15	100
Phenyl β -naphthylamine (Neozone D)	1
Stearic acid	1
Zinc oxide (Kadox 15)	5
Benzothiazyl disulfide (Altax)	1.5
Tetramethyl thiuram disulfide (Methyl Tuads)	0.15
Sulfur	1.5
EPC carbon black (Spheron #9)	50

CURE: variable

- 189 -
WADC TR 52-197 Pt 3

Contrails

APPENDIX

B -

CURING FORMULAE FOR COMPRESSION SET STUDIES

Poly-FBA - Silicate Cure

Poly-FBA - Oxide Cure

Same as in Appendix A

Cure: 5 hrs. at 310°F.

Cure: 2 hrs. at 310°F.

FBA:But. Copolymer - Sulfur Cure

	<u>Gum Stock</u>	<u>Reinforced F=Stockred</u>
32:68 FBA:butadiene copolymer	100	100
Phenyl β-naphthylamine (Neozone D)	1 1	1
Stearic acid	1	1
Zinc oxide (Kadox 15)	5	5
Benzothiazyl disulfide (Altax)	1.5	1.5
Tetramethyl thiuram disulfide (Methyl Tuads)	0.15	0.15
Sulfur	2	2
EPC carbon black (Spheron #9)	-	35

CURE: 20 min. at 300°F.

Hycar OR-15 - Sulfur Cure

	<u>Gum Stock</u>	<u>Reinforced Stock</u>
Hycar OR-15	100	100
Phenyl β-naphthylamine (Neozone D)	1	1
Stearic acid	1	1
Zinc oxide (Kadox 15)	5	5
Benzothiazyl disulfide (Altax)	1.5	1.5
Tetramethyl thiuram disulfide (Methyl Tuads)	0.15	0.15
Sulfur	1.5	1.5
EPC carbon black (Spheron #9)	-	50

Cure: 20 min. at 300°F.

- 190 -

WADC TR 52-197 Pt 3

APPENDIX

B - Cont'd.

Paracril 18 - Sulfur Cure

	<u>Reinforced Stock</u>
Paracril 18	100
Phenyl β -naphthylamine (Neozone D)	1
Stearic acid	1
Zinc oxide (Kadox 15)	5
Benzothiazyl disulfide (Altax)	1.5
Tetramethyl thiuram disulfide (Methyl Tuads)	0.15
Sulfur	1.5
EPC carbon black (Spheron #9)	50

CURE: 45 min. at 300°F.

Contracts

APPENDIX

C. Raw Materials Provided During Report Period for Polymer Studies

1,1-Dihydroperfluorobutyl vinyl ether
1,1-Dihydroperfluorohexyl vinyl ether
Perfluorocyclohexene
1,1-Dihydroperfluorobutene-1
Perfluoropropylene *
Perfluoroacrylonitrile*
Perfluoroacrylyl fluoride
1,1-Dihydroperfluoroamyl acrylate
1,1,5-Trihydroperfluoroamyl acrylate
1,1,3-Trihydroperfluorobutyl acrylate
 β -(1,1-Dihydroperfluoroethoxy) ethyl acrylate
 β -Hydroperfluoroethoxyethyl acrylate
 δ -Hydroperfluoroethyl diethylene glycol acrylate
(1,1-Dihydroperfluorobutoxy)ethyl acrylate
 β -(2-Perfluorofuryl)-1,1-dihydroperfluoroethyl acrylate
 γ -(Perfluoromethoxy)-1,1-dihydroperfluoropropyl acrylate
 γ -(Perfluoroethoxy)-1,1-dihydroperfluoropropyl acrylate*
 γ -(Perfluoropropoxy)-1,1-dihydroperfluoropropyl acrylate
 γ -(Perfluorobutoxy)-1,1-dihydroperfluoropropyl acrylate
3,3,3-Trichloroperfluoropropene-1
1,1-Dichloroperfluoropropene
1,1,3,3,3-Pentachloroperfluoropropene-1
2-Hydroperfluoropentene

* Materials first prepared during earlier report periods; further quantities prepared during this period.

Contrails

APPENDIX

D. Samples Sent to Wright Air Development Center

*FBA Monomer	- 1 lb.	August 24, 1952
Poly-FBA	- 4.75 lbs.	November 10, 1952
*Trifluoroethanol	- 4 oz.	November 10, 1952
*FBA Monomer	- 1 lb.	November 18, 1952
Perfluorobutadiene:Ethy- lene Copolymer (described p.6, Report #14)	- 3.5 g.	February 11, 1953
Poly-FBA	- 15 lbs.	February 20, 1953
*Methyl Perfluoro- butyrate	- 2 lbs.	March 6, 1953
*FBA-Monomer	- 2 lbs.	May 6, 1953

* These samples represent material not within the scope of the Research Contract No. AF33(038)-515. They were prepared and submitted at the request of various representatives of the Wright Air Development Center. The basis for cooperation in furnishing these samples is given in detail in the letter from Dr. W. H. Pearlson to the attention of Col. M. E. Sorte, dated April 24, 1951.