TI-1915

Part 3 SYNTHETIC RUBBERS FROM CARBON-FLUORINE COMPOUNDS

F. A. Bovey

Minnesota Mining and Manufacturing Company

September 1953

WRIGHT AIR DEVELOPMENT CENTER

20020611069

NOTICES

○○○○○○○○○○

Part 3   SYNTHETIC RUBBERS FROM CARBON-FLUORINE COMPOUNDS

F. A. Bovey

Minnesota Mining and Manufacturing Company

September 1953

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 $350^\circ F.$, 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.

<center>PUBLICATION REVIEW</center>

This report has been reviewed and is approved.

FOR THE COMMANDER:

J.W.Cummings Lt.Col.USAF

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

TABLE OF CONTENTS

vii

LIST OF ILLUSTRATIONS

LIST OF TABLES

LIST OF TABLES (Continued)

x

Page

LIST OF TABLES (Continued)

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 flex-
ibility, 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

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 flex-
ibility 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 temper-
atures, 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

- 3 -

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, $R_f CFHCF_2OCH:CH_2$, give plastic polymers having only limited elastic behavior and no further work with these is contemplated. The 1,1-dihydroperfluoroalkyl vinyl ethers, $R_f CH_2OCH:CH_2$, 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.

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

- 5 -

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

- 6 -

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. <u>Fluorine-Containing Acrylates</u>

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, $R_fOCF_2CF_2CH_2OCOCH:CH_2$. 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

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 improve-
ment over the butadiene copolymers of the earlier
acrylates has been realized. As an example of the
properties observed, the homopolymer of γ-(perfluoro-
methoxy)-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,

vinyl triethoxysilane, and acrylic acid. These
studied 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 vulcan-
izates, 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

- 9 -

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

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

- 11 -

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.

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-dihydroperfluoro-alkyl 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 bascity to such a degree that Lewis acids do not interact appreciably with it. In the hydro-carbon 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

- 13 -

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:

	Parts by Weight	
	A	B
Monomer	100	100
Water	180	180
Duponol ME	3	---
Ammonium perfluoro-octanoate	---	6
$Na_2S_2O_8$	1	1
Na_2HPO_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

- 14 -

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

- 15 -

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 hydr...., washed with acetone, and dried. A total of three grams of poly......... obtained. It was a very soft, tacky ....ples were heat d 200°, after a p.. ...., a combined of s....r, .1 wax . (essentially the same recipe as on page 34). and a combination of .van.. Stabilizer E-6B and phenyl-β-naphthylamine. The results of measurements of weight loss with 1 part phenyl-'-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

- 16 -

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 under-
gone 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

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. <u>Perfluorocyclohexene</u> was studied, with regard
to both homopolymerization and copolymerization.
Likewise, <u>1,1-dihydroperfluorobutene-1</u>, $CH_2=CFCF_2CF_3$
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-dihydroperfluoro-
butene-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 perfluoro-
acrylonitrile, trifluorochloroethylene, and

WADC TR 52-197 Pt 3

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. <u>Perfluoropropylene</u> 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

- 20 -

TABLE I

COPOLYMERIZATION OF C_3F_6 WITH STANDARD MONOMERS

Tube No.	Comonomer M_1	$M_2(C_3F_6)$, Mol Charge Ratio	Reaction Conditions	Ac_2O_2 Catalyst %	Conversion %	Copolymer Analysis	Wt. % C_3F_6	Mol % M_1	Mol % C_3F_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

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.

WADC TR 52-197 Pt 3

TABLE II

COPOLYMERIZATION OF C_3F_6 AND ISOBUTYLENE

Mol Ratio C_3F_6-iC_4H_8	Catalyst	Reaction Conditions	% Conversion	Mol% C_3F_6 in Polymer	Nature of Polymer
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.

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

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 <u>vinylidene fluoride</u> and with <u>trifluorochloroethylene</u> by both methods. With <u>vinyl 1,1-dihydroperfluorohexyl ether</u> (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 <u>vinylidene chloride,</u> perfluoroacrylonitrile gave a white powdery product in a yield of less than 50%. This material softened at 150-170°C. and appeared to be

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 megaroentgens of Co 60 gamma radiation at Brookhaven

TABLE III

PERFLUOROACRYLONITRILE – VINYL ETHER COPOLYMERS

Tube	Vinyl Ether	Perfluoroacrylo- nitrile:Vinyl Ether Charge Ratio, Molar	Nature of Polymer	% Yield	% F	Mole % perfluoro- acrylonitrile
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.

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 % perfluoro-acrylyl fluoride) was produced. This material was insoluble in benzene and acetone but dissolved slowly in dilute base. When heated, it became rubbery at 75°C. and charred above 250°C. without softening further.

- 29 -

V. PERFLUOROBUTADIENE

In the last annual report, copolymers of per-
fluorobutadiene 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 perfluoro-
butadiene 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 perfluoro-
butadiene 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

The product after 48 hours at 80-85°C. was
rubbery but was formed in only 20% yield. It con-
tained 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
$Na_2S_2O_8$	- 1
$NaHSO_3$	- 0.5
Borax	- 0.5
$t-C_{12}$ mercaptan	- 1.0

Two polymerizations were carried out. One

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

- 32 -

tabulated in Table IV.

TABLE IV

SWELLING OF PERFLUOROBUTADIENE:ETHYLENE COPOLYMER

Solvent	δ	Swelling %
c-$C_8F_{16}O$	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 diffi-
cult 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 C_8 ether, c-$C_8F_{16}O$, 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 inter-
action between carbonyl groups and hydrogens on

- 33 -

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

- 34 -

TABLE V

AGING OF PERFLUOROBUTADIENE:ETHYLENE (FB-C_2H_4) AND OTHER POLYMERS AT 200°C.

Polymer	Cure	Anti-oxidant	Time of Hardening Hours[1]	Wt. Loss % 64 Hrs.	Wt. Loss % 140 Hrs.	Relative Moduli 21 Hrs.	42 Hrs.	64 Hrs.	87 Hrs.	177 Hrs.	140 Hrs.	162 Hrs.	185 Hrs.
FB:C_2H_4 Bulk	None	None	75	11%	18%	2.47	3.18	7.56	78.0	114			
FB:C_2H_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_2H_4 Bulk	None	None	65	10	19	3.34	4.83	16.8	254	300			
FB:C_2H_4 Bulk Extracted	Sulfur	None	95	7	14	1.46	1.87	3.14	37.6	66.5			
FB:C_2H_4 Bulk Extracted	None	None	175	15	20	1.18	1.52	2.10	2.86	4.80	4.94	7.95	18.1
FB:C_2H_4	None	PBNA Agerite D + PEA	190	15	19	1.12	1.37	1.68	2.42	2.88	3.10	3.88	
FB:C_2H_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_2H_4	Sulfur	None	110	18	26	3.92	5.32	8.32	8.88	18.9			
FB:C_2H_4	Sulfur	PBNA Agerite D + PEA	70	16	23	4.85	6.05	8.30	32.0	68.0	109	437	595
FB:C_2H_4	Sulfur	Agerite D + PEA	70	16	24	4.15	5.56	8.40	50.7	127			
pFBA	M_gO	None	70	22	39	--	0.20	8.15	38.0				
						1 Hr.	3 Hrs.						
Paracril 18	Sulfur	None	2	--	--	1.53	89.5						
Paracril 18	Sulfur + Carbon Black	PBNA	3	--	--	0.95	9.50						
Hycar OR-15	Sulfur Carbon Black	Agerite Resin D	2	--	--	1.39	25.6						

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

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 perfluoro-butadiene: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 per-fluorobutadiene copolymers.

- 36 -
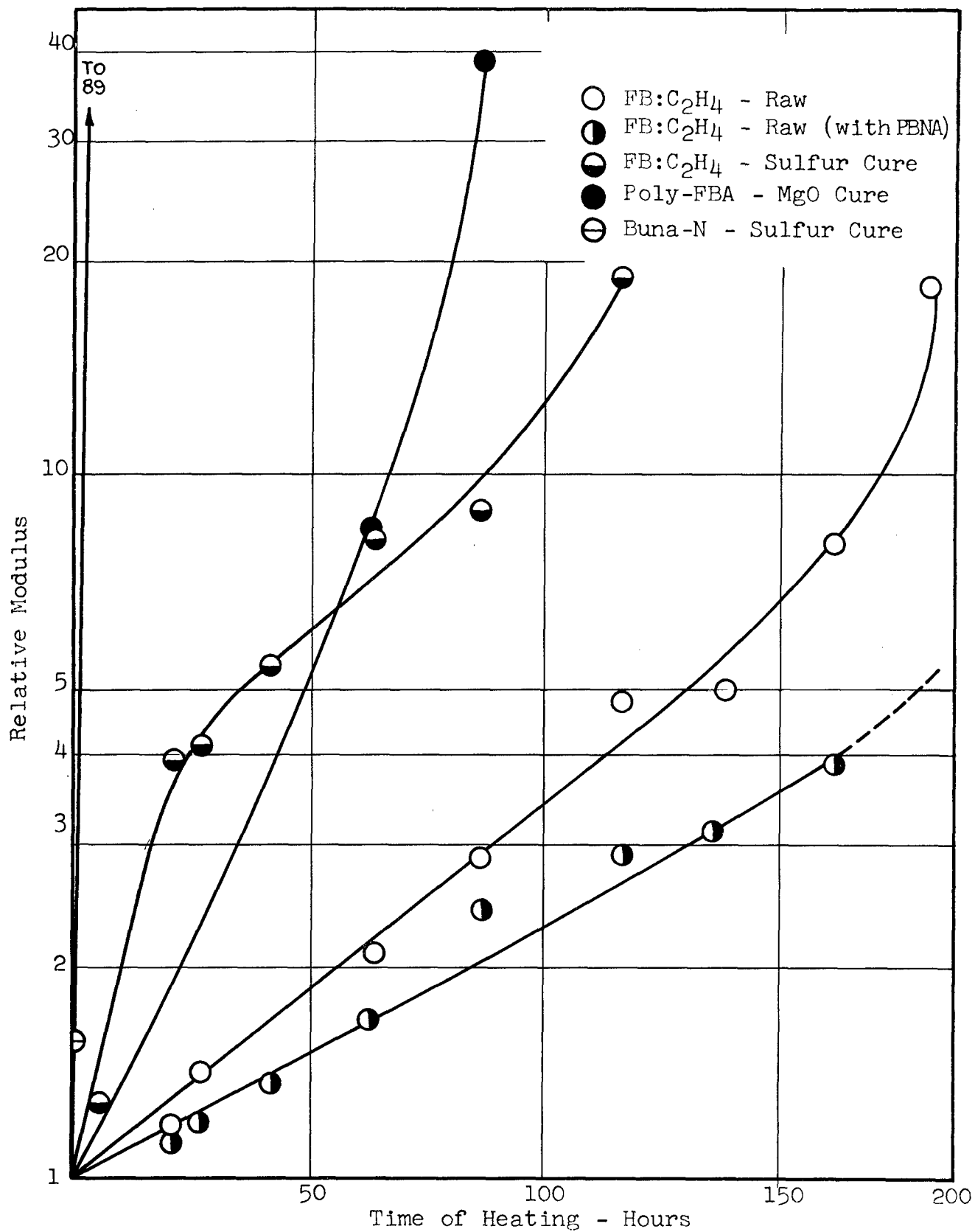
FIGURE 1

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 obtain-
ing elastic products at conversions above 20-25%.

B.   Perfluorobutadiene:1,1-Dihydroperfluoroalkyl Ethers

1. Preparation

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

- 38 -

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

Run No.	Charge (Molar Ratio)	Catalyst	Reaction Time and Conditions	Fluorine (%)	Composition (Wt.% FBd)	(Mol % FBd)	Nature of Product
FB-1A	1:1 FB:VFBE	1% Ac_2O_2	25 hrs.at 50°	62.2	28.1	35.2	Soft,non-tacky rubber
1B		1% Bz_2O_2	40 hrs.,U.V.	64.6	49.2	57.5	Cheesy rubber
FB-2A	1:1 FB:VFHE	1% Ac_2O_2	25 hrs.at 50°	64.2	1.6	3.2	Good rubber
2B		1% Bz_2O_2	40 hrs. U.V.	66.1	32	49	Fair rubber

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:

WADC TR 52-197 Pt 3

TABLE VII

EMULSION COPOLYMERIZATION OF PERFLUOROBUTADIENE AND VINYL 1.1-DIHYDROPERFLUOROBUTYL ETHER(VFBE) AT 50°C.

Tube No.	Mercap-tan %	Reaction Time (Hours)	Yield %	Nature of Polymer
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.

- 42 -

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

	Parts
Perfluorobutadiene	100
VFHE	180
H_2O	3
Duponol ME	1
$Na_2S_2O_8$	0.5
$NaHSO_3$	0.5
Borax	0.2
$n-C_{12}$ Mercaptan	50°
Temperature	

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

- 43 -

TABLE VIII

POLYMERIZATION OF PERFLUOROBUTADIENE AND VFHE IN VARYING RATIOS

Tube No.	Amt. FBd	Amt. VFHE	Molar Charge Ratio FBd:VFHE	Length of Reaction at 50°C.	Yield Gms.	%	Nature of Polymers
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 perfluoro-
butadiene: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 stiff-
ening rate. It seems, however, that the

- 45 -

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 de-
scribed 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 effec-
tive ingredient in the "cure" recipe. The in-
clusion 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

- 46 -
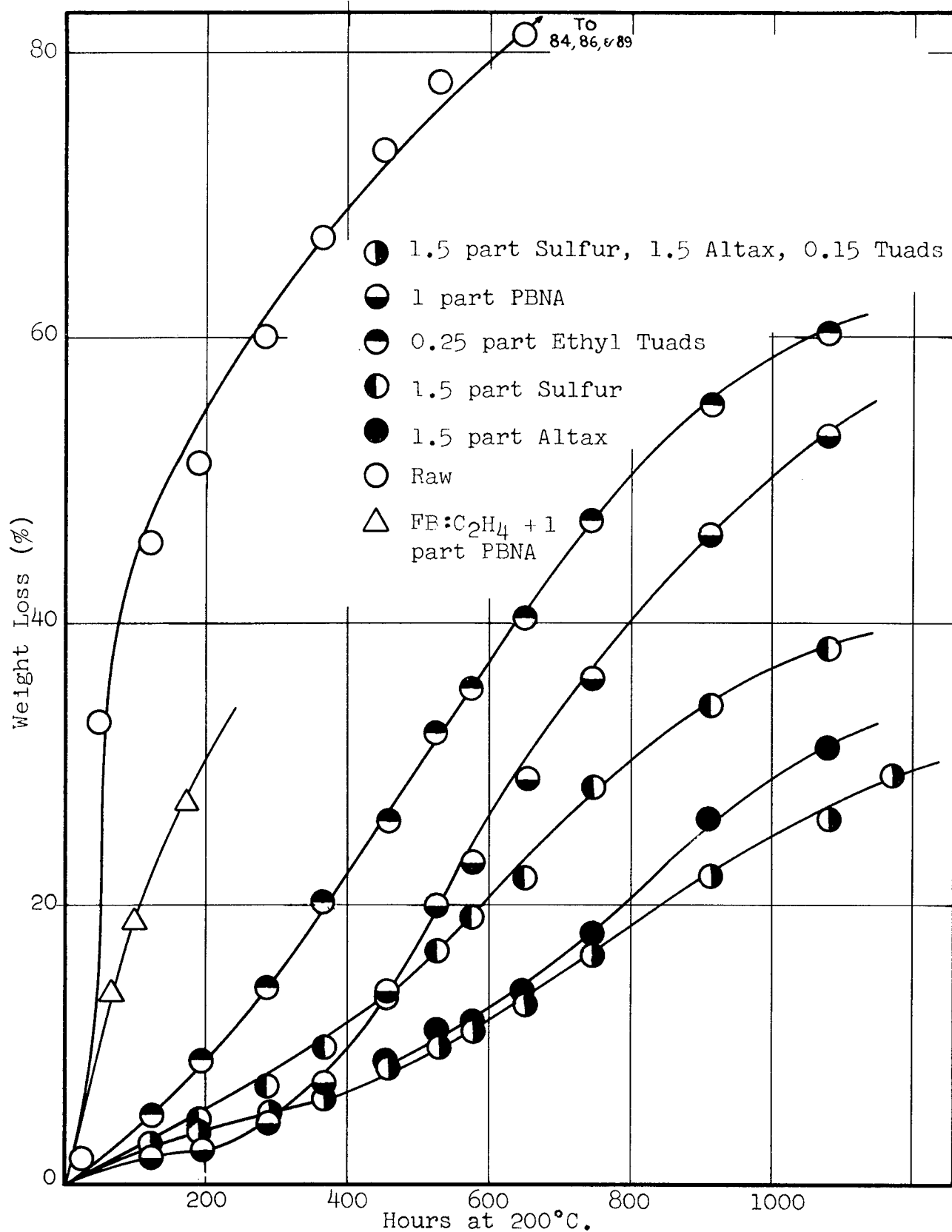
FIGURE 2

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

- 47 -
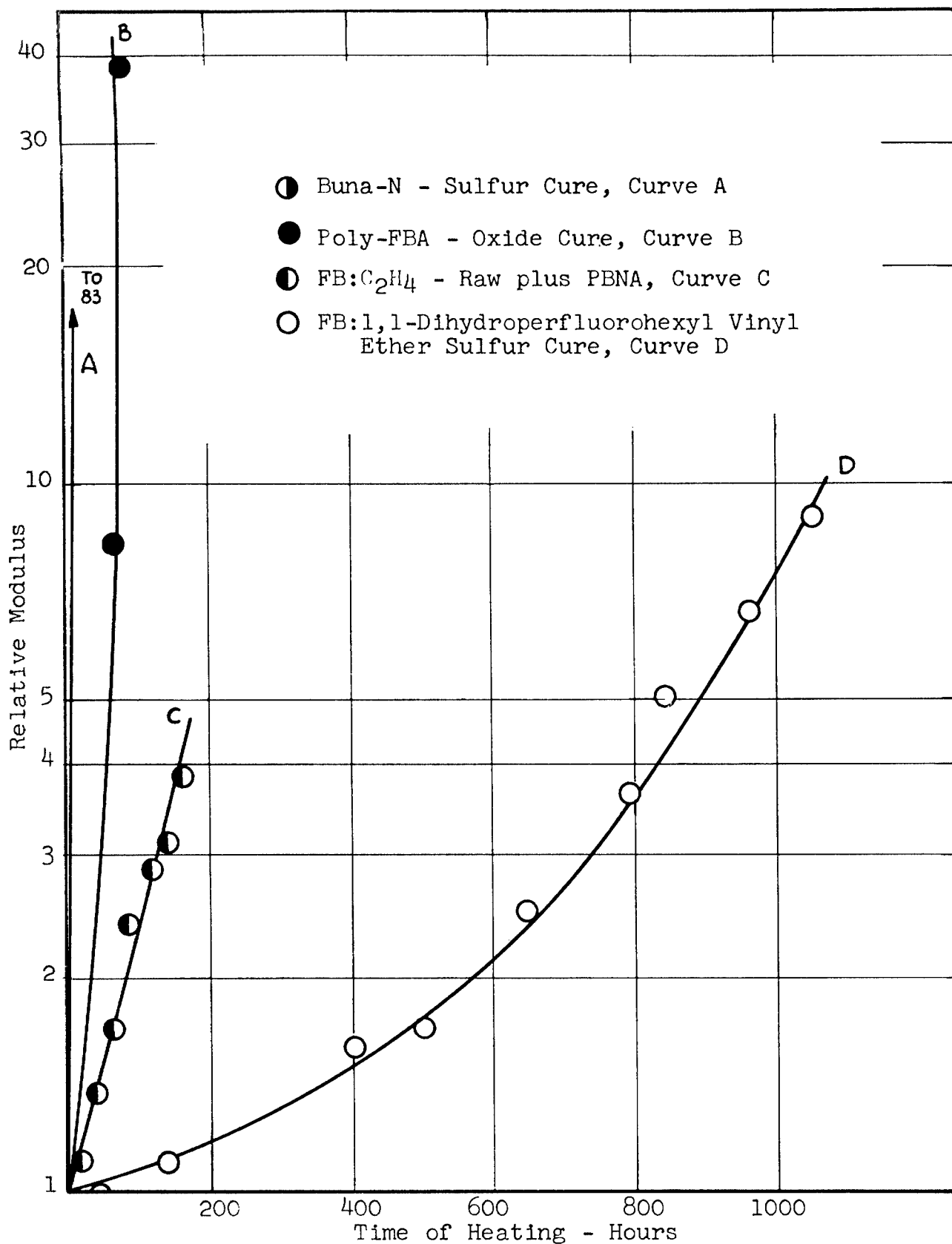
FIGURE 3

RATE OF STIFFENING OF PERFLUOROBUTADIENE COPOLYMERS AT 200°C.

WADC TR 52-197 Pt 2
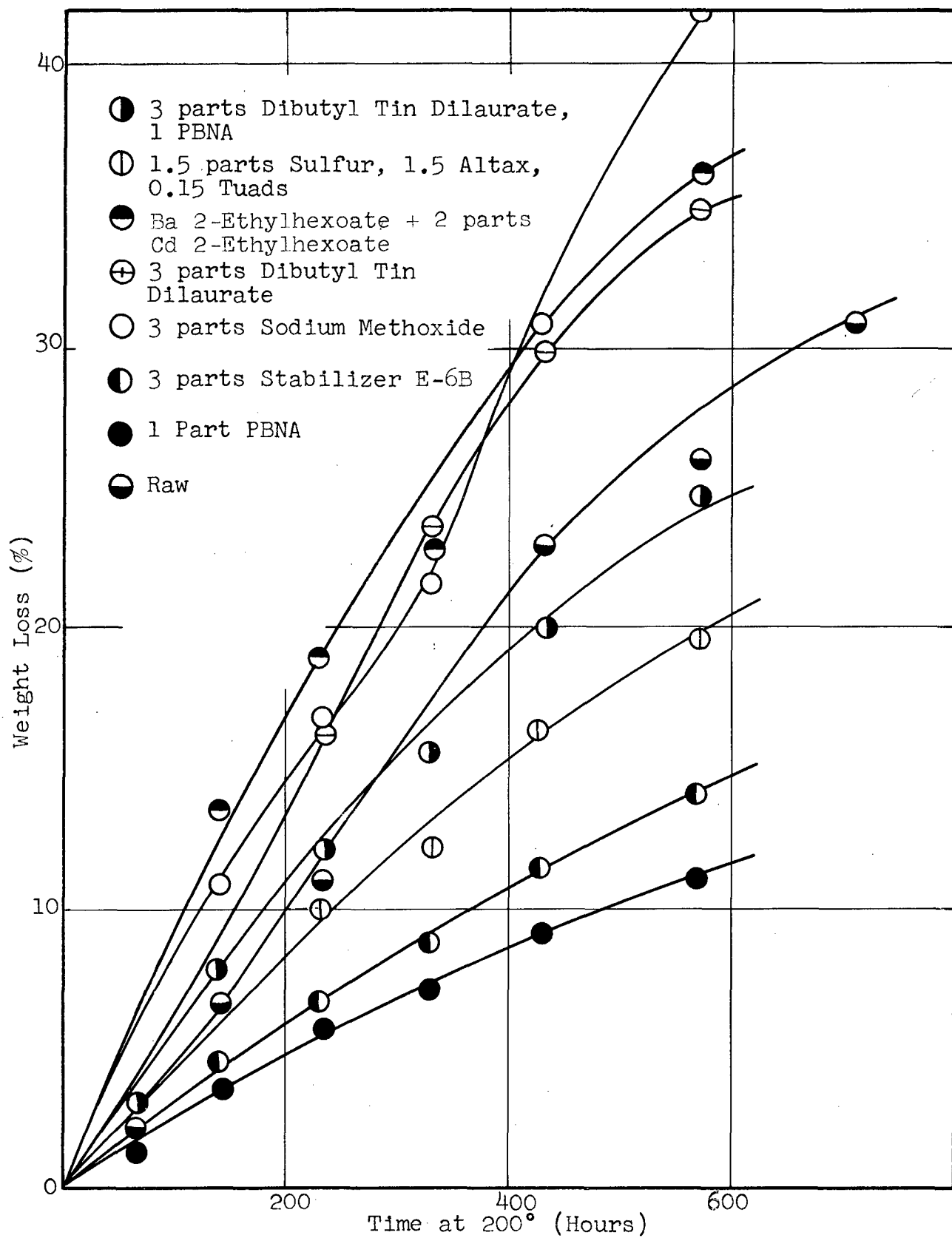
FIGURE 4

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

- 49 -

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 di-
laurate and Advance's Stabilizers E-6B and #52.
In addition, phenyl-ƒ-naphthylamine, methyl
phenyl polysiloxane (an effective material for
retarding oxidation in lubricating oils), a
number of hydroxy- and amino-substituted anthra-
quinone dyes, a combination of dibutyl tin di-
laurate and phenyl-ƒ-naphthylamine, and a com-
bination of sulfur, Altax and Tuads were eval-
uated as stabilizers. The results of many of

- 50 -

these tests are presented in Figure 4. The poly-
vinyl chloride stabilizers all proved very dis-
appointing, with the possible exception of
Advance's Stabilizer E-6B (a material of undis-
closed 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 substi-
tuted 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 copoly-
mer is compared with that for similarly stabilized
samples of the 1:1 and 3:1 copolymers, as well as
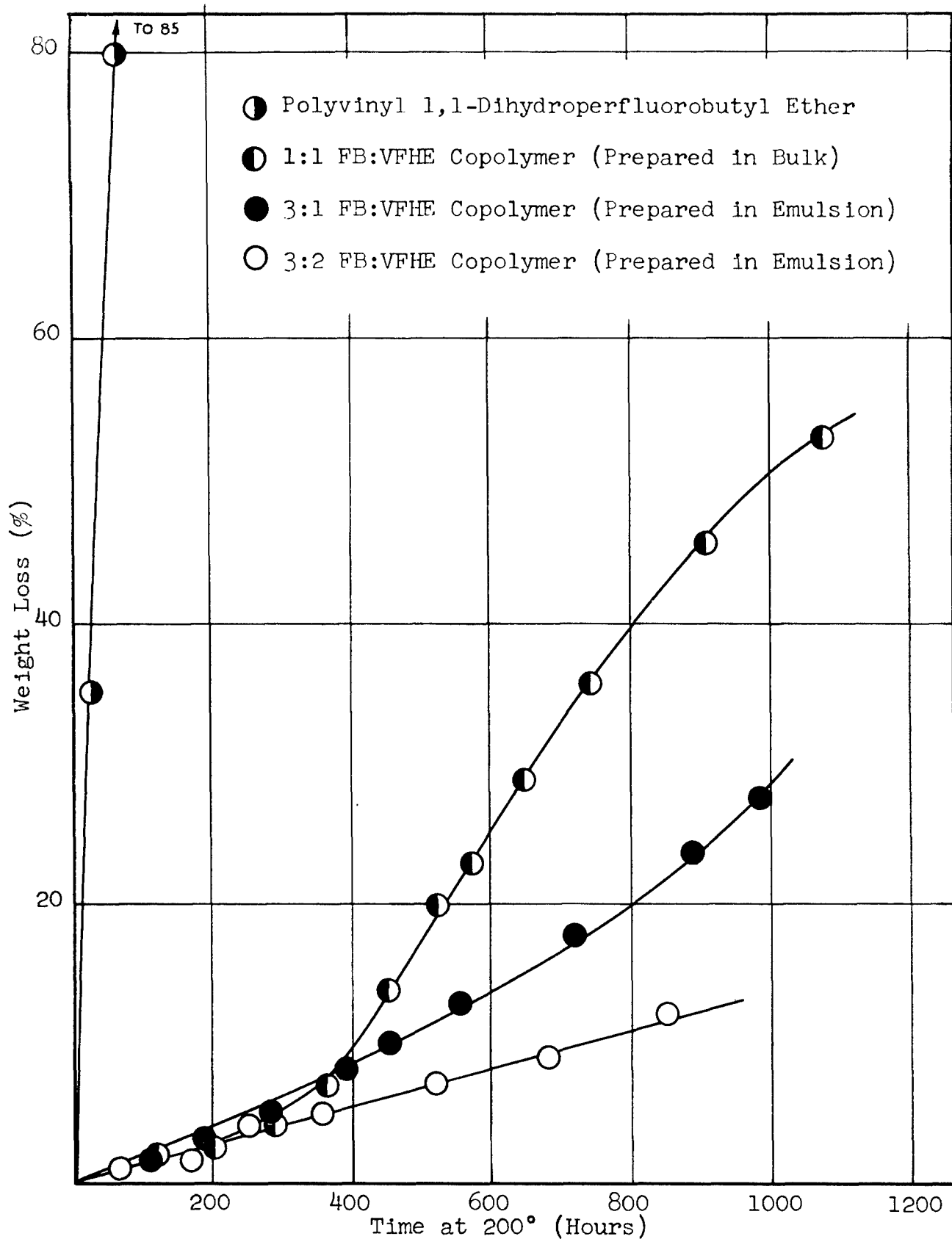
WADC TR 52-197 Pt 3

FIGURE 5

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

WADC TR 52-197 Pt 3
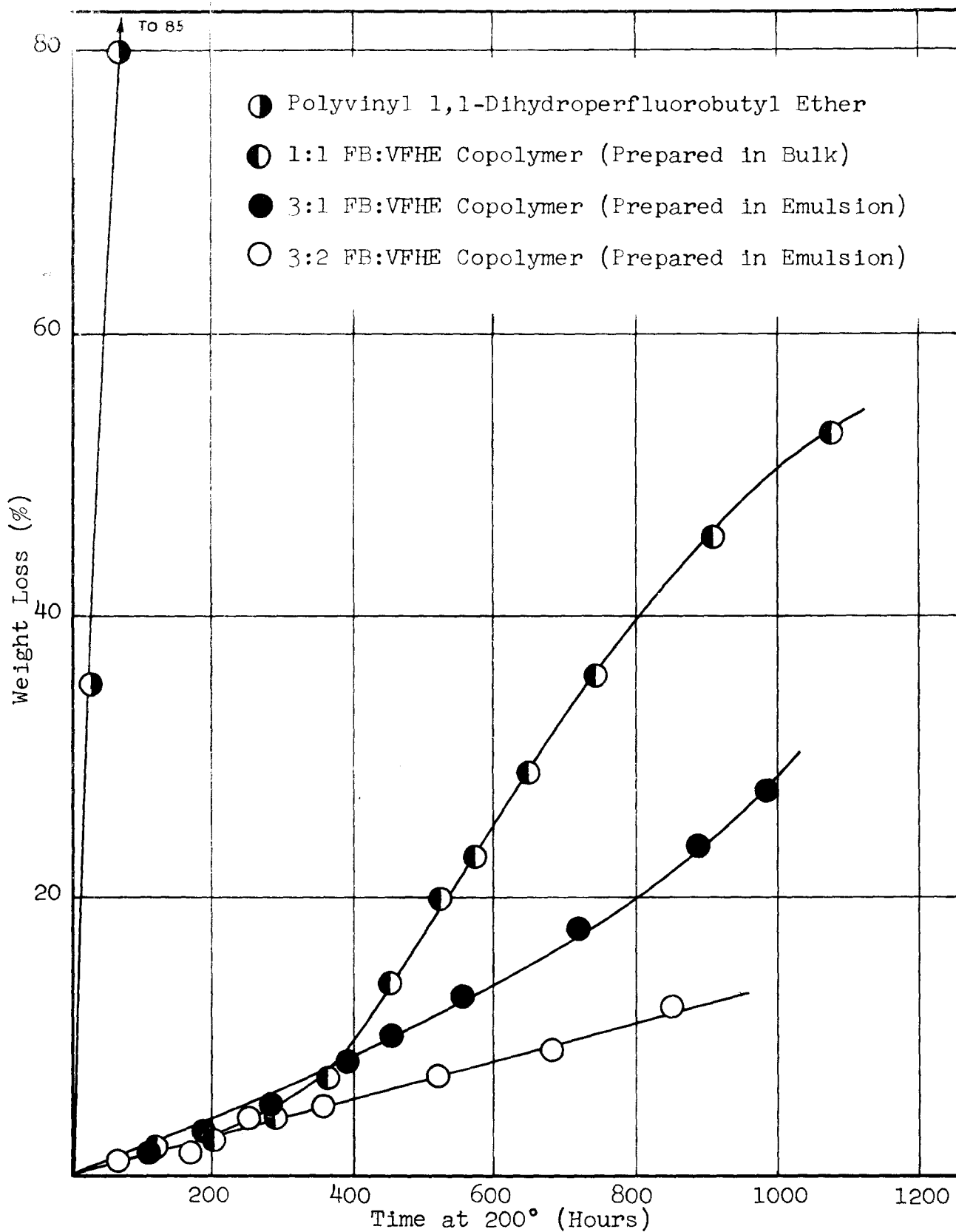
FIGURE 5

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

- 52 -

with that for the homopolymer of vinyl 1,1-dihy-
droperfluorobutyl 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 behav-
ior. 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 connec-
tion with the description of the pyrolysis exper-
iments.

3. Pyrolysis of Perfluorobutadiene:VFHE Copolymers

Some experiments have been carried out in
which unstabilized perfluorobutadiene:VFHE copoly-
mers 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

- 53 -

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:VFHE 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-C_4F_8, 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 C_5F_{11} group of the copolymer (as in the homopolymer), in addition to the loss of HF.

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 de-crease to about 1.95; whereas the ratio drpps 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 $-CF_2CH_2-$ 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 stiff-ening.

(c) Chain scission. Simple depolymeriza-tion, 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 exclu-sion of oxygen by immersion of the rubber in liquids, such as dioctyl sebacate, results in

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 elas-
ticity have been relatively poor. Consequently,
some effort has been devoted to obtaining poly-
mers with better mechanical properties. First,
a study was made of the effect of modifier con-
centration 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 signif-
icant improvement in the polymer.

Next it was thought that polymerization
at lower temperatures might produce better poly-
mer. 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.

- 56 -

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

Recipe #1

	Parts
Perfluorobutadiene	43 (60:40
VFHE	57 mole ratio)
Water	200
Duponol ME	4
Cumeme Hydroperoxide	0.36
$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$	0.05
$Na_4P_2O_7 \cdot 10H_2O$	0.50
Fructose	0.50
$n-C_{12}$ Mercaptan	0 or 0.2

Recipe #2

Perfluorobutadiene	43 (60:40
VFHE	57 mole ratio)
Water	200
Ammonium Perfluoro-octanoate	5
Cumeme Hydroperoxide	0.36
$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$	0.50
$Na_4P_2O_7 \cdot 10H_2O$	0 or 0.50
Fructose	0.50
$n-C_{12}$ Mercaptan	0.2

- 57 -

TABLE IX (Cont'd.)

REDOX RECIPES USED IN THE PREPARATION OF
PERFLUOROBUTADIENE:VFHE COPOLYMERS

Recipe #3

	Parts
FBd	43 (60:40
VFHE	57 mole ratio)
Water	200
SF Flakes	5
Cumeme Hydroperoxide	0.36
$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$	0.5
$Na_4P_2O_7 \cdot 10H_2O$	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_2O	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_2O	200
SF Flakes	5
KCl	0.5
$Na_2S \cdot 9H_2O$	0.12
$Fe(NO_3)_2 \cdot 9H_2O$	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.

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 Perfluoro-butadiene: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

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:

TABLE X

PROPERTIES OF PERFLUOROBUTADIENE:VFHE COPOLYMERS

	60:40 Perfluoro-butadiene:VFHE, Raw Polymer	60:40 Perfluoro-butadiene:VFHE, Polyac Cure, Gum	60:40 Perfluoro-butadiene:VFHE, Polyac Cure With Carbon Black
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) synthetic lubricant	7	--	12
Dioctyl 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

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

recipes all cause severe blowing and only moder-
ate 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 perfluoro-
butadiene with vinyl n-butyl ether (VNBE) and
vinyl isobutyl ether (VIBE). The conditions and
results of these experiments are detailed in
Table IX.

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°C.

    b. Heat aging at 200°C.

        21 hrs. - 3% wt. loss
        68 hrs. - 10% wt. loss
            Polymer hard and brittle

    c. Swelling volumes

        benzene - 470%
        acetone - 680%

- 64 -

TABLE XI

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

Tube No.	Amt. FB	Amt. VE	FB:VE	Yield %**	Nature of Polymer	% F	Mol % Perfluoro-butadiene
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-C$_{12}$ mercaptan
** Tube 7 was reacted 144 hours at 50°C., the rest reacted 42 hours.

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-Dihydro-perfluorobutyl 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

- 66 -

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

E. Miscellaneous Copolymerizations of Perfluoro-butadiene

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 perfluoro-butadiene 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

- 67 -

TABLE XII

PERFLUOROBUTADIENE COPOLYMERS

Comonomer	Reaction Time (Days)	Nature of Product	% F	Composition (Mol %)	Comments
Vinyl β-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	unavailable	--	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:

	Parts
Perfluorobutadiene	100
Water	180
Ammonium Perfluoro-octanoate	6
$Na_2S_2O_8$	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.

Exposure of perfluorobutadiene sealed under vacuum in a Pyrex ampoule to 200 megaroentgens 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 perfluoro-butyrate, 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.

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.)

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: $R_f CH_2 OCOCH = CH_2$, where
R_f denotes a perfluoroalkyl group. The newer
ones belong to other homologous series. Partic-
ular 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 summar-
ized in Table XIII, in which members of the
$R_f CH_2 OCOCH:CH_2$ series have been included for com-
parison. Glass temperatures, Tg, have been
determined refractometrically, as described in
earlier reports. The T_{10} values are, as before,
determined on the German Torsional modulus
apparatus. Likewise in Table XIII have been
included the properties of certain non-fluorinated

- 72 -

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°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 (FAH$_3$A)**

The glass temperature for this homopolymer,
-35°C., is similar to that for poly-FAA, -37°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°F. with 35 parts of
Spheron #9 black.

- 73 -

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 (FBH_3A)

FBH_3A 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 $Al_2(SO_4)_3 \cdot 18H_2O$ 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 (FEH_2EA)

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

- 74 -

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 resis-
tance 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-FEH$_2$EA, 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
(FEHE$_2$A)

This is similar to FEHEA, but with two
-OCH$_2$CH$_2$- 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 FEH$_2$EA, is
superior to it in both low temperature flexibility

- 75 -

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 (FFEA)

This monomer has the following structure:

$$\overset{\boxed{F}}{\underset{O}{\bigcirc}} - CF_2CH_2O\underset{O}{C}CH=CH_2$$
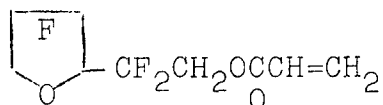
The polymer was prepared in the standard Duponol:persulfate emulsion recipe. As might be expected for a polymer containing cyclic groups in the side chains, the T_{10} for this material is rather high, 2°C. The nearest equivalent in a straight chain acrylate is poly-γ-(perfluoroethoxy)-1,1-dihydroperfluoropropyl 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:

- 76 -

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°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

- 77 -

Table XIII

PROPERTIES OF FLUOROACRYLATE HOMOPOLYMERS

Structure	Abbreviation	% F.	Tg, °C.	T_{10}, °C.	% Swell 70:30 iso-oct. Toluene	% Swell Benzene
$CF_3CH_2OCCCH = CH_2$	FEA	37.0	-10	--	--	
$CF_3CF_2CH_2OCCCH = CH_2$	FPA	46.6	-26	-7	20-30	
$CF_3(CF_2)_2CH_2OCCCH=CH_2$	FBA	52.3	-30	-7	10-15	
$CF_3CFHCF_2CH_2OCOCH = CH_2$	FBH_3A	48.3	-5	-5	10-15	
$CF_3(CF_2)_3CH_2OCOCH = CH_2$	FAA	56.2	-37	-7	5-10	
$CF_2H(CF_2)_3CH_2OCOCH = CH_2$	FAH_3A	53.1	-35	-17	5-10	
$CF_3(CF_2)_4CH_2OCOCH = CH_2$	FHA	59.0	-39	-7	0-5	
$CF_3(CF_2)_6CH_2OCOCH = CH_2$	FOA	62.7	+37*	--	0	
$CF_3(CF_2)_8CH_2OCOCH = CH_2$	FDA	65.1	--	--	0	
$CF_3CH_2CCH_2CH_2OCOCH = CH_2$	FEH_2FA	28.8	--	-5	15	210
$CF_2HCF_2OCH_2CH_2OCOCH = CH_2$	FEHEA	35.2	-22	-9	20	
$CF_2HCF_2(OCH_2CH_2)_2OCOCH = CH_2$	FEHE_2A	29.2	-40	-15	10	100
$CF_3CF_2CF_2CH_2OCH_2CH_2CCOCH = CH_2$	FBEA	44.6	-45	-20	20	50
F$-CF_2CH_2OCOCH = CH_2$	FFFA	60.2		+2	0-5	0-5

Table XIII (Cont'd)

PROPERTIES OF FLUOROACRYLATE HOMOPOLYMERS

Structure	Abbreviation	% F.	Tg, °C.	T_{10}, °C.	70:30 iso-oct. Toluene	% Swell Benzene
$CF_3OCF_2CF_2CH_2OCOCH = CH_2$	FMFPA	49.2	-55	-32	10	16
$CF_3CF_2OCF_2CF_2CH_2OCOCH = CH_2$	FEFPA	53.4	-49	(-23**)	10-15	7-12
$CF_3(CF_2)_2OCF_2CF_2CH_2OCOCH = CH_2$	FPFPA	56.4	-68	-35	12	13
$CF_3(CF_2)_3OCF_2CF_2CH_2OCOCH = CH_2$	FBFPA	58.8	-68	-31	2	29
Hydrocarbon Acrylates						
$CH_3OCH_2CH_2OCOCH = CH_2$	MEA		-50	-20	30	660
$CH_3CH_2OCH_2CH_2OCOCH = CH_2$	EEA		-50	-35	50	very high
$CH_3CH_2OCH_2CH_2CH_2OCOCH = CH_2$	EPA		-65			

* Probably 1st order transition
** Silicate cure; -34° in oxide cure

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-FEH$_2$EA; 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-FEH$_2$EA, (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

- 80 -

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.

- 81 -

TABLE XIV

FLUORINATED ALKOXY-ACRYLATE:BUTADIENE POLYMERS

Series	Charge Ratios Molar Acry-late:B	Wt. Acry-late:B	Reaction Time (Hrs.)	Approx. % Con-version	Analytical Ratios Molar Acry-late:B	Wt. Acry-late:B	Appear. of raw polymer	% Swelling 70:30 Iso-octane toluene	Iso-octane	Ben-zene	Gehman T_{10} °C.
FMFFA	100:0	100:0	2	100	--	--	Good rubber	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

TABLE XIV (continued)

FLUORINATED ALKOXY-ACRYLATE:BUTADIENE POLYMERS

Series	Charge Ratios Molar Acry-late:B	Wt. Acry-late:B	Reaction Time (Hrs.)	Approx. % Con-version	Analytical Ratios Molar Acry-late:B	Wt. Acry-late:B	Appear. of raw polymer	% Swelling 70:30 Iso-octane toluene	Iso-octane	Ben-zene	Gehman T$_{10}$ °C.
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 - 7	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 - 7	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

TABLE XIV (continued)

FLUORINATED ALKOXY-ACRYLATE:BUTADIENE POLYMERS

Series	Charge Ratios Molar Acry-late:B	Wt. Acry-late:B	Reaction Time (Hrs.)	Approx. % Con-version	Analytical Ratios Molar Acry-late:B	Wt. Acry-late:B	Appear. of raw polymer	% Swelling 70:30 Iso-octane toluene	Iso-octane	Ben-zene	Gehman T10 °C.
FPFPA	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 Molar Acrylate:B	Wt. Acrylate:B	Reaction Time (Hrs.)	Approx. % Conversion	Analytical Ratios Molar Acrylate:B	Wt. Acrylate:B	Appear. of raw polymer	% Swelling 70:30 Iso-octane toluene	Iso-octane	Benzene	Gehman T_{10} °C
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

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

- 86 -
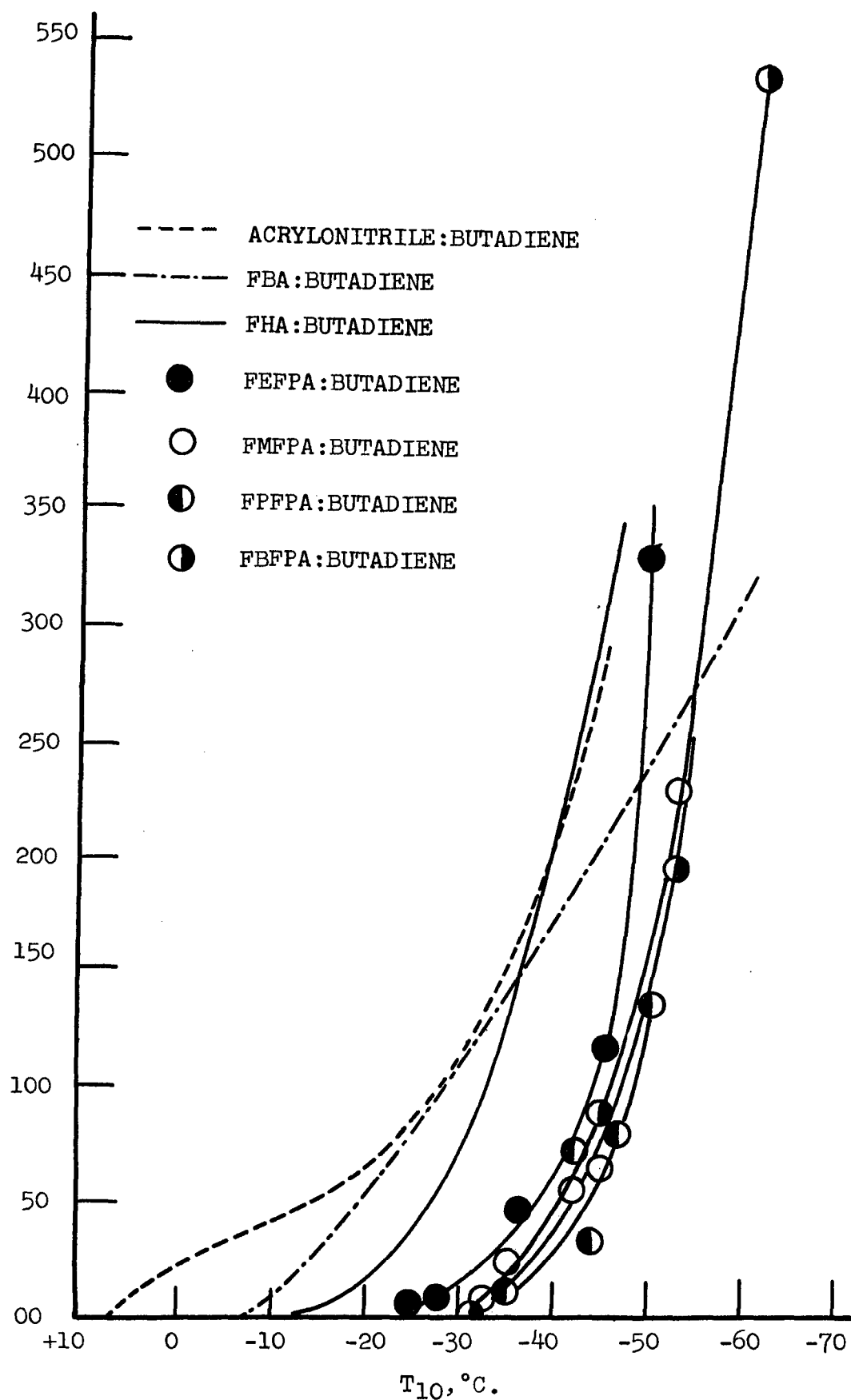
FIGURE 6

GEHMAN T_{10} VS. PERCENT SWELLING IN 70:30 ISO-OCTANE TOLUENE

87

TABLE XVI (continued)

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

	Poly-FBA Polyamine Cure	Poly-FBA Standard Oxide Cure	Poly-FHA Standard Oxide Cure	Poly-FEFPA Standard Oxide Cure	Poly-FMFPA 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	2-7	8.3	4.2
150 hours at 350°F. in air	5.9	—	—	—	4.6

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 in 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.

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

Charge Ratio				Approx.	Analytical Results				
Wt. %		Mol. %		% Con-	Wt. %		Mol. %		Quantity
FEFPA	Buta.	FEFPA	Buta.	version	FEFPA	Buta.	FEFPA	Buta.	Prepared
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

	20:80 FEFPA:Bd.	48:52 FEFPA:Bd.
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-(Perfluoroethoxy)-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

- 93 -

TABLE XVIII

COPOLYMERS OF FLUOROPRENE (FP) WITH 1,1-DIHYDROPERFLUOROHEXYL
ACRYLATE (FHA) AND ⌐ (PERFLUOROETHOXY)
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}	Benzene	Swelling Volumes* 70:30 Iso-octane: Toluene	Iso-octane
FHA & FP	5:1	1:1	60 to 75%	51%	75:25	38:62	-21°C.	45	45	15
FEFPA & FP	4:1	1:1	65 to 80%	41%	54:46	21:79	-39°C.	149	100	37

C. <u>Poly-1,1-Dihydroperfluorobutyl Acrylate (Poly-FBA)</u>

1. Preparation of Poly-FBA: Six homopolymer-
izations 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

- 95 -

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 nonionic reagent, permitted high conversions but also caused almost complete preecoagulation. 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

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 encount-
ered. 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 diffi-
cult to mold. With other curing recipes, higher mole-
cular 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

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 $(Al_2(SO_4)_3 \cdot 18H_2O)$ 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 -

TABLE XVIX

FBA:2-CHLOROBUTADIENE COPOLYMERS

| Sample No. | Charge, Parts by Wt. | | | % Conversion | $\langle \eta \rangle$ * |
	FBA	2-chloro-butadiene	t-C_{12} Mercaptan		
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 copoly-
mer 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 ali-
phatic or aromatic hydrocarbons, and polyethoxyethyl
acrylate showed surprisingly low swell in 70:30 iso-
octane:toluene.

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

- 100 -

	Parts
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.

TABLE XX

COPOLYMERS OF FBA AND ALKOXYALKYL ACRYLATES

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

*EEA = ethoxyethyl acrylate

MPA = methoxypropyl acrylate

c. Copolymers of FBA with Vinyl Triethoxysilane

FBA was copolymerized with vinyl triethoxy-
silane 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 hydroly-
sis 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 $Na_2CO_3.10H_2O$,
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 $Na_2CO_310H_2O$. 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.

- 103 -

TABLE XXI

COPOLYMERS OF FBA AND VINYL TRIETHOXYSILANE

Tube No.	Weight % Vinyl Silane Charged	System	Reaction Conditions	% Yield	(η)*	Weight % Vinyl Silane in Copolymer	Remarks (Samples milled with 10% $Na_2CO_3 \cdot 10H_2O$)
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, Duponol 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 precoagulates, 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

- 106 -

TABLE XXII

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

% Swelling Volumes, 48 hours at Room Temperature

Sample	70:30 Iso-octane: Toluene	Iso-octane	Benzene	Acetone	Skydrol	Synthetic Lubricant Di-(2-Ethylhexyl) Sebacate Base	T_{10} °C	Hours at 150°C. to reach 10% Wt. Loss
A-FHA:AcAc, 10 wt. % (35 mol %) AcAc charged, 6.3 wt. % (25 mol %) AcAc Found	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

TABLE XXIII

COPOLYMERIZATION OF FBA WITH BUTADIENE*

Tube No.	Charge Composition Mol % Bd	FBA	Reaction Time at 50°C., Min.	% Conversion	% C Found	Copolymer Composition Mol % 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 % MMA	FBA	Reaction Time at 50°C., Hr.	% Conversion	% C Found	Copolymer Composition Mol % 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

WADC TR 52-197 Pt 3
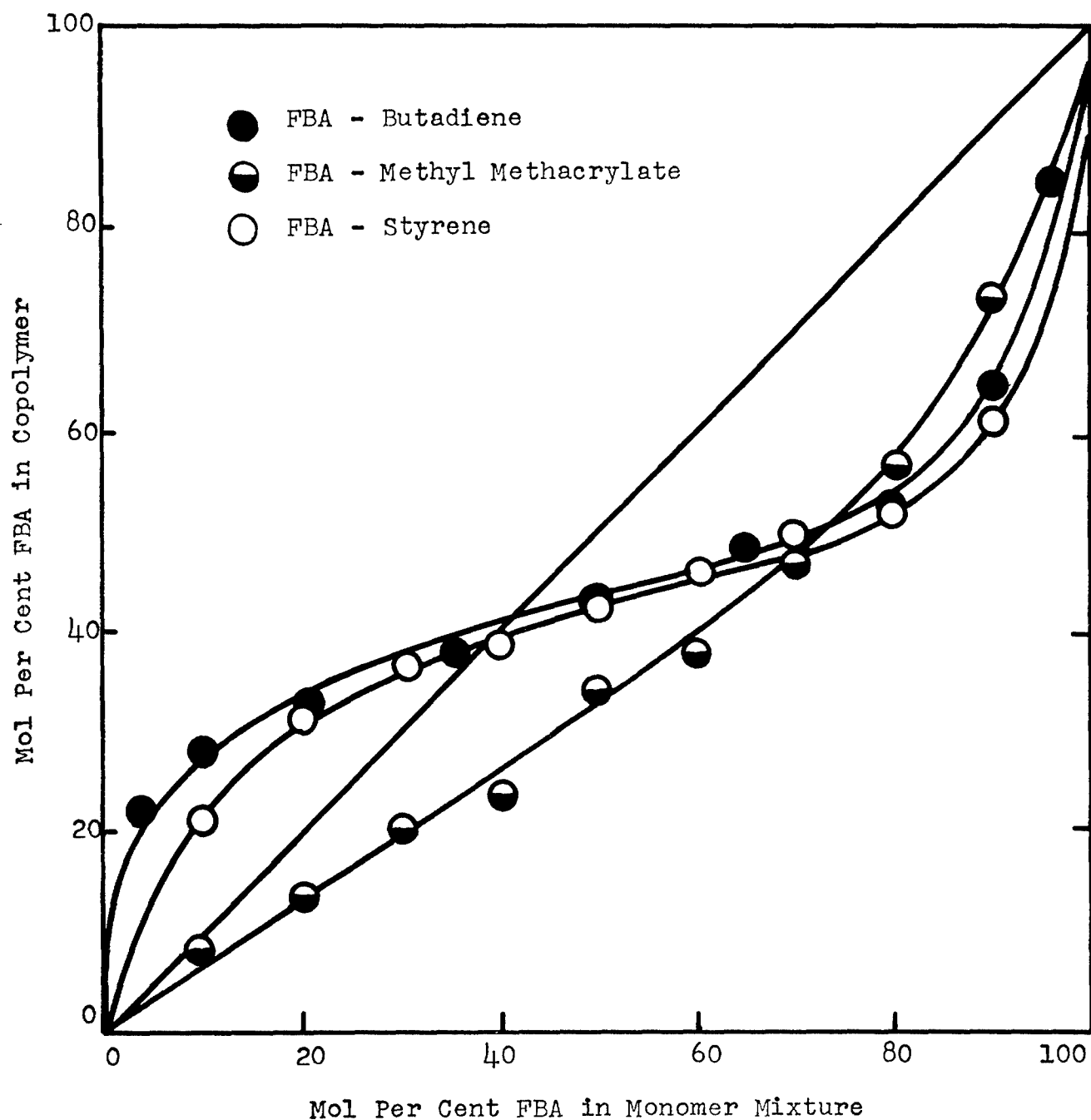
add three times as fast to FBA as to butadiene, and FBA radicals have a fourteen-fold preference for butadiene.

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.

- 111 -

4. <u>Compounding and Vulcanization of Poly-FBA and Poly-FHA</u>

   a. <u>Vulcanization in Silicate and Oxide Recipes:</u>
      <u>Effect of State of Cure</u>

   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.

(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 absissa scale was chosen to represent the state of cure.

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

WADC TR 52-197 Pt 3

FIGURE 8

TENSILE STRENGTH

MODULUS AT 100 % ELONGATION

(See Text P.117)

INCREASING CURE →

WADC TR 52-197 Pt 3   - 114 -

FIGURE 9

COMPRESSION SET, 70 HOURS AT 100°C

SHORE A-2 HARDNESS

INCREASING CURE ⟶   (See Text P. 117)

FIGURE 10

SWELLING VOLUME IN 70:30 ISOOCTANE:TOLUENE

SWELLING VOLUME IN BENZENE

INCREASING CURE ⟶ (See Text P. 117)
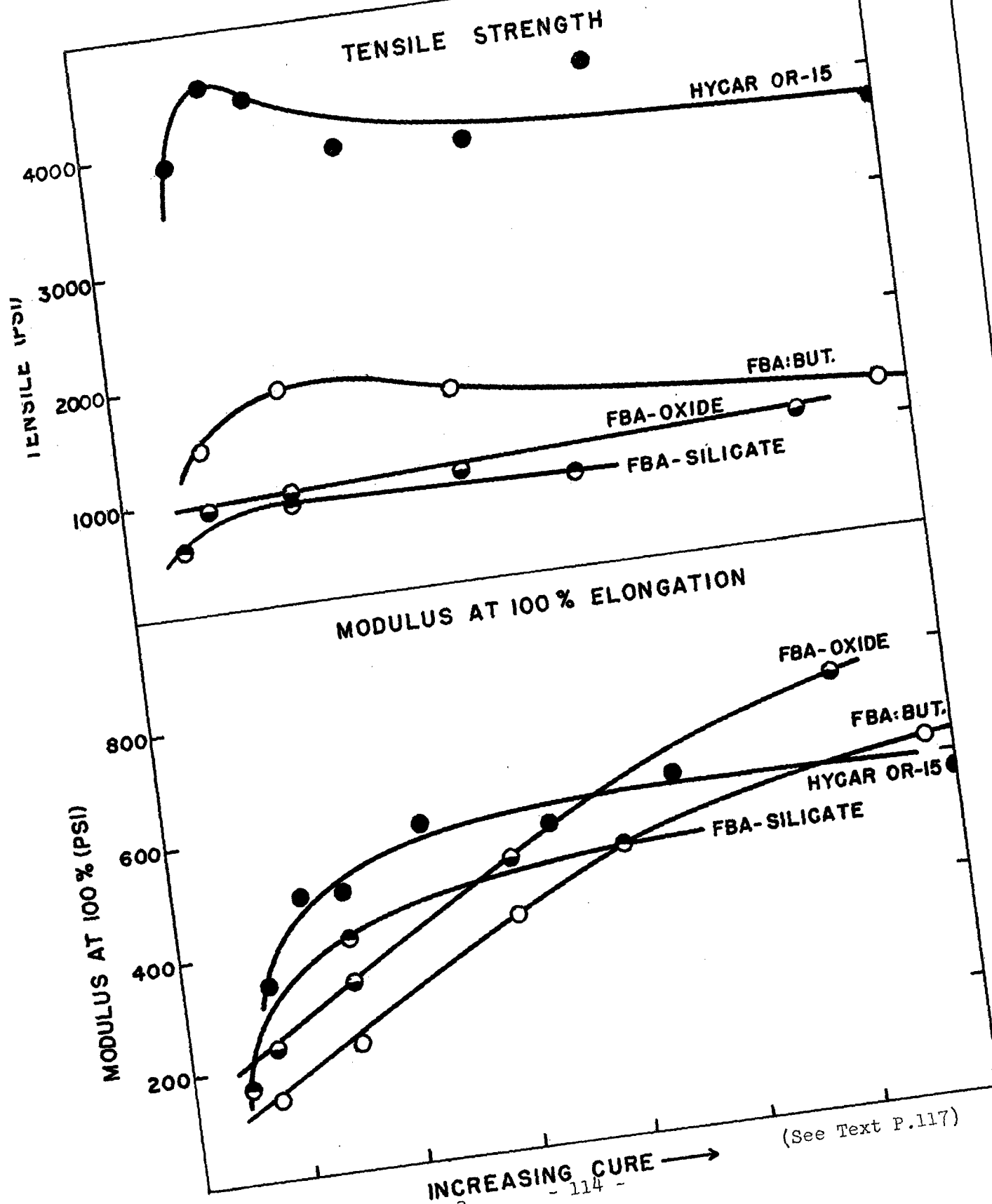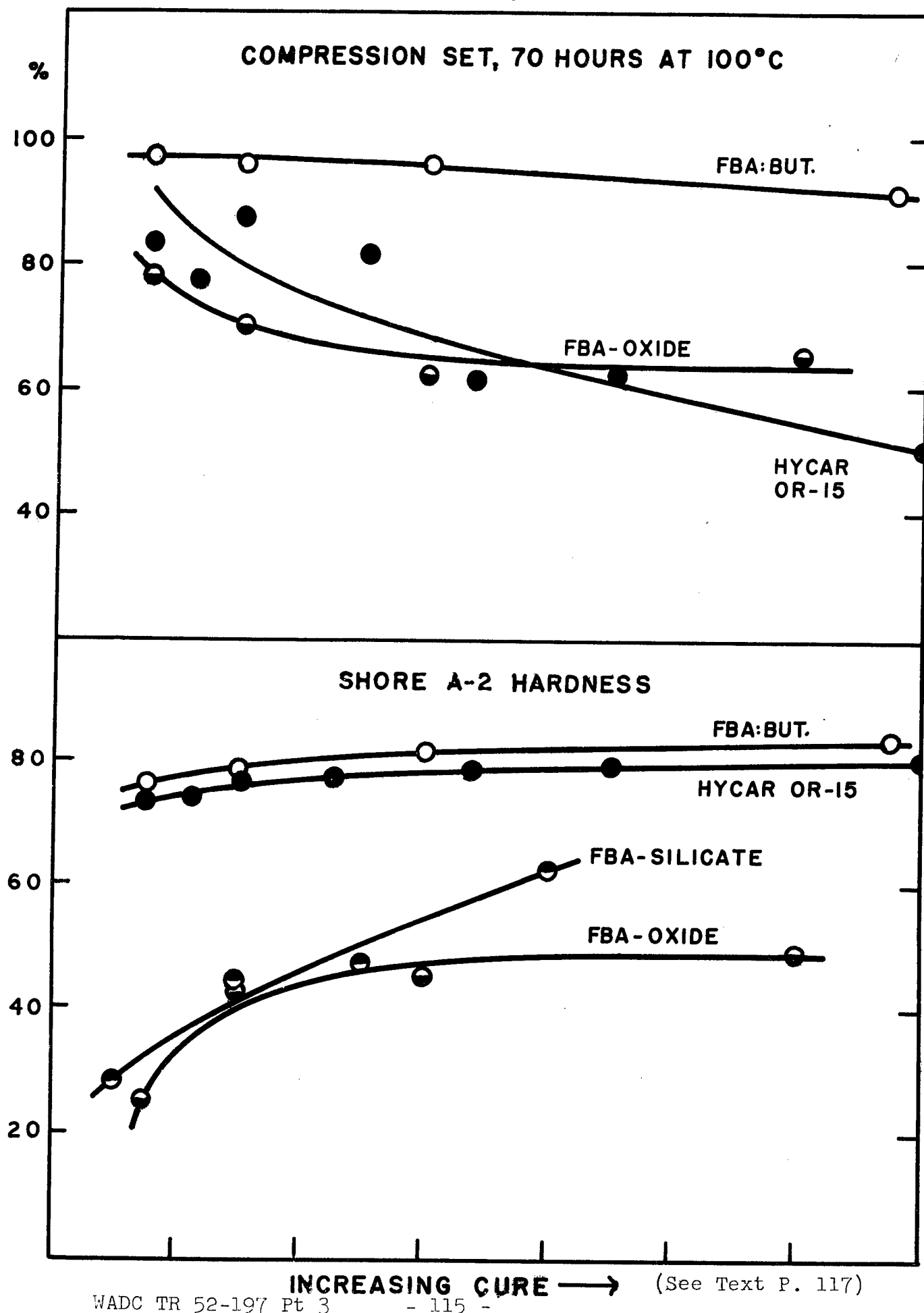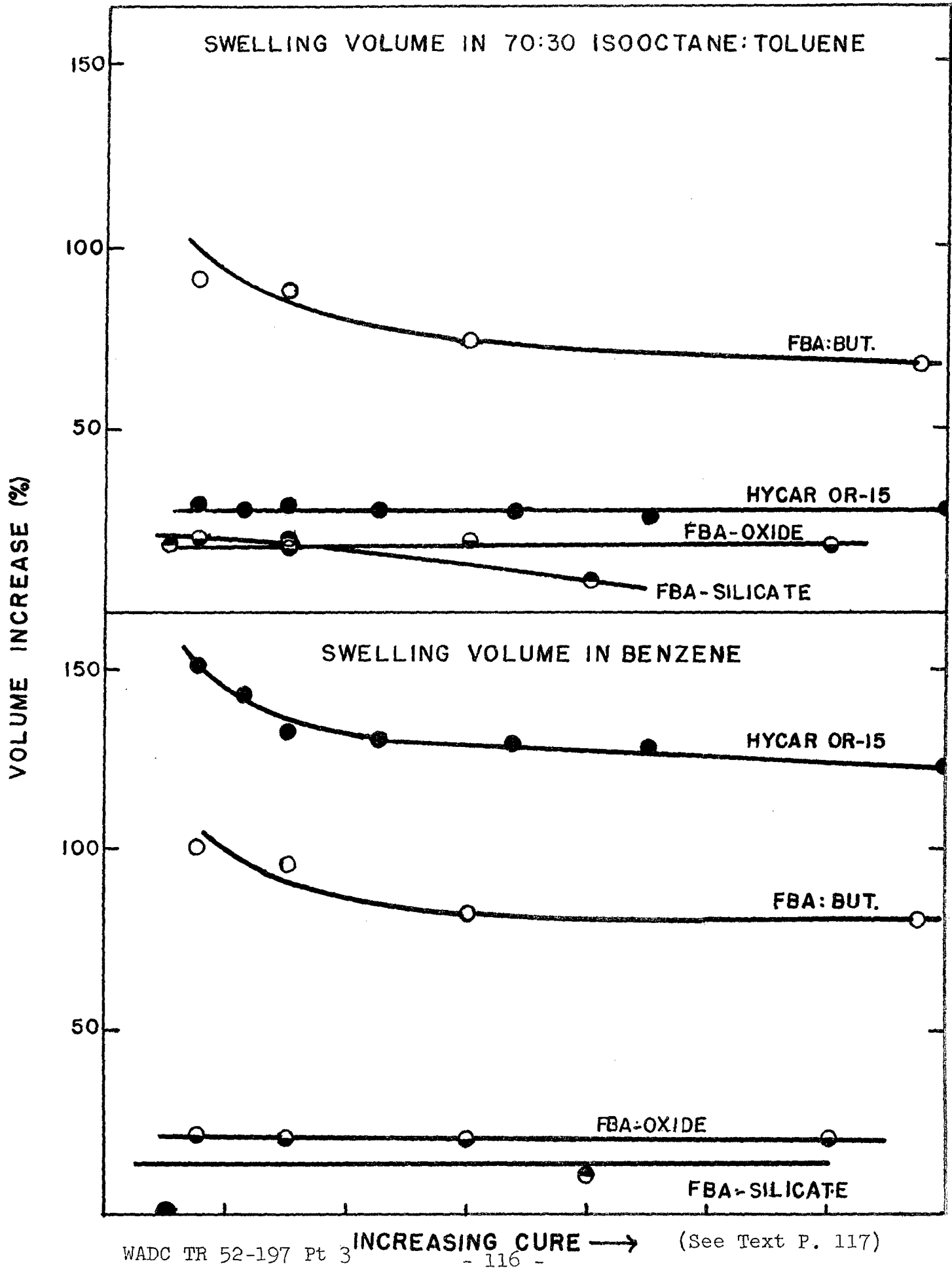
Hycar OR-15   13-1/3 min at 300°F.

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.

WADC TR 52-197 Pt 3

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 swelliin 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:

| | Recipes | |
	A	B
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

TABLE XXVII

PROPERTIES OF POLYAMINE VULCANIZATES OF POLY-FBA

Recipe No.	A	B
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_2SO_4	0	3
10% NaOH	225	186
Fuming HNO_3	In good condition.	In good 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

- 120 -

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

HAF Black, Parts	0	20	30	40	50
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

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

WADC TR 52-197 Pt 3

FIGURE 11

HEAT AGING OF POLY-FBA

——— POLY-FBA — OXIDE CURE

– – – COMM. BUT.:AN.—
TMTD CURE

WADC TR 52-197 Pt 3
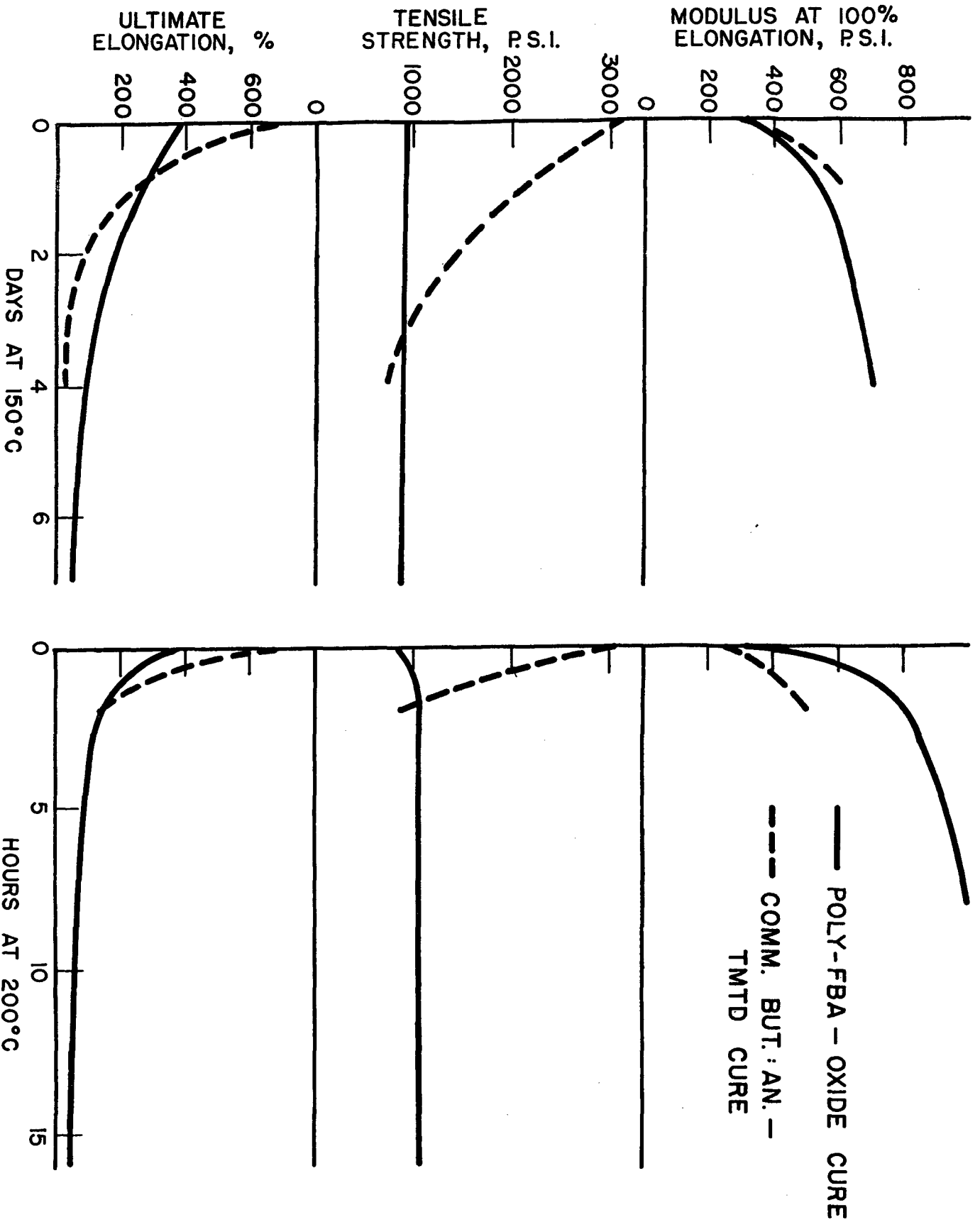
of butadiene.

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 -

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

- 126 -

TABLE XXIX

PYROLYSIS OF POLY-FBA - PO 227, LOT 3

Original weight poly-FBA = 1.3338 grams

Original = 3.12

Immersion Time, mm.	Temperature °C.	Pressure mm.	Noncumulative Weight Loss g's per 1/2 Hr.	Color of Residue
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
$(Na_2SiO_3 \cdot 9H_2O + Ca(OH)_2$

Original weight of poly-FBA = 1.0354 grams

Immersion Time, mm.	Temperature °C.	Pressure mm.	Noncumulative Weight Loss g's per 1/2 Hr.	Color of Residue
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

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, %	8.3	5.6	7.2
180° bend	OK	OK	OK
1000 hrs. at 300°F.			
wt. loss, %	14.0	8.8	13.7
180° bend	OK	OK	OK
1200 hrs. at 300°F.			
wt. loss, %	16.0	10.5	17.4
180° bend	Fails	OK	Fails
250 hrs. at 350°F.			
wt. loss, %	14.0	5.9	13.9
180° bend	OK	OK	OK
500 hrs. at 350°F.			
wt. loss, %	29.6	14.6	24.7
180° bend	Fails	OK	Fails
750 hrs. at 350°F.			
wt. loss, %	42.5	24.6	33.2
180° bend	Fails	Fails	Fails

TABLE XXXII

RETENTION OF PROPERTIES AT 350°F.

	Poly- FBA		Hycar 4021	
	Recipe A Pg.119	Recipe B Pg.119	Recipe A Pg.119	Recipe B Pg.119
Original Properties				
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
Aged in Air at 350°F. - 100 hrs.				
Weight loss, %	3.7	6.3	7.2	3.3
Modulus at 300% Elongation, psi	350	----	---	---
Tensile Strength, psi.	380 (-67%)	540 (-56%)	Very low; degraded.	1720 (-11%)
Ultimate Elongation, %	430 (+19%)	155 (-48%)		250 (-24%)
Hardness (Shore Duro A)	73 (+17)	88 (+21)	65 (+6)	
180° bend	OK	OK	OK	OK
Aged in Air at 350°F. - 250 hrs.				
Weight loss, %	5.9	8.9	13.5	10.5
Modulus at 300% Elongation, psi.	--	--	--	--
Tensile Strength, psi.	Very low; degraded.	230 (-81%)	brittle	310 (-84%)
Ultimate Elongation, %		25	--	150 (-55%)
Hardness (Shore Duro A)	72 (+16)	87 (+20)	68 (+9)	81 (+20)
180° bend	OK	OK	FAILS	OK
Aged in Sebacate * at 350°F. - 100 hrs.				
Volume Change, %	0	-3	+64	+40
Modulus at 300% Elongation, psi.	--	--	495	--
Tensile Strength, psi.	1070 (-7%)	1050 (-15%)	630 (-75%)	430 (-78%)
Ultimate Elongation, %	195 (-46%)	50 (-83%)	330 (-27%)	110 (-67%)
Hardness (Shore Duro A)	67 (+11)	90 (+23)	31 (-28)	56 (-5)
180° bend	OK	OK	OK	OK
Aged in Sebacate * at 350°F - 250 hrs.				
Volume Change, %	-2	-6	+85	+52
Modulus at 300% Elongation, psi	--	--	210	--
Tensile Strength, psi.	930 (-19%)	1150 (-6%)	270 (-89%)	390 (-80%)
Ultimate Elongation, %	230 (-36%)	30 (-90%)	360 (-20%)	80 (-76%)
Hardness (Shore Duro A)	62 (+6)	95 (+28)	28 (-31)	60 (-1)
180° bend	OK	OK	OK	OK

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

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 vulcani-
zates at 350°F. in air is poor. Compound A seems to
degrade excessively whereas Compound B hardens too

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-dihydro-perfluoroalkyl 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

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 polymer-
ization. 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 XXXIII. 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 XXXIII are shown
test values for three lots of FHA:butadiene copolymers.
Again one lot is inferior because of high conversion;

TABLE XXXIII

FBA AND FHA COPOLYMERS OF BUTADIENE

Sample Number	Mol % FHA or FBA		Conversion %	Tensile Strength psi.	Ultimate Elongation %	Swelling %		Gehman Brittle Point		Conclusion
	Charged	Found in Polymer				70:30 Iso:Tol.	Ben-zene	T_{10} °C.	Point °C.	
PP-68, Lot 1 (FBA)	55	50	79	750	180	80	85	-21	-27	Poor physical properties 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 properties due to high conversion.
PP 67, Lots 3 & 4 (FHA)	55	40	60	1700	350	65	60	-26	-36	Representative rubber

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 in-
crease 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. Vulcan-
izates 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.

- 134 -

TABLE XXXIV

SWELLING OF VULCANIZATES IN "SKYDROL"

Polymer	Type of Cure	Carbon Black	Swell (%) (7 days at 75°C.)
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

Polymer	PO-268, Lot 2 31:69 FHA:But.	PO-213, Lot 2 32:68 FBA:But.
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

Original Properties

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

TABLE XXXV (continued)

Polymer	PO-268, Lot 2 31:69 FHA:But.	PO-213, Lot 2 32:68 FBA:But.
% 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.

	PO-268, Lot 2	PO-213, Lot 2
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.

	PO-268, Lot 2	PO-213, Lot 2
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

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

TABLE XXXVI

COMPARISON OF T_{10}'s AND BRITTLE POINTS OF FHA:BUTADIENE AND

FBA:BUTADIENE VULCANIZATES IN VARIOUS CURING SYSTEMS

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

TABLE XXXVII

TENSILE PROPERTIES OF FHA:BUTADIENE AND FBA:BUTADIENE VULCANIZATES

Polymer	Curing System	EPC Carbon Black	Tensile Strength psi.	Ultimate Elongation %	Compression Set % (70 hr. at 100°C.)
27:73 FHA:	Sulfur-Altax	None	300	360	85
But. (PP-67	Sulfur-Altax	35 pts.	1900	310	82
Lot 1)	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:	Sulfur-Altax	None	300	450	81
But. (PP-67,	Sulfur-Altax	35 pts.	1700	410	88
Lot 4)	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:	Sulfur-Altax	None	600	440	81
But. (PP-68,	Sulfur-Altax	35 pts.	2100	370	83
Lot 2)	Oxide	None	1100	610	48
	Oxide	35 pts.	1600	290	72
	Silicate	None	900	100	91
	Silicate	35 pts.	1600	310	69

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

- 141 -
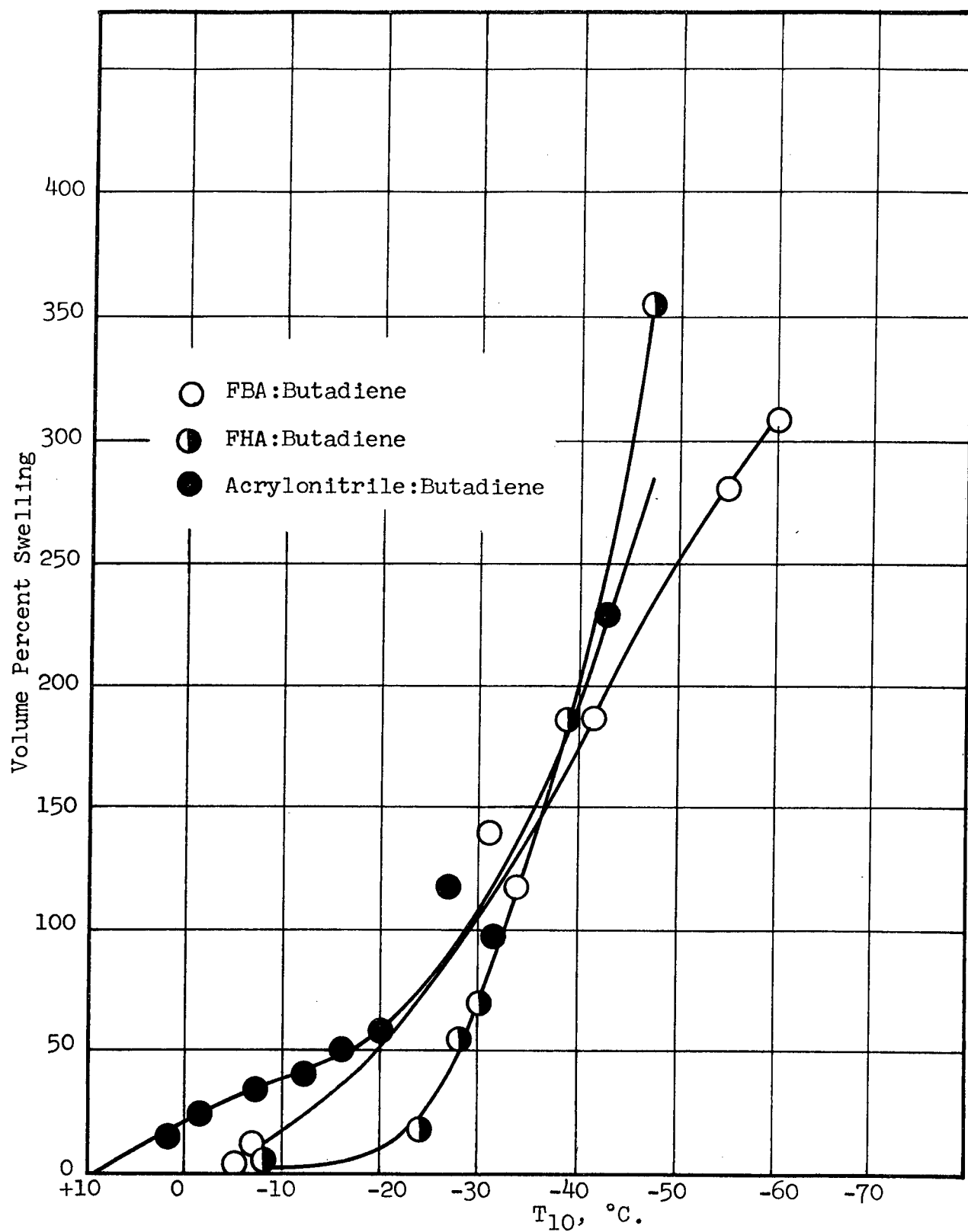
FIGURE 12

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

- 142 -
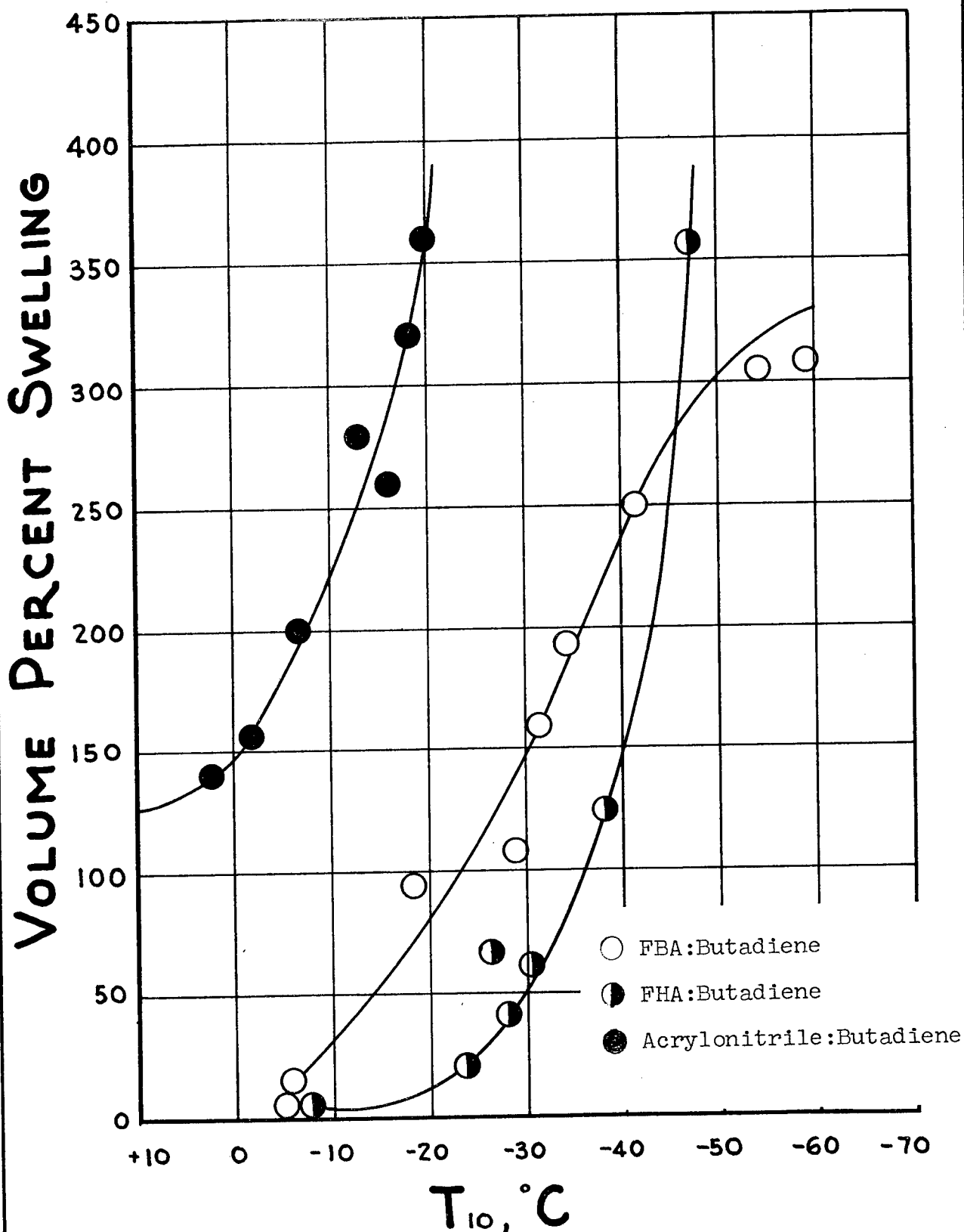
FIGURE 13

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

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

- 144 -

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 strength is muchrsmaller 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, evaporationoof 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

TABLE XXXVIII

EFFECT OF SOLVENT UPON PHYSICAL PROPERTIES

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

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

WADC TR 52-197 Pt 3

TABLE XXXIX

PLASTICIZERS FOR POLY-FBA

EXTRACTIBILITY AND LOW TEMPERATURE FLEXIBILITY

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

Plasticizer	Plasticizer Added (% by Volume)	Gehman T_{10} (°C.)	Extraction by 70:30 Iso-octane: Toluene* (% of Plasticizer Removed)
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.

TABLE XXXIX   (continued)

PLASTICIZERS FOR POLY-FBA

EXTRACTIBILITY AND LOW TEMPERATURE FLEXIBILITY

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

Plasticizer	Plasti-cizer Added (% by Volume)	Gehman T_{10} (°C.)	Extraction by 70:30 Iso-octane: Toluene* (% of Plasticizer Removed)
Perfluorotributylamine bottoms	25	-15	68
Cyclo-$C_{10}F_{20}O$	27	-27	B.P. -143°C. added to strip for swelling.
$C_8F_{16}O_2$	26	-32	B.P. -101°C. (swelled)
$C_4F_9OC_2F_4OC_4F_9$	26	-21	B.P. -135°C. "
$C_2F_5(CC_2F_4)_2OC_2F_5$	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-$C_8F_{13}Cl_3O$	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

$$CF_2 - CF_2$$
$$CF \quad CFCF_2COOCH_2C_7F_{10} \qquad 25 \qquad -- \qquad \text{Poor samples obtained.}$$
$$\diagdown_O\diagup$$

- 149 -

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 strengthsgths above 800 psi. were obtained and, surprisingly, no improvement in low temperature flexibility resulted.

TABLE XL

COMPOUNDING OF POLY-FBA WITH THIOKOL LP-3

	A	B	C
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.

	A	B	C
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 relax-
ometer, like that described by McDonald and Ushakoff
(Anal. Chem. 20 713 (1948)). This instrument records
the relaxation of cylindical 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.

Compression set measurements over a temperature range of -40° to +100°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.

- 153 -

TABLE XLI

COMPRESSION SET OF OIL RESISTANT COMPOUNDS

COMPRESSION SET (%)*

Temperature °C.	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.

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

- 155 -

TABLE XLII

COMPRESSION SET AT -20°C.*

Polymer	Type of Cure	Channel Black, pts. per 100 pts. Polymer	Compression Set, %	T_g of Uncured Polymer
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.

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

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 vulcan-
izate. These data can be interpreted in terms of gasket
performance and are therefore important in evaluating
our fluorine-containing rubbers. Samples can be com-
pressed almost instantaneously, but since the recorder
response is slow, the initial stress (S_o) is taken as
the stress after 0.01 hours (t_o). The data obtained at
25° and at 100° are shown in Table XLIII and plotted in
Figures 14 and 15.

Table XLIII

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
$S_o/S_{max.}$	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
$S_o/S_{max.}$	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.

Curve No.	Polymer	Type of Cure	Reinforcement
1	Hycar OR-15	sulfur	none
2	Hycar OR-15	sulfur	50 p. EPC black
3	Poly-FBA	silicate	none
4	Poly-FBA	oxide	none
5	31:69 FHA:But.	sulfur	35 p. EPC black

Time in Hours
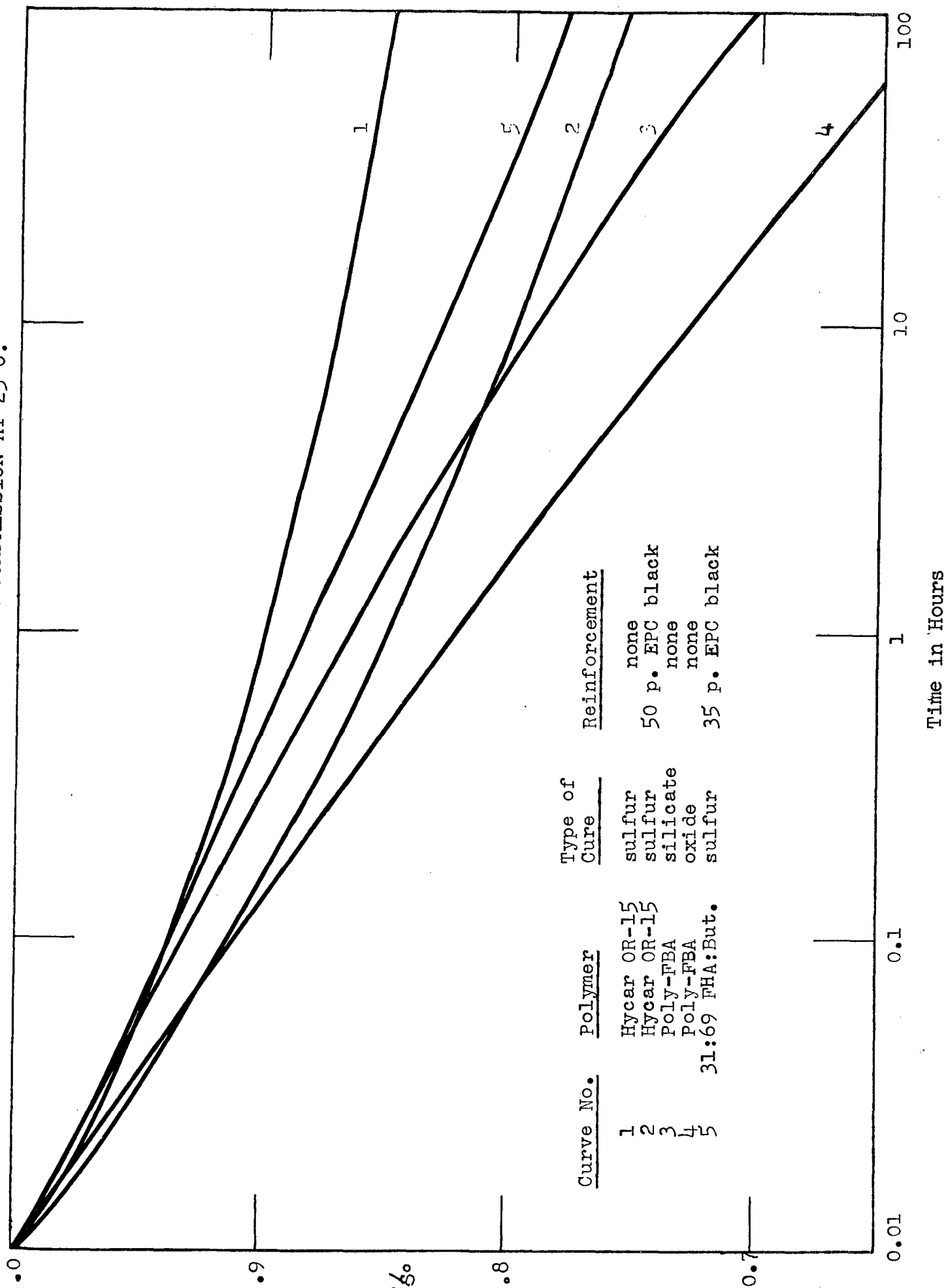
FIGURE 15

STRESS DECAY IN COMPRESSION AT 100°C.

Curve No.	Polymer	Type of Cure	Reinforcement
1	Hycar OR-15	sulfur	none
3	Poly-FBA	silicate	none
4	Poly-FBA	oxide	none

Time in Hours

$S/S°$
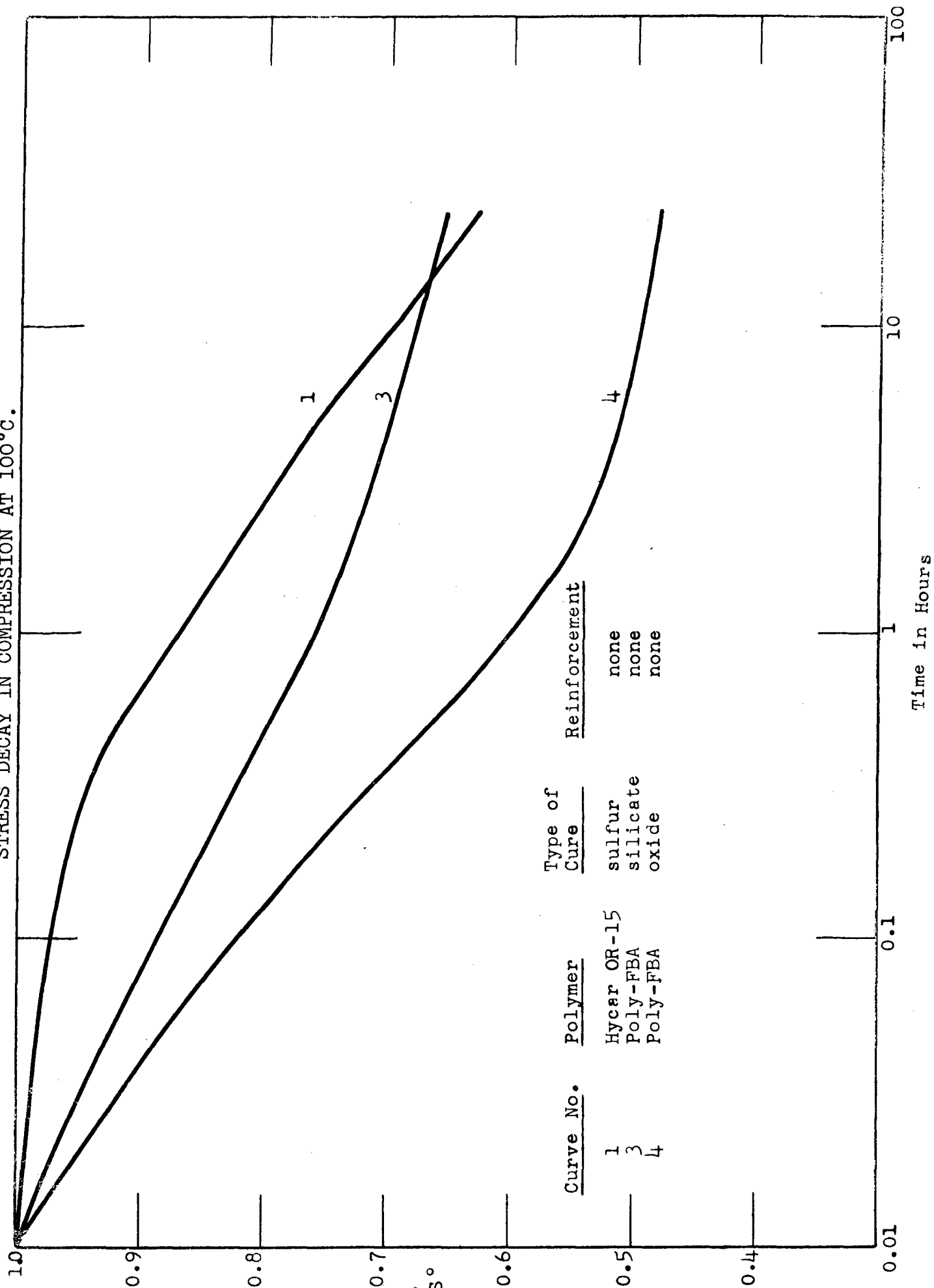
The data appear to indicate that the stress decay is due nearly entirely to reversible relaxation processes in all cases. This is shown by the percent recovery, which is close to 100%. A satisfactory material should show a rapid stress relaxation during the first few seconds but after this period the change of stress with time should be relatively slow and the stress should maintain a high value even after a long period. The Hycar OR-15 vulcanizate used in these tests shows a nearer approach to this ideal behavior than the FBA:butadiene or FHA: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 OR-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 OR-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

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

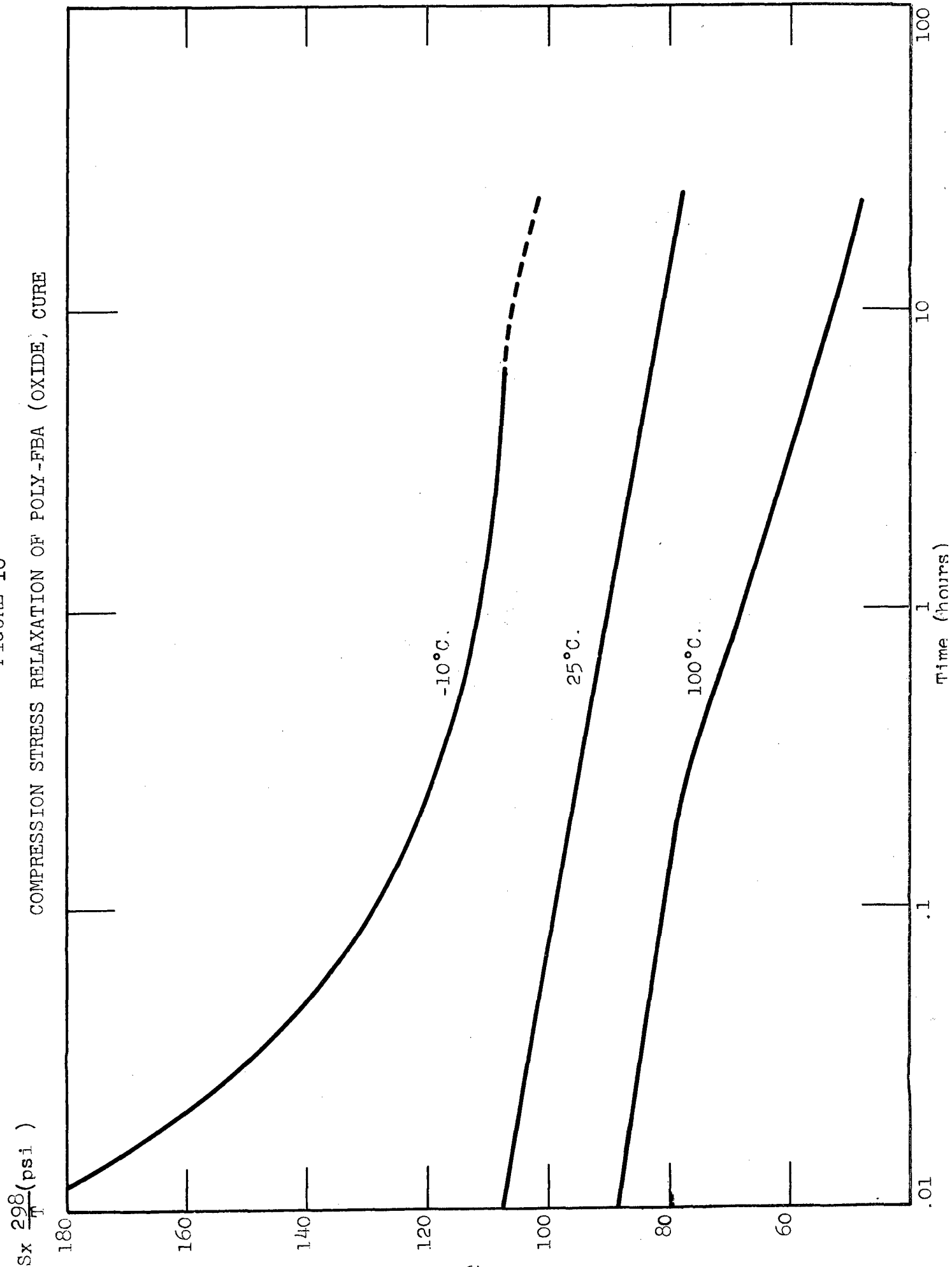COMPRESSION STRESS RELAXATION OF POLY-FBA (OXIDE, CURE

FIGURE 17

COMPRESSION STRESS RELAXATION OF POLYACRYLIC RUBBERS

WADC TR 52-197 Pt 3

- 165 -
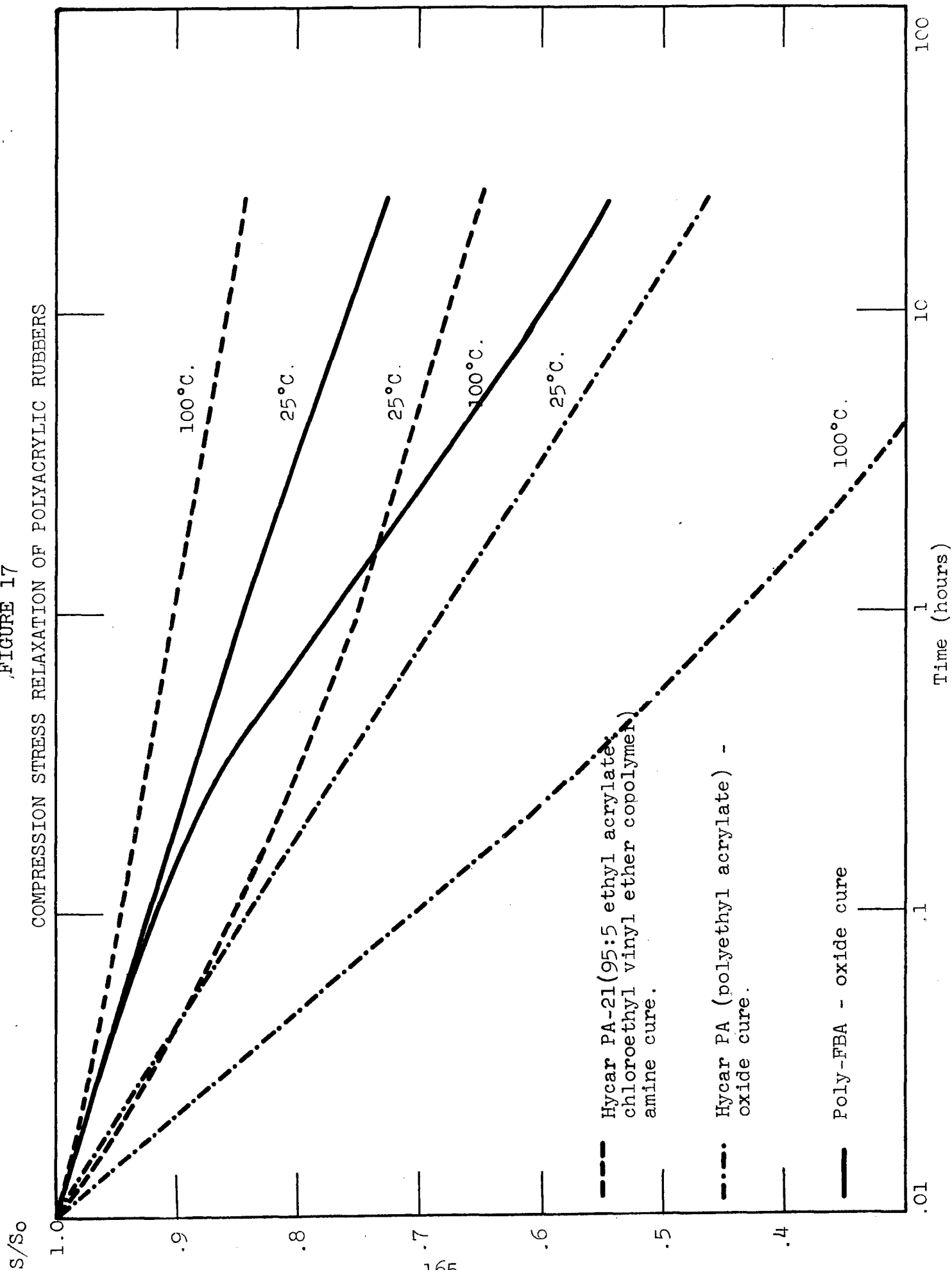
vulcanizates, discussed in the previous section on the polyamine cure. These vulcanizates have not yet been examined for their stress relaxation characteristics as carefully as the earlier cures, but indications are promising.

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:

	Parts
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.

- 166 -
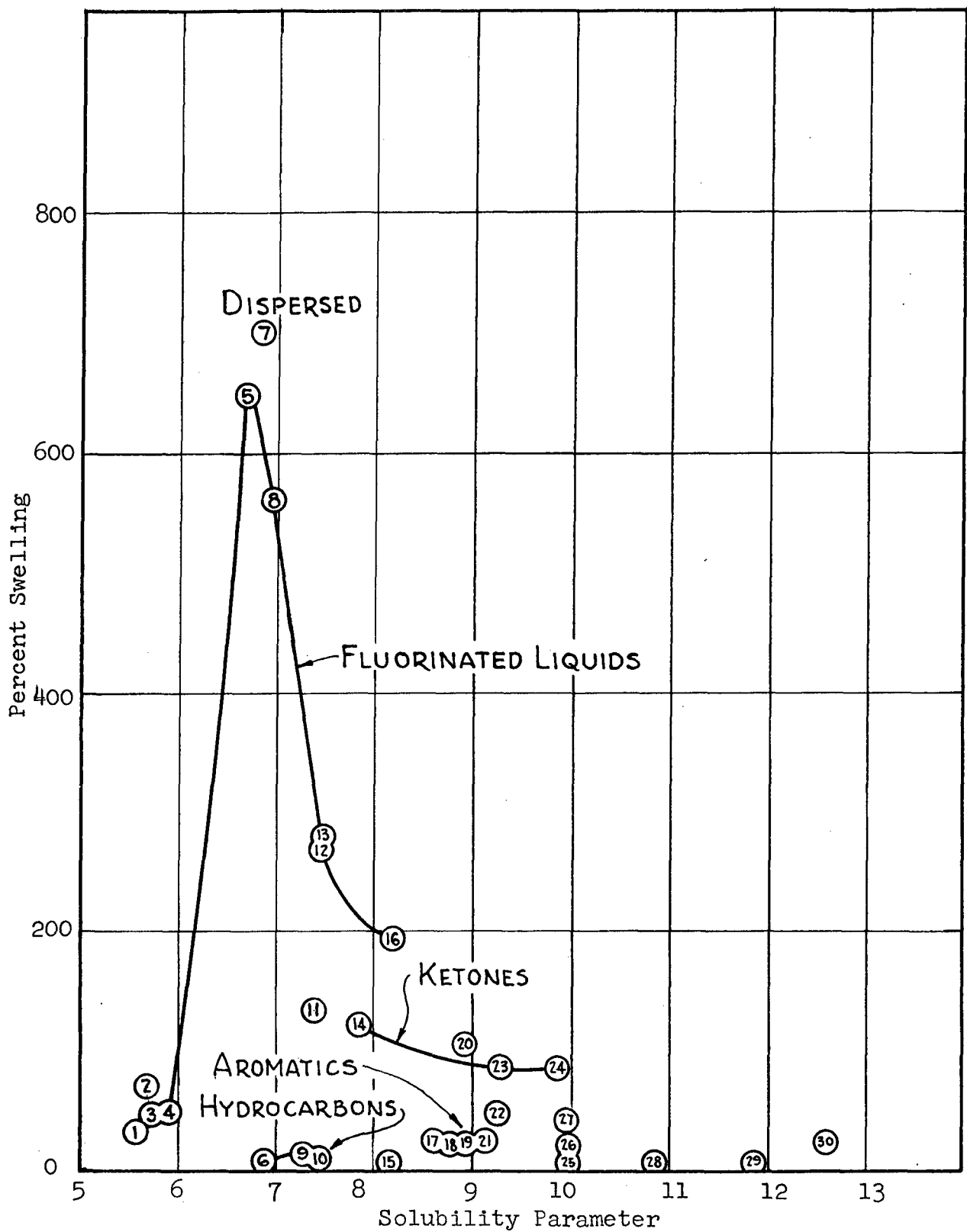
FIGURE 18

PERCENT SWELLING OF SILICATE CURED FBA VS. SOLUBILITY PARAMETER

TABLE XLIV

SWELLING OF POLY-FBA

No.	Solvent	δ	% Swelling
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.	$\underline{c}\text{-}C_8F_{16}O$	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 dispersed
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

- 168 -

Table XLIV (Cont'd)

SWELLING OF POLY-FBA

No.	Solvent	δ	% Swelling
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
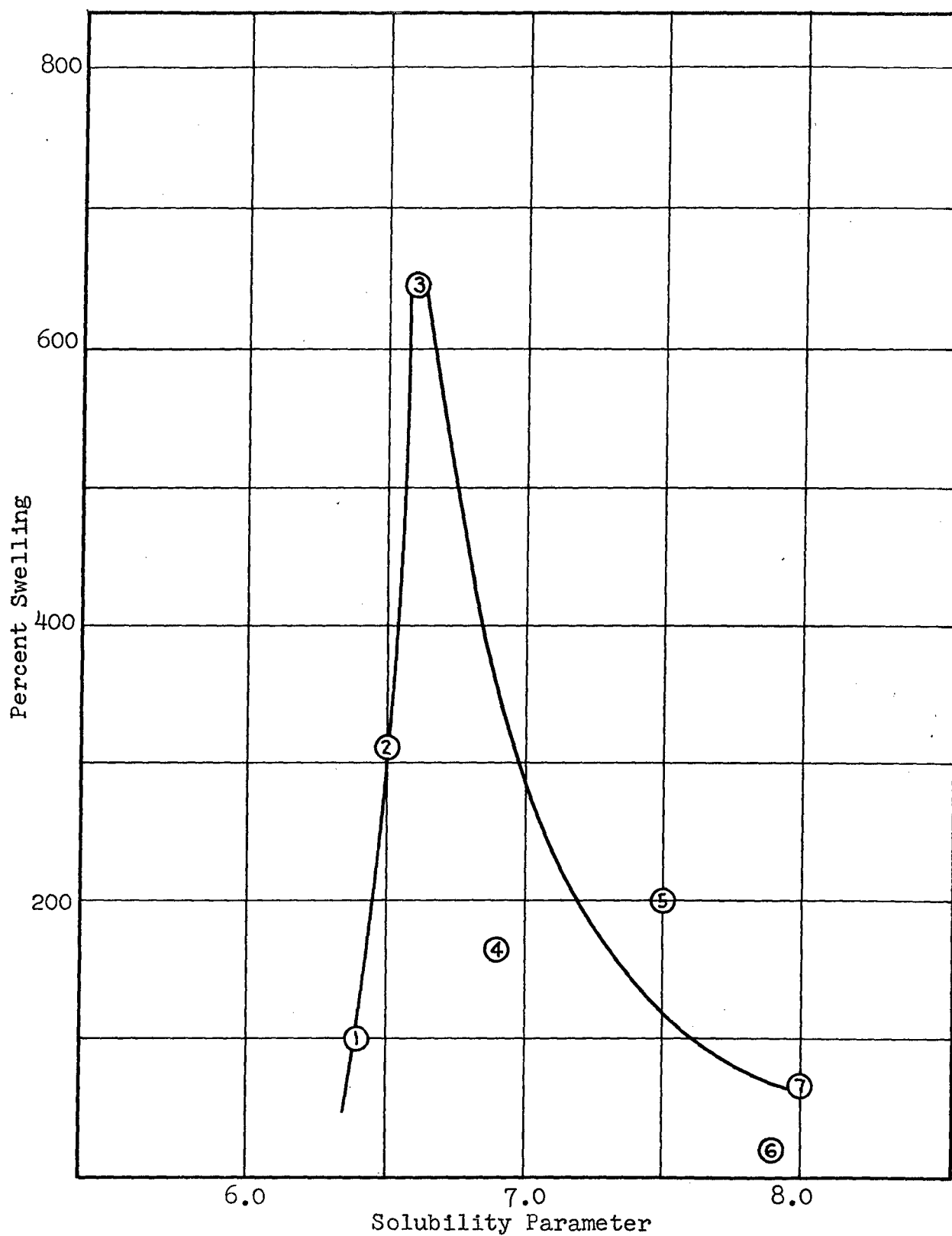
FIGURE 19

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

TABLE XLV

SWELLING OF POLY-FBA IN MIXED SOLVENTS*

Mixture	Average Solubility Parameter	Arithmetic Mean of Swelling in Pure Components	Swelling Volume	Identification Number in Figures
c-C_8F_{16}O:iso-octane	6.4	28	100	1
c-C_8F_{16}O:C_3F_6HCC$_3$H$_7$	6.5	344	313	2
c-C_8F_{16}O:Ethyl ether	6.6	90	644	3
$(C_4F_9)_2$O:$(C_2H_5)_2$O:1.4 Hexane	6.9	54	165	4
c-C_8F_{16}O:Methyl ethyl ketone:Hexane	7.5	45	200	5
Toluene:iso-octane	7.9	15	20	6
c-C_8F_{16}O:Amyl Alcohol: Hexane	8.0	22	67	7

* Equal volumes of each liquid unless marked otherwise.

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

- 172 -

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
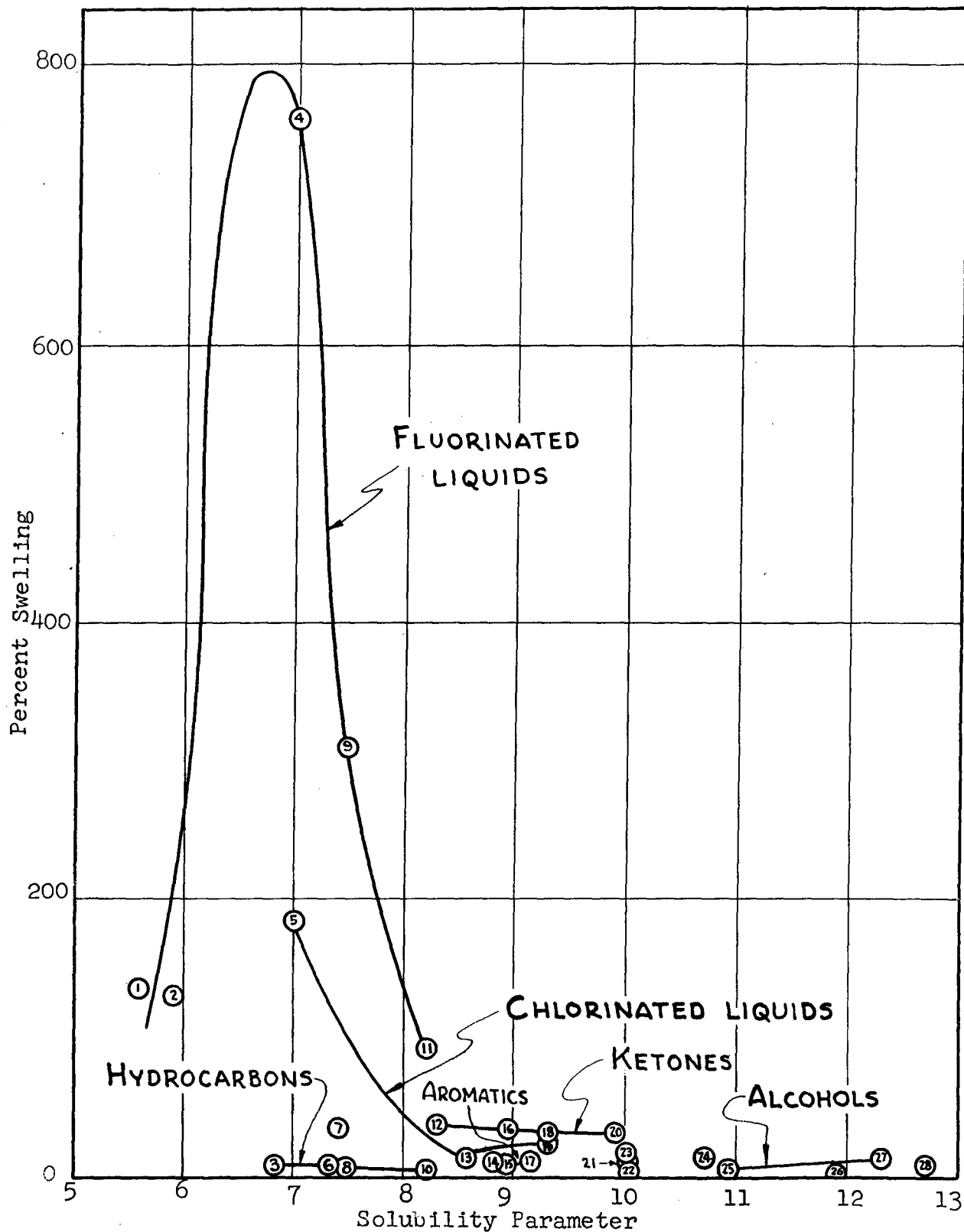
FIGURE 20

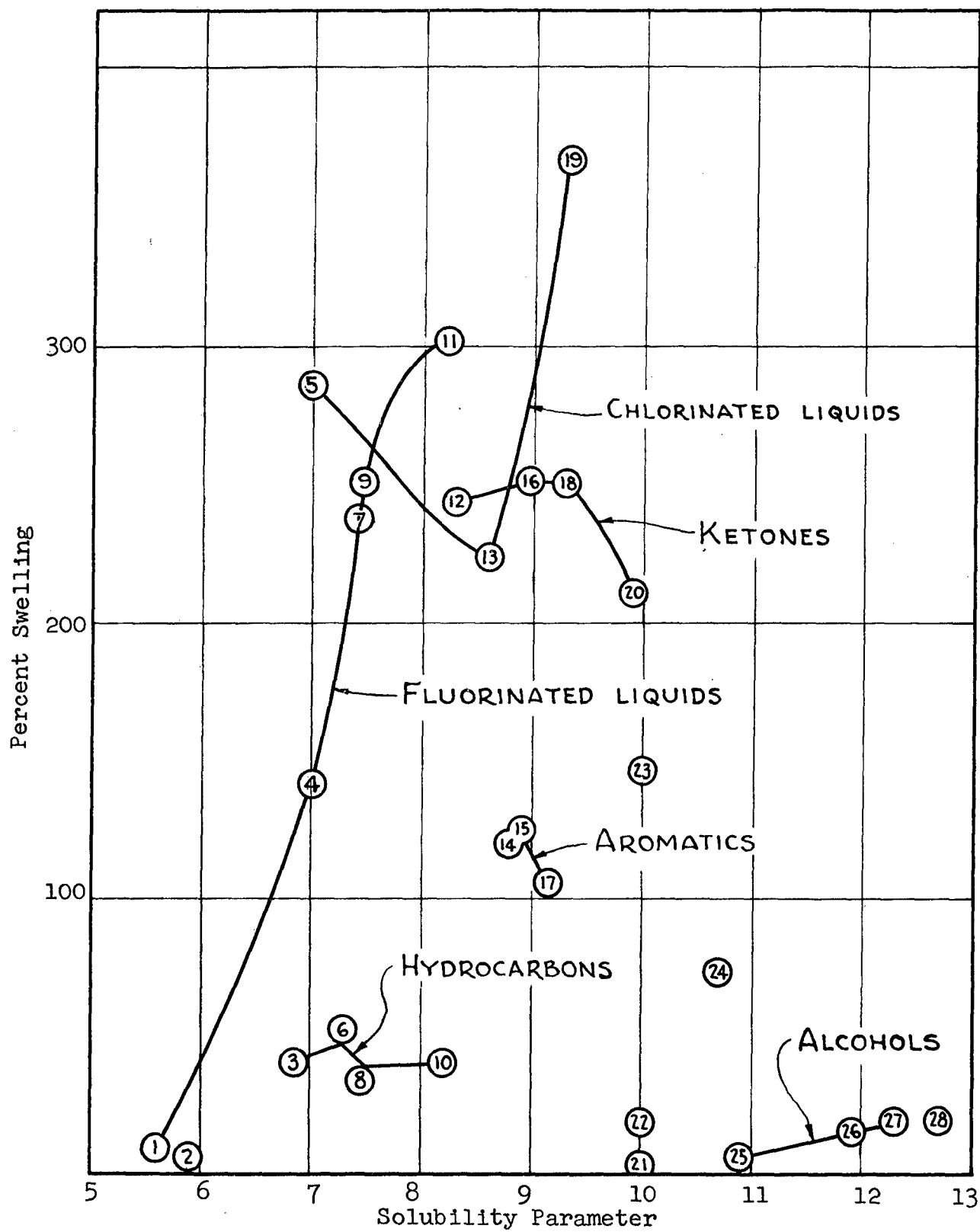PERCENT SWELLING OF SILICATE CURED FHA VS. SOLUBILITY
PARAMETER OF SOLVENT

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

- 175 -

TABLE XLVI

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

No.	Solvent	Per cent Swelling		
		Poly-FHA	Poly-FBA:Bd	δ
1	Perfluorohexane	137	9	5.6
2	Cyclo-$C_6F_{16}O$	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) 48		14.3
		50 (Amt. extrac.) 25		
31	Oleic acid	1	6	7.3
32	Glacial acetic acid	95	64	10.0
33	Skydrol T-17	0	16	
34	Dioctyl sebacate	0	12	
35	Water	12	16	24.0

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 inter-action 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

poly-FHA or FBA:butadiene even after heating the
solutions for one week at 100°C. Although β values
are not available for these molecules, they probably
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 poly-
butadiene is 8.5. As a result, many liquids with solu-
bility 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

- 178 -

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
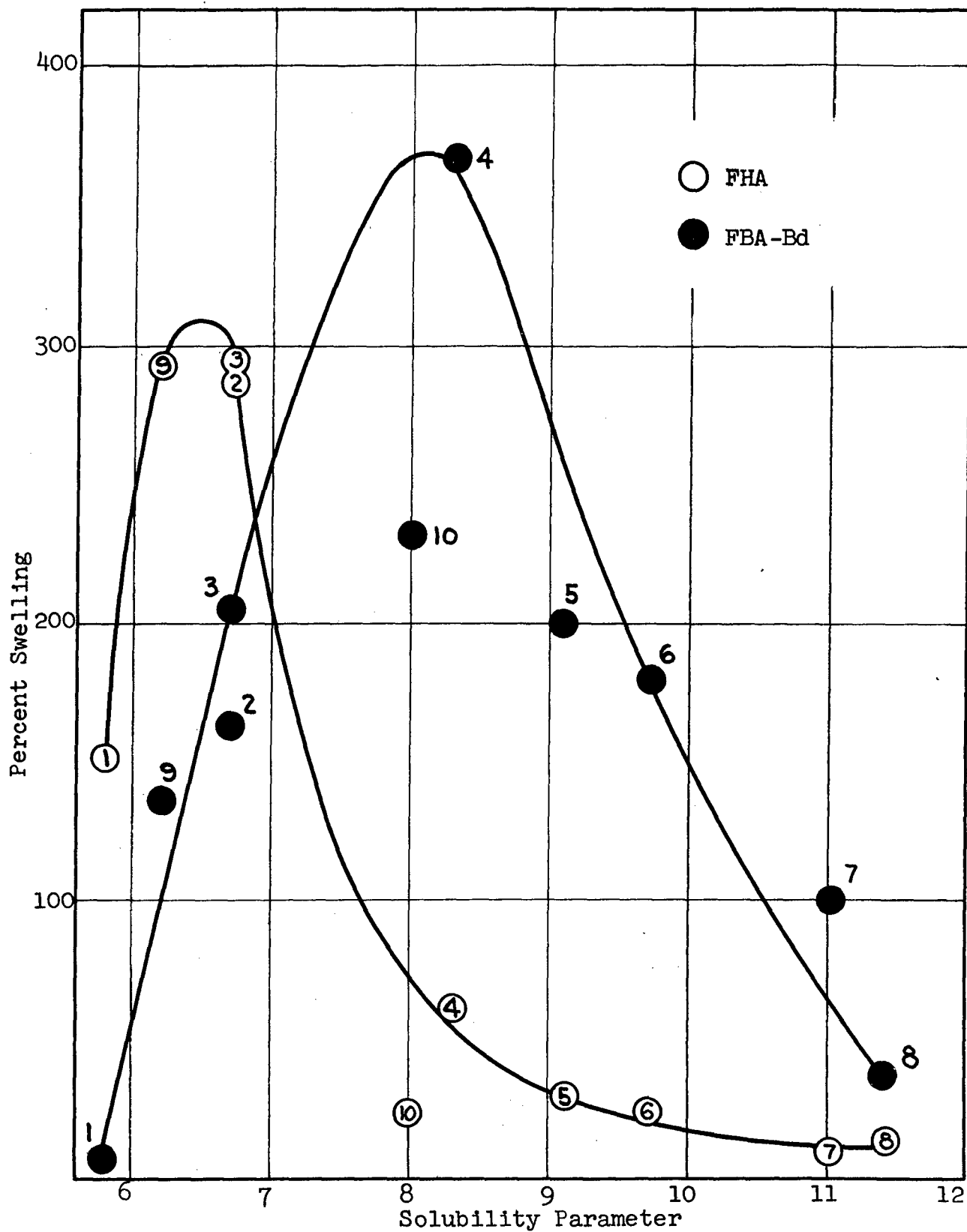
- 179 -

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 relation-
ships were found in this solvent:

$$[\eta] = 1.3 \times 10^{-4} \times M^{0.56} \text{ at } 26.6°$$
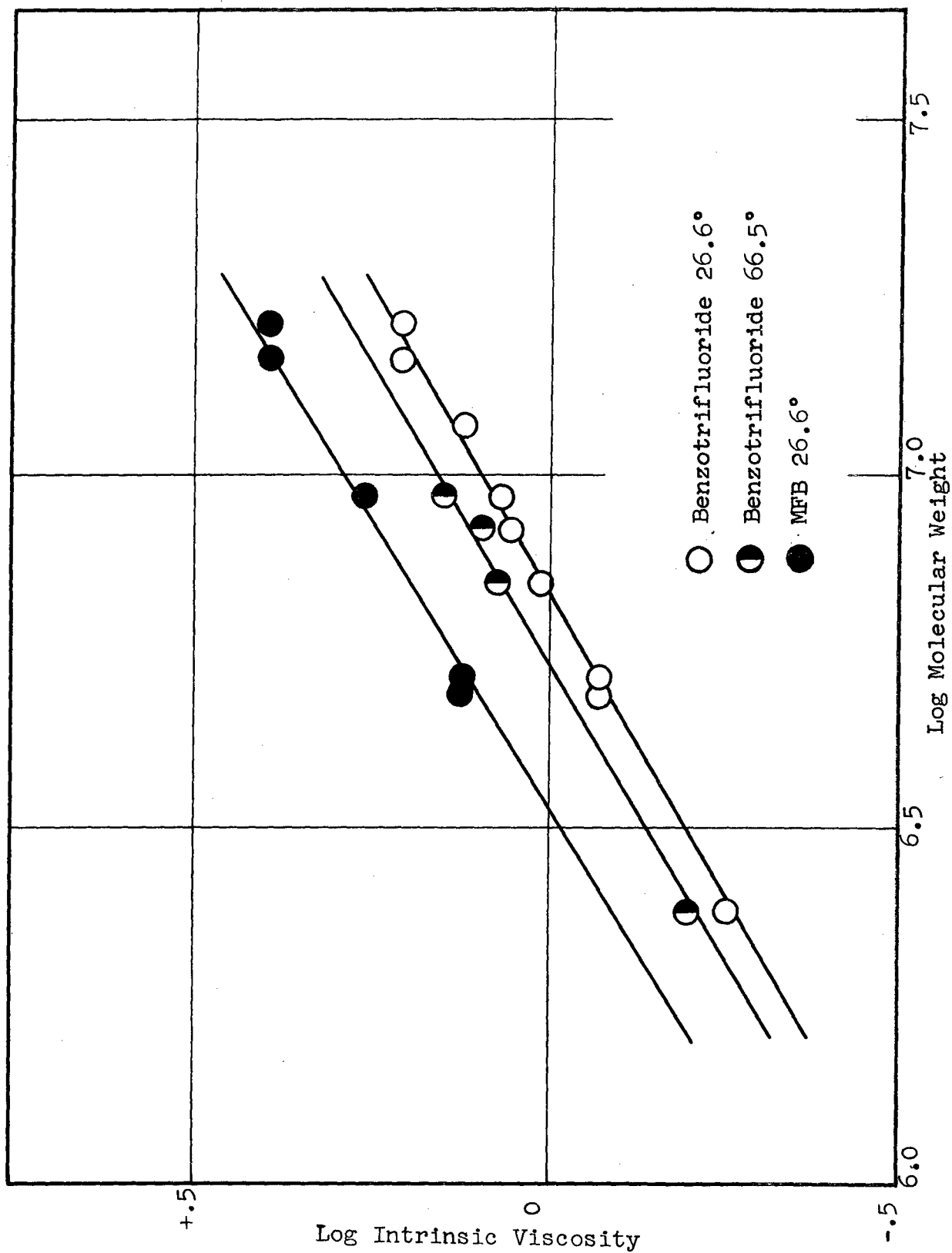$$[\eta] = 1.4 \times 10^{-4} \times M^{0.57} \text{ at } 66.5°$$

In methyl perfluorobutyrate:

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

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

- 181 -

FIGURE 23

INTRINSIC VISCOSITY VS. MOLECULAR WEIGHT FOR FRACTIONATED FBA

WADC TR 52-197 Pt 3

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

WADC TR 52-197 Pt 3

TABLE XLVII

MOLECULAR WEIGHTS AND INTRINSIC VISCOSITIES OF POLY-FBA FRACTIONS

$[\eta]$				md. wt. x 10⁶		Molecular length, Å, L		$\dfrac{dn_D}{dc}$ x 10²	$\dfrac{L^3}{M}$ x 10¹⁷
benzotrifluoride 26.6°	benzotrifluoride 66.5°	fluorobutyrate 26.6°	fluorobutyrate 70.0°	benzotri- fluoride	methyl per- fluorobutyrate	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

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

- 185 -

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.

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.

APPENDIX

A -

CURING FORMULAE FOR STATE OF CURE STUDIES

Poly-FBA - Silicate Cure		Poly-FBA - Oxide Cure	
Poly-FBA	100	Poly-FBA	100
Calcium hydroxide	2.72	Stearic acid	1
Sodium metasilicate		Litharge	5
nonohydrate	6.72	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

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

	Gum Stock	Reinforced Stock
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

	Gum Stock	Reinforced Stock
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.

B - Cont'd.

Paracril 18 - Sulfur Cure

	Reinforced Stock
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.

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

β-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.

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:Ethylene Copolymer (described p.6, Report #14)	- 3.5 g.	February 11, 1953
Poly-FBA	- 15 lbs.	February 20, 1953
*Methyl Perfluorobutyrate	- 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.