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Report No. RL-52-209

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Petroleum and Chemical Research Department

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⑥ Arctic Rubber.

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For the Period April-June, 1952

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Petroleum and Chemical Research Department
Laboratory Division, Jersey City, N.J.

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PROGRESS REPORT

Subject: Arctic Rubber - U.S. Army Contract DA-44-109-qm-222

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- - - -

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E F Schwarzenbek

E. F. SCHWARZENBEK

CONTENTS

Page No.

I. Introduction 4

- A. Purpose of the Project 4
- B. Research Program 4
- C. Past Progress 4

II. Summary of Current Progress 5

III. Experimental Section 6

- A. Monomer Synthesis 6
- B. Polymer Preparation 7
  1. Copolymers of $CF_2=CFCl$ and $CF_2=CH_2$ 8
  2. Copolymers of $CF_2=CFCl$ and Butadiene 8
  3. Copolymers of $CF_2=CFCl$ and Isoprene 9
  4. Copolymers of $CF_2=CCl_2$ and Butadiene 9
  5. Copolymers of $CF_2=CCl_2$ and Isoprene 10
  6. Copolymers of $CF_2=CFCl$ and n-Butyl Acrylate 10
  7. Copolymers of $CF_2=CF-CF=CF_2$ with Butadiene and Isoprene 10
  8. Copolymers of $CF_2=CF_2$ and Butadiene 11
  9. Copolymers of $CF_2=CFCl$ and Chloroprene 14
  10. Copolymers of $CH_2=CFCl$ 14
  11. Copolymers of $CF_2=CFCl$ and $CF_2=CHF$ 16
  12. Miscellaneous Butadiene Copolymers 16
  13. Exploratory $CF_2=CH_2$ Copolymerizations 17
  14. Fluoroprene Polymers 19
  15. Miscellaneous Exploratory Copolymerizations 19
  16. Polysulfide Polymer 21
  17. Gel Content 21
- C. Polymer Evaluation 22
  1. Copolymers of $CF_2=CCl_2$ and Isoprene 22

IV. Plans for Future Work 24

I. Introduction

A. Purpose of the Project

The primary purpose of this project is the development of a fluorine containing oil- and fuel-resistant elastomer which will retain its rubbery properties between -70°F. and +160°F.

B. Research Program

To achieve this goal, the M. W. Kellogg Company has been authorized by the Quartermaster Corps to conduct a broad investigation of fluorocarbon polymers involving (1) monomer synthesis; (2) polymer preparation; and (3) polymer evaluation. Emphasis has been placed upon polymer preparation and especially upon the copolymerization of fluoro-olefins and fluoro-chloro-olefins among themselves and with olefinic and diolefinic hydrocarbons.

Monomer synthesis at Kellogg has been restricted largely to products arising from the thermal dimerization of $CF_2{=}CFCl$, namely, $CF_2{=}CF{-}CF{=}CF_2$, $\overline{CF_2{-}CF{=}CF{-}CF_2}$ and $CF_3{-}CF{=}CF_2$. Other monomers not available commercially have been requested from Dr. Paul Tarrant of the University of Florida, Dr. Aldrich Syverson of the Ohio State University, and Dr. W. T. Miller of Cornell University, or obtained on an exchange basis from Minnesota Mining & Manufacturing Co.

Polymer preparation has proceeded through three phases: (a) Exploratory copolymerization of new monomer pairs; (b) determination of the relative reactivities of monomers successfully copolymerized into elastomers; and (c) synthesis of compositionally homogeneous, pound batches of these elastomers in several co-monomer ratios for evaluation.

Polymer compounding, testing, and evaluation have been made the responsibility of Mr. C. B. Griffis of the Chemical & Plastics Laboratory of the Philadelphia Quartermaster Depot.

C. Past Progress

1. Quarters completed as of March 31, 1952: 7
2. Monomers available for copolymerization: 25
    - a. Purchased: 12
    - b. Minnesota Mining & Mfg. Co.: 2
    - c. Dr. Tarrant: 3
    - d. Dr. Syverson: 3
    - e. M. W. Kellogg Co.: 5
3. Copolymer systems investigated: 53
4. Rubberlike copolymers selected for evaluation: 21

5. Monomer reactivity ratios determined: 5

M_1	M_2	r_1	r_2
$CF_2=CFCl$	butadiene	0.00	1.35
$CF_2=CFCl$	isoprene	0.11	1.41
$CF_2=CFCl$	$CF_2=CH_2$	0.52	1.17
$CF_2=CCl_2$	isoprene	0.00	0.45
$CF_2=CCl_2$	butadiene	0.00	0.80

6. Rubbers Evaluated: /1/

System	Combined Molar Ratio	Tensile	Elongation	% Swell SR-6	% Swell SR-10	TR-10	TR-70
$CF_2=CFCl$/butadiene	10/90	1360 psi	180%	218	168	-61°C.	-47°C.
$CF_2=CFCl$/isoprene	13/87	1750	250	226	196	-43	-33
$CF_2=CFCl/CF_2=CH_2$	50/50	-	-	10	2	-	-
$CF_2=CCl_2$/isoprene	23/77	2800	260	149	101	-24	-13
" "	39/61	3310	320	161	106	-14	-1
$CF_2=CCl_2$/butadiene	10/90	1700	205	140	100	-55	-40
" "	23/77	3100	310	148	92	-28	-16
$CH_2=CFCl$ only	-	Too soft to process on rubber mill. No further evaluation planned.					

7. Alfin and anionic (Na) polymerizations of fluoro-olefins unsuccessful.

8. No glass transition temperature observed for Teflon, KEL-F, polyperfluorobutadiene, or polytrifluoroethylene from -150°C. to +85°C.

9. Progress made in vulcanization of "saturated" rubbers such as the 50/50 molar $CF_2=CFCl/CF_2=CH_2$ copolymers. Polysulfide and peroxide-amine recipes most promising.

10. Copolymers of $CF_2=CFCl$/n-butyl acrylate seem to be of "grafted" type with an acrylate backbone and fluorocarbon side chains.

II. Summary of Current Progress

The number of monomers available for copolymerization studies has increased to 30, the number of copolymer systems investigated to 81, and the number of rubberlike systems to 26. Monomer reactivity ratios have been calculated for three additional systems, $CF_2=CF-CF=CF_2$/butadiene, $CF_2=CF-CF=CF_2$/isoprene, and $CF_2=CF_2$/butadiene.

/1/ Well-cured, general purpose black stocks except for $CF_2=CFCl/CF_2=CH_2$ rubber, for which raw gum values are presented.

Tests have been completed on the $CF_2=CCl_2$/isoprene system at three levels, 10/90, 25/75, and 40/60 molar. Low temperature properties become worse and solvent resistance is not improved as greater amounts of $CF_2=CCl_2$ are combined. In the $CF_2=CCl_2$/butadiene, $CF_2=CFCl$/butadiene and $CF_2=CFCl$/isoprene series, all samples required to complete the screening tests have been sent to the Depot. Data for all four systems will be correlated as soon as the tests are completed.

Compounding and vulcanization studies of "saturated" rubbers exemplified by the $CF_2=CFCl/CF_2=CH_2$ copolymers near 50/50 molar have continued, but no significant degree of cross-linking has been achieved.

Copolymers of $CF_2=CFCl$/chloroprene, $CF_2=CF_2$/butadiene, and $CF_2=CF-CF=CF_2$/butadiene have been sent to the Depot for test, but data are not yet available. The $CF_2=CFCl$/n-butyl acrylate copolymers, which seem to be of the "grafted" type, have been made on a pound scale, but none of the samples has contained enough $CF_2=CFCl$ to justify evaluation.

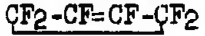
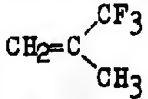
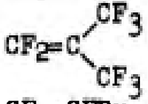
Exploratory copolymerizations have been attempted with many new monomer pairs: In most cases the yields have been very poor, but some new rubberlike systems have been found, notably $CF_2=CF_2/CF_2=CH_2$; $CF_2=CFCl/CH_2=CF-CH=CH_2$; $CF_2=CCl_2/CH_2=CF-CH=CH_2$, and $CF_2=CF_2$/n-butyl acrylate.

Five new monomers have been added to the list and the production of $CF_2=CF-CF=CF_2$ has been resumed on a limited scale.

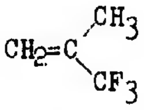
III. Experimental Section

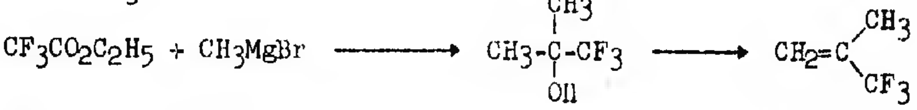
A. Monomer Synthesis

Thirty monomers are now available for copolymerization studies:

1. $CF_2=CFCl$
2. $CF_2=CH_2$
3. $CH_2=CH-CH=CH_2$
4. $CF_2=CF-CF=CF_2$
5. $CH_2=C(CH_3)-CH=CH_2$
6. $(CH_3)_2C=CH_2$
7.  $\underbrace{CF_2-CF=CF-CF_2}$
8. $CH_2=CHCl$
9. $CF_2=CCl_2$
10. $CH_3-CH=CH_2$
11. C_6H_5
12. $CH_2=CCl_2$
13. $CH_2=CCl-CH=CH_2$
14. $CF_3-CF=CF_2$
15. $CF_2=CF-CN$
16. $CH_2=CF-CN$
17. $CH_2=CH-COO \cdot C_4H_9$ (n)
18. $CF_2=CHCl$
19. $CF_3-CCl=CCl-CF_3$
20. $CF_3-C\equiv C-CF_3$
21. $CF_2=CHF$
22. $CH_2=CFCl$
23. <u>cis</u> $CF_3-CH=CH-CF_3$
24. $CF_2=CF_2$
25. <u>trans</u> $CF_3-CH=CH-CF_3$
26. $CH_2=CH-C_6H_4-CH=CH_2$
27.  $CH_2=C\begin{matrix} CF_3 \\ CH_3 \end{matrix}$
28. $CH_2=CF-CH=CH_2$
29.  $CF_2=C\begin{matrix} CF_3 \\ CF_3 \end{matrix}$
30. $CF_2=CFBr$

During the current quarter, Dr. Tarrant has submitted three new monomers prepared as follows:

1.  $CH_2{=}C\begin{matrix}CH_3\\CF_3\end{matrix}$, 316 gm., b. 6°-8°C.



$$CF_3CO_2C_2H_5 + CH_3MgBr \longrightarrow CH_3-\underset{OH}{\overset{CH_3}{C}}-CF_3 \longrightarrow CH_2{=}C\begin{matrix}CH_3\\CF_3\end{matrix}$$

2. $CH_2{=}CF-CH{=}CH_2$, 361 grams, b. 10.5°-13.0°C.

$$CH_3-CCl{=}CH-CH_3 + HF \longrightarrow CH_3-CFCl-CH_2-CH_3 + Cl_2 \longrightarrow$$

$$CH_3-CFCl-CH_2-CH_2Cl \xrightarrow[375-400^\circ C.]{\text{soda lime}} CH_2{=}CF-CH{=}CH_2$$

3. $CF_2{=}CFBr$, 1 lb., b. -3.0° to -1.0°C.

$$CF_2Br-CHFCl \xrightarrow{Zn} CF_2{=}CHF \xrightarrow{Br_2} CF_2Br-CHFBr$$

$$\xrightarrow[H_2O]{KOH} CF_2{=}CFBr.$$

In exchange for an equal quantity of $CF_2{=}CF-CF{=}CF_2$, the Minnesota Mining & Mfg. Co. has sent us 250 grams of $CF_2{=}C\begin{matrix}CF_3\\CF_3\end{matrix}$, b. 7°C.

A small quantity of divinyl benzene (#26) has been purchased.

Additional quantities of $CF_2{=}CF_2$ and $CF_2{=}CHF$ have been prepared in our laboratory as needed from CF_2Br-CF_2Br and $CF_2Br-CHFCl$, respectively. The synthesis of $CF_2{=}CF-CF{=}CF_2$ has been resumed to the extent that all of the $CF_2{=}CFCl$ dimerization products on hand are being worked up to provide 10-12 lbs. of the pure monomer.

B. Polymer Preparation

The twenty-three copolymer systems considered rubbery enough for evaluation are the following (where the numbers refer to the monomers listed in section III-A): 1-2, 1-3, 1-5, 1-13, 1-17, 1-22, 2-4, 2-22, 2-24, 3-4, 3-9, 3-14, 3-18, 3-19, 3-21, 3-22, 3-24, 4-5, 5-9, 9-12, 9-13, 9-17 and 22.

Recent experimental data relative to these and other copolymer systems are set forth below.

1. Copolymers of $CF_2=CFCl$ (KF) and $CF_2=CH_2$ (VF_2)

Additional pound batches of approximately 50/50 molar KF/VF_2 rubber have been sent to the Depot periodically for vulcanization studies (cf. Section III-C). The yields of this copolymer have been erratic when the polymerizations have been carried out in the persulfate-bisulfite suspension recipe in the 1-gallon stainless steel autoclave. Because of the acidity of this recipe, excessive and variable quantities of soluble iron have been suspected. An $(NH_4)_2SO_4$-$(NH_4)HSO_4$ buffer and "Versene Fe-3 Specific" sequestering agent have been helpful but they have not brought all the variables under control. The best procedure now involves scrupulous exclusion of hydrocarbons (such as oils and greases from packings), vigorous steaming of the pot between runs, and the addition of very small amounts of $FeSO_4 \cdot 7H_2O$ to the recipe. With these precautions, conversions have been consistently high.

Attempts have been made to introduce small amounts of a third monomer into this system to provide better sites for cross-linking. Both runs were made in the persulfate-bisulfite recipe at 20°C.

Code	Moles Charged	Moles Found	% Conversion	Hours Polymerization	Appearance
		$KF/VF_2/CF_2=CF-CF=CF_2$			
605A	50/45/5	-	zero	96	-
		$KF/VF_2/CF_2=CFBr$			
627	30/65/5	33/63/4	91	22	rubbery

As soon as a satisfactory vulcanizing agent is found for the $CF_2=CFCl/CF_2=CH_2$ rubbers or for the terpolymers, homogeneous batches of the 60/40, 50/50, and 40/60 molar products will be prepared on a pound scale for final evaluation.

2. Copolymers of $CF_2=CFCl$(KF) and Butadiene (BD)

A homogeneous 10/90 molar KF/BD copolymer has already been tested; more recently, there have been a number of attempts to prepare the homogeneous 25/75 and 40/60 molar products in the gallon autoclave by increment feeding. For the most part, these experiments have been difficult and time-consuming. At the 25/75 level, one apparently homogeneous batch was prepared in the Mutual recipe at 50°C. by increment feeding (527-G). The yield of polymer was 456 gm. compared with an expected yield of 480 gm. Its composition was 22/78 molar KF/BD. For comparative purposes, a deliberately heterogeneous copolymer (529-G) was prepared in the same recipe at 50°C. by the single charge technique. It was carried to 75% conversion where the butadiene was virtually exhausted from the monomer phase and the polymerization at a standstill. Its composition was 21/79 molar KF/VF$_2$, almost identical with that of 527-G. Both batches have been sent to the Depot for test.

At KF levels higher than 25 mole %, the difficulties of preparing homogeneous copolymers on a pound scale have been even greater. One of the products (556-A-G), prepared in the Mutual recipe at 50°C. by increment feeding, has been sent to the Depot for test. The actual yield was 225 gm., compared with an expected yield of 170 gm.; its composition was 39/61 molar. Although probably not as homogeneous as desired, this sample will serve for the initial evaluation of KF/BD rubbers at high KF levels.

In this series, as well as in other series where monomer reactivities are of the same order, copolymer homogeneity will be attained in the future mainly by restricting the conversions of single-charge polymerizations to the optimum level. Increment feeding will be considered only in those systems where the properties of the initial batches justify the subsequent preparation of a number of pound lots under more or less identical conditions.

3. Copolymers of CF_2=CFCl (KF) and Isoprene (I)

Although a homogeneous 10/90 molar KF/I copolymer has already been tested, difficulties have been encountered in preparing homogeneous products at the 25/75 and 40/60 molar levels (cf. discussion in KF/BD section immediately above). Six runs have recently been carried out by the increment feeding and single charge techniques, but in only one instance (607-G) was the product considered suitable for evaluation. This batch was prepared by carrying a single charge of 40/60 molar KF/I monomer to 39% conversion in the Mutual recipe at 50°C. The composition of the product was 24/76 molar KF/I; it has been sent to the Depot for test. There will be no further attempts to make KF/I rubbers at KF levels higher than 25 mole %.

4. Copolymers of CF_2=CCl_2 (G) and Butadiene (BD)

Adequately homogeneous 10/90 and 23/77 molar G/BD copolymers have already been tested. At higher G levels, copolymer homogeneity can best be realized by short-stopping the polymerization at relatively low conversions. This point has been demonstrated by a comparison of the gross physical properties of three G/BD copolymers prepared from the same charge (60/40 molar G/BD) in the Mutual recipe at 50°C.

Code	Moles G/BD combined	% Conversion	Appearance
500-G	44/56	53	Dry, powdery solid
579-G	38/62	36	" " "
555-G	46/54	19	Spongy rubber

Batches 500-G and 555-G have been sent to the Depot for test.

5. Copolymers of $CF_2=CCl_2$ (G) and Isoprene (I)

Of the three G/I copolymers scheduled for test, two, at the 23/77 and 39/61 molar G/I levels, have already been evaluated. The third, at the 10/90 level, has now been tested (cf. Section III-C for results and general comments on the G/BD and G/I series). All three G/I copolymers were prepared in the Mutual recipe at 50°C. by the single charge technique.

6. Copolymers of $CF_2=CFCl$ (KF) and n-Butyl Acrylate (BA)

These copolymers seem to be of the "grafted" type, i.e., copolymers composed of an initially formed acrylate backbone to which KF side chains are attached during the latter stages of polymerization by chain transfer to the polymer. The first two attempts to prepare a batch of approximately 25/75 molar KF/BA rubber for evaluation failed because the reactions were not carried to high enough conversions. Both runs were made in the persulfate-bisulfite recipe at 20°C.

Code	Moles KF/BA Charged	Moles KF/BA Found	% Conversion	Hours Polymerization	Appearance
571-G	25/75	1/99	67	41	rubber
611-G	25/75	4/96	68	20	rubber

A third run is being conducted in 8-10 glass polymerization tubes where conversions have been consistently higher than in the gallon autoclave, and where larger amounts of KF have been successfully incorporated in smaller batches of the copolymer.

7. Copolymers of $CF_2=CF-CF=CF_2$ (FBD) with Butadiene (BD) and Isoprene (I)

Monomer reactivity ratios have now been computed for the FBD/BD and FBD/I systems on the basis of the following data and data previously reported:

Code	FBD/BD Moles Charged	FBD/BD Moles Found	% Conversion	Hours Polymerization	Appearance
566	30/70	22/78	28	6	Rubbery crumb
567	"	21/79	27	6	"
568	40/60	24/76	27	6	"
569	"	23/77	28	6	"

The parameters for these two systems are:

M_1	M_2	r_1	r_2
$CF_2=CF-CF=CF_2$	butadiene	0.0 ± 0.1	1.35 ± 0.2
$CF_2=CF-CF=CF_2$	isoprene	0.0 ± 0.1	0.75 ± 0.2

Instantaneous composition diagrams and composition-conversion plots for these systems are presented in Figures 1 and 2, respectively. In only one of the cases, FBD/I, is there an azeotrope, where the copolymer composition is identical with that of the feed from 0-100% conversion. For all practical purposes, however, copolymers from 0/100 to 25/75 molar FBD/I may be considered azeotropic. These reactions may be carried to high conversions (e.g. 90%) without excessive heterogeneity. At higher FBD levels (e.g., 40 mole %) conversions should be limited to about 50% for adequate (± 2.5 mole %) homogeneity.

The reactivity ratios for FBD/BD resemble those previously calculated for KF/BD. Above 10 mole % FBD, reasonably homogeneous copolymers can be prepared by increment feeding or by limiting the conversions markedly (40% for 25/75 FBD/BD and 30% for 40/60 FBD/BD).

The first pound batch of FBD/BD rubber scheduled for test has now been prepared in the gallon autoclave and sent to the Depot (623-G). This copolymer was carried to 32% conversion in the Mutual recipe at 50°C. and has a composition of 18/82 molar FBD/BD. It is probably not as homogeneous as it should be. Additional batches of more homogeneous FBD/BD rubber are to be made at the 10/90, 25/75, and 40/60 molar levels as soon as enough FBD monomer becomes available.

8. Copolymers of CF_2=CF_2 (TFE) and Butadiene (BD)

Monomer reactivity ratios for this system have now been calculated on the basis of the following polymerizations carried out in the Mutual recipe at 50°C.

	TFE/BD		%	Hours	
Code	Moles Charged	Moles Found	Conversion	Polymerization	Appearance
573	25/75	14/86	23	6	Rubbery crumb
574	25/75	14/86	23	6	" "
523	30/70	13/87	31	7	" "
547	40/60	20/80	31	8	" "
522	50/50	19/81	28	6	" "
575	"	21/79	21	6	" "
576	60/40	24/76	16	6	" "
549 /1/	70/30	33/67	36	7	" "

/1/ In a cumene-redox recipe at 20°C.

FIGURE 1

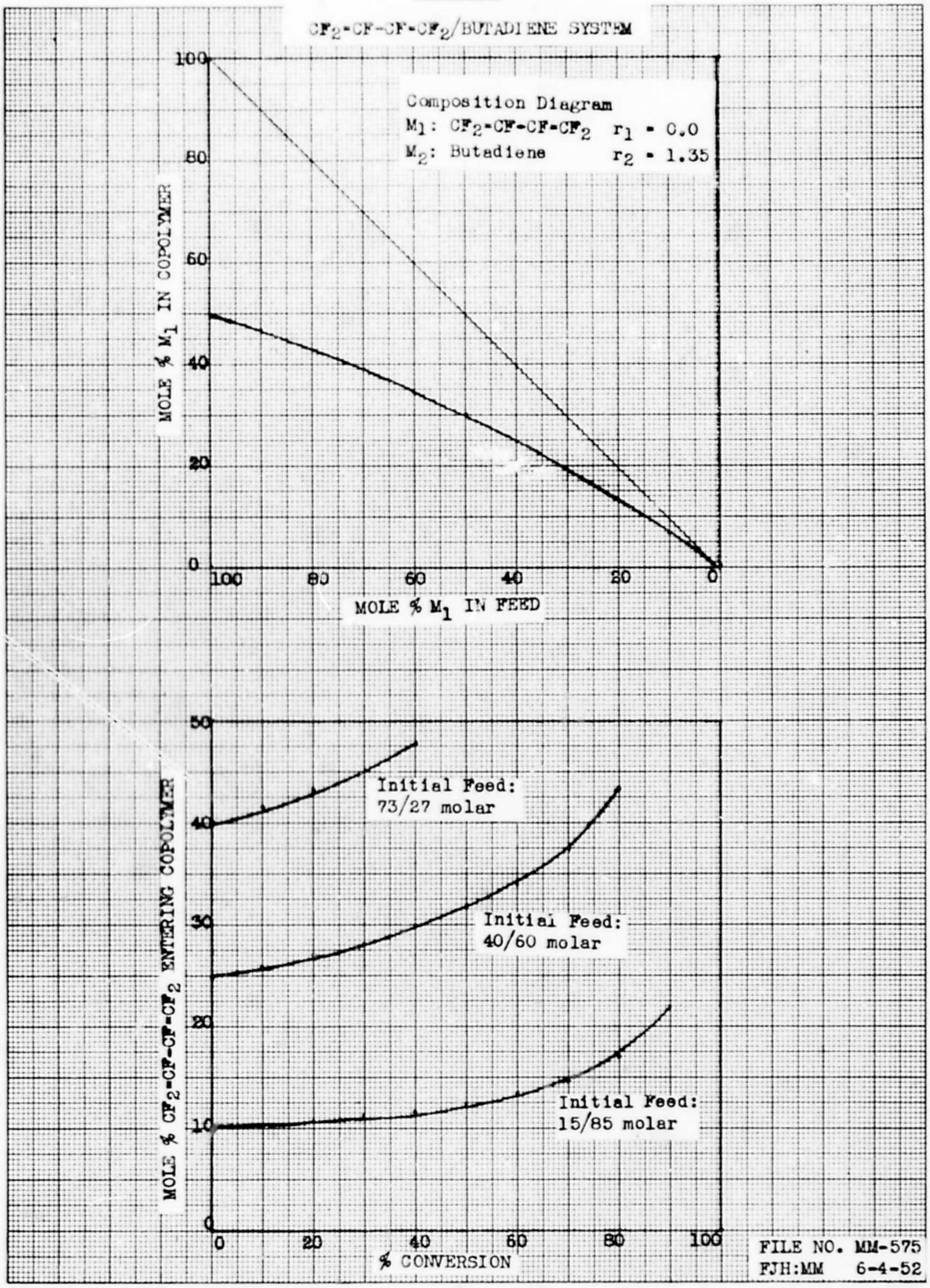


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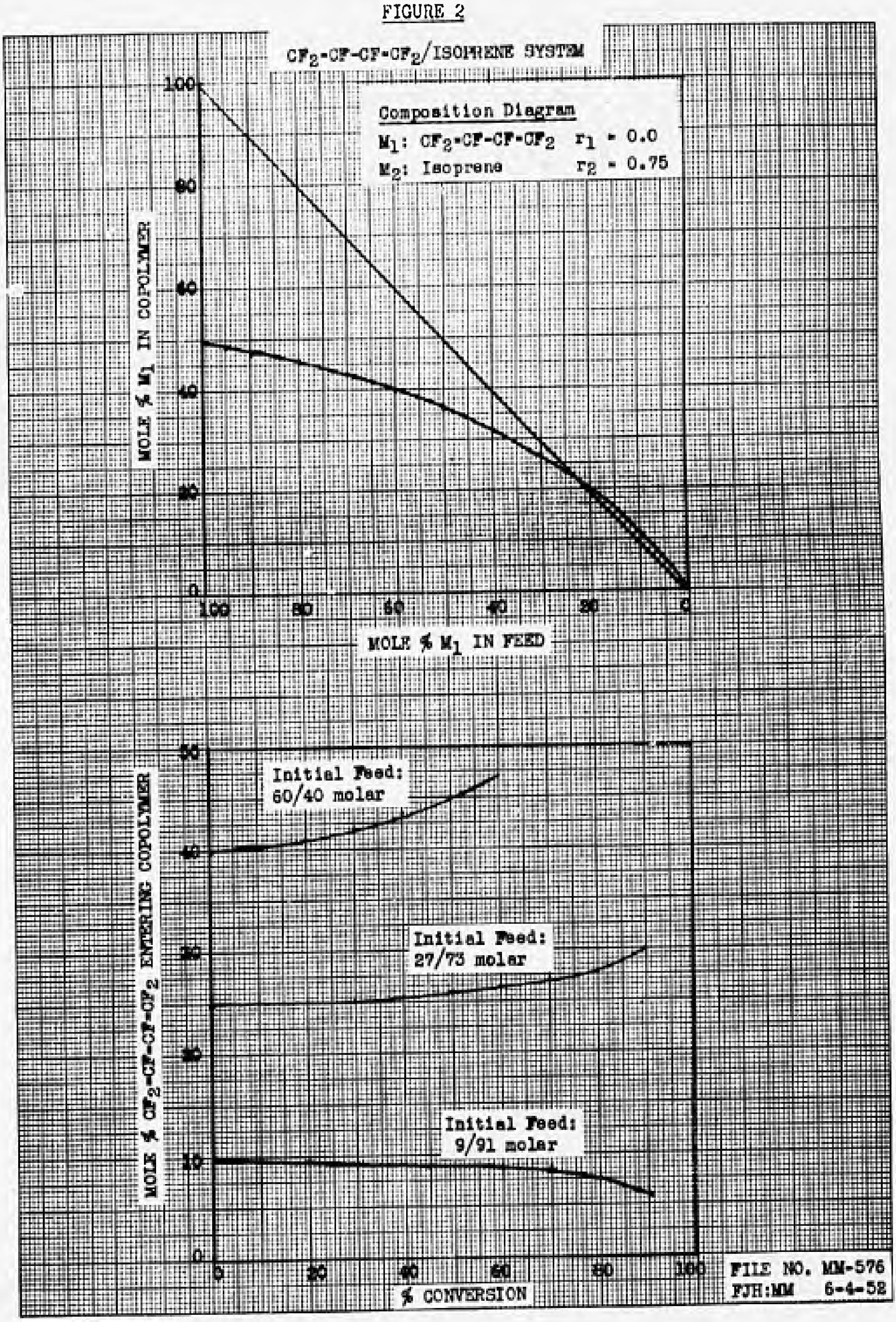
FIGURE 2



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The parameters for this system are tabulated below, together with those for the KF/BD and G/BD systems. It is interesting to note the decrease in r_2 with the increase in the number of chlorine atoms in the monomer. Correlation of data of this kind should provide considerable insight into the effect of fluorocarbon structure upon its tendency to polymerize.

M_1	M_2	r_1	r_2
$CF_2=CF_2$	butadiene	0.0±0.2	1.75±0.1
$CF_2=CFCl$	"	0.0±0.05	1.35±0.08
$CF_2=CCl_2$	"	0.0±0.06	0.80±0.05

Instantaneous composition and composition-conversion diagrams for the TFE/BD system are presented in Figure 3. Because of the comparatively large value of r_2, the copolymer curve deviates markedly from the azeotropic line and homogeneous (±2.5 mole %) copolymers can be made by the single charge technique only by severely limiting the conversions (60% at 10/90, 35% at 25/75 and 25% at 40/60 molar TFE/BD).

One pound of 10/90 molar TFE/BD rubber, carried to 31% conversion in the Mutual recipe at 50°C., has now been sent to the Depot for test (624-G). Other batches at the 25/75 and 40/60 molar levels will follow.

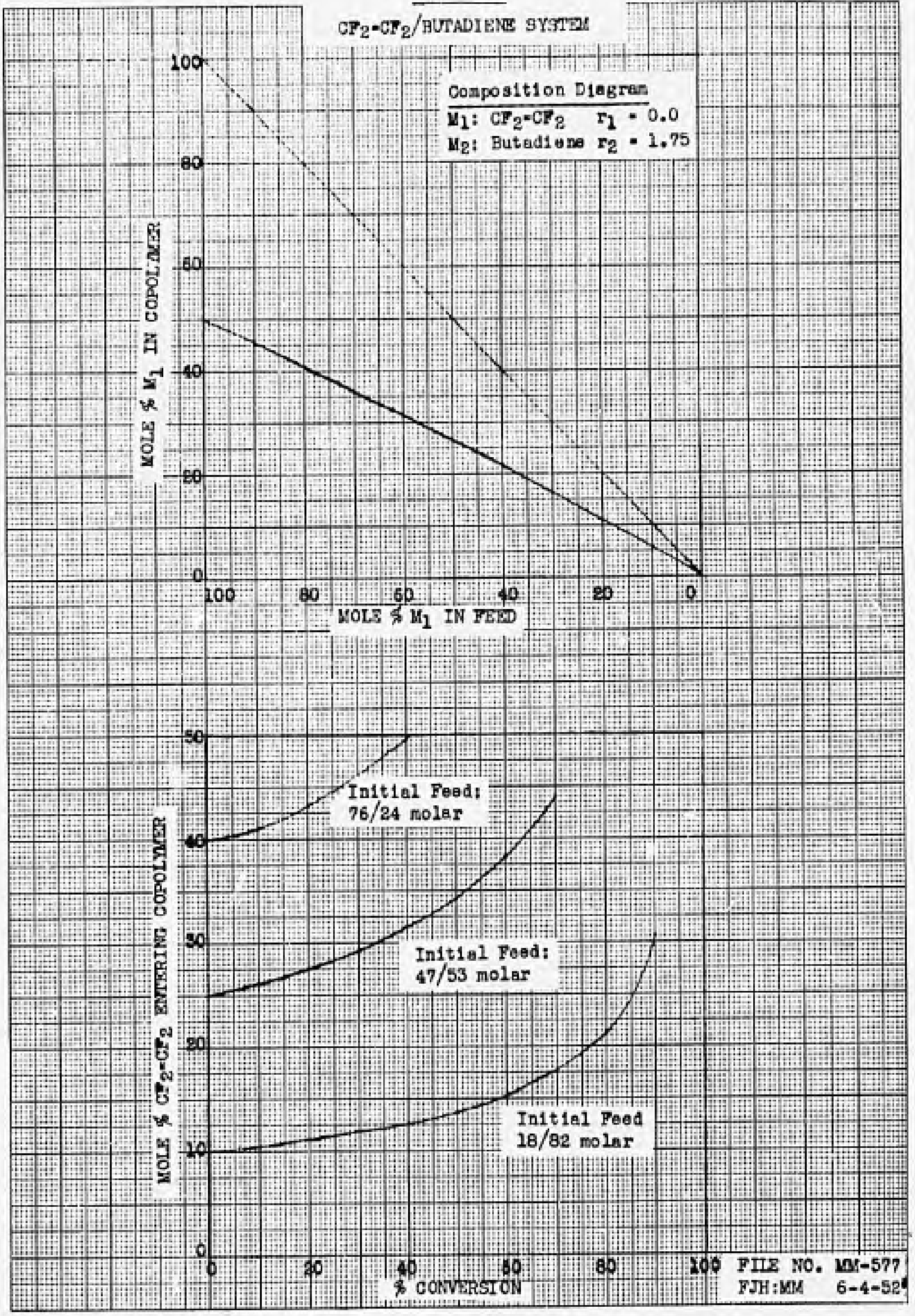
9. Copolymers of $CF_2=CFCl$ (KF) and Chloroprene (CP)

Because of the great relative reactivity of CP, special techniques must be employed to incorporate more than a few mole per cent of KF into KF/CP copolymers. In run 610-G, a KF/CP copolymer was prepared in the Mutual recipe at 50°C. by charging all of the KF monomer initially to the gallon autoclave and feeding an equimolar quantity of CP into the reactor over an 11 hour period. To maintain a high average molecular weight, the initiator was charged in increments over the polymerization period. The product, which has a composition of 14/86 molar KF/CP, has been sent to the Depot for test.

10. Copolymers of $CH_2=CFCl$

The homopolymer of $CH_2=CFCl$ is somewhat rubberlike, but it is so soft, tacky and difficult to process that it will probably not be further evaluated. Among the copolymers of $CH_2=CFCl$, those containing $CF_2=CFCl$ and $CF_2=CH_2$ have been studied most. To a great extent, these copolymers resemble the homopolymer, in that they are moderately rubbery, soft, tacky, low-melting and show some tendency to lose F and Cl while drying at 35°-40°C. in vacuo. Whether or not these products are further evaluated as rubbers will depend upon the successful vulcanization of another, more easily processed type of "saturated" rubber, the $CF_2=CFCl/CF_2=CH_2$ system.

FIGURE 3



CF_2-CF_2/BUTADIENE SYSTEM

FILE NO. MM-577
FJH:MM 6-4-52

The most recent data on $CH_2=CFCl$ copolymers are summarized below:

Code	Moles Charged	Moles Found	% Conversion	Hours Polymerization	Remarks
			$CF_2=CFCl/CH_2=CFCl$ /1/		
561	70/30	-	-	4	Soft, tacky rubbers. Although yields are obviously good, composition-conversion data are not too reliable because of loss of F & Cl during drying.
562	65/35	-	-	4	
563	50/50	-	-	4	
564	40/60	-	-	4	
565	35/65	-	54	4	
			$CF_2=CH_2/CH_2=CFCl$ /1/		
578	50/50	-	17	5	Sl. tacky rubber.

/1/ Persulfate-bisulfite suspension recipe at 20°C.

11. Copolymers of $CF_2=CFCl$ (KF) and $CF_2=CHF$ (TRFE)

Products containing substantial proportions of both KF and TRFE seem to be true copolymers rather than mixtures, since they are completely soluble in acetone at room temperature. The homopolymer of KF is, of course, acetone-insoluble. These products are not sufficiently rubberlike to justify further study at this time, however.

12. Miscellaneous Butadiene (BD) Copolymers

Butadiene is a convenient comonomer since its copolymers are usually rubberlike and vulcanizable, and provide some basis for comparing the properties of various fluorocarbon structures even when these structures cannot be prepared by direct homopolymerization of the appropriate fluorinated monomer. Data are compiled below for some recent polymerizations. The $CF_2=CHF$/BD system seems promising at first glance because its products are rubberlike, but the amount of $CF_2=CHF$ which can be incorporated in the copolymer is so small that the system will probably not be studied further. Apparently the H in $CF_2=CHF$, like that in $CF_2=CHCl$, is an effective chain transfer agent.

Code	Moles Charged	Moles Found	% Conversion	Hours Polymerization	Appearance
			$CF_2=CHF/BD$ /1/		
544	30/70	1/99	34	24	Resilient rubber
545	40/60	2/98	23	24	Rubber
543	50/50	4/96	15	24	Tacky rubber
546	60/40	-	very low	24	-
550 /2/	70/30	6/94	21	24	Rubbery crumb
			trans $CF_3-CH=CH-CF_3/BD$ /1/		
582	50/50	-	very low	24	-

/1/ Mutual recipe at 50°C.
/2/ Cumene redox recipe at 20°C.

13. Exploratory $CF_2=CH_2$ (VF_2) Copolymerizations

VF_2 is an interesting monomer because its methylene group imparts to an otherwise stiff fluorine polymer chain "points of flexibility" which contribute to kinetic elasticity and rubberiness. Data are compiled below for a number of recent VF_2 copolymerizations.

Code	Moles Charged	Moles Found	% Conversion	Hours Polymerization	Appearance
			$CF_2{=}CF_2/VF_2$ /1/		
572	50/50	65/35	57	18	Sl. rubbery crumb
			$CH_2{=}C(CH_3)_2/VF_2$ /1/		
591	50/50	-	zero	24	-
			n-butyl acrylate/VF_2 /1/		
600	50/50	96/4	65	18	Rubber
			$CF_2{=}CCl_2/VF_2$ /1/		
598	50/50	0/100	36	19	Powder
			$CH_2{=}CHCN/VF_2$ /1/		
601	50/50	100/0	46	16	Powder
			$CF_2{=}CHCl/VF_2$ /1/		
582	50/50	-	trace	21	-
			$CF_2{=}CHF/VF_2$ /1/		
581	49/51	56/44	88	23	Brittle solid
			(cis) $CF_3{-}CH{=}CH{-}CF_3/VF_2$ /1/		
583	50/50	-	zero	21	-
			$CF_3{-}CCl{=}CCl{-}CF_3/VF_2$ /1/		
597	50/50	-	zero	24	-
			chloroprene/VF_2 /2/		
613	50/50	92/8	62	16	Rubber
			$CF_2{=}CF{-}CF{=}CF_2/VF_2$ /3/		
609	50/50	-	zero	24	-

/1/ Persulfate-bisulfite suspension at 20°C.
/2/ Cumene-redox at 20°C.
/3/ Persulfate-emulsion at 50°C.

Of the products obtained, the $CF_2{=}CF_2/CF_2{=}CH_2$ copolymer (572) seems most interesting. The 50/50 molar product should be even more rubberlike, if this system follows the pattern set by $CF_2{=}CFCl$ and $CF_2{=}CH_2$.

14. Fluoroprene (FP) polymers

Fluoroprene, $CH_2{=}CF{-}CH{=}CH_2$, is the first fluorinated diene other than perfluorobutadiene to be synthesized for this program. According to published data, FP is intermediate in reactivity between butadiene and chloroprene. Its homopolymer and presumably many of its copolymers are rubberlike. Its fluorine content is great enough to provide some aliphatic solvent resistance. For these reasons, FP will open a new area of copolymerization which should provide some interesting products for evaluation as Arctic Rubbers. The few runs completed to date are shown below:

Code	Moles Charged	Moles Found	% Conversion	Hours Polymerization	Appearance
			FP only		
616 /1/	-	-	2	24	soft, soapy solid
620 /2/	-	-	trace	40	-
			$CF_2{=}CCl_2/FP$ /1/		
626	50/50	29/71	19	73	rubbery
			$CF_2{=}CFCl/FP$		
615 /3/	50/50	-	2	17	soapy
625 /1/	50/50	22/78	18	73	rubbery

/1/ Mutual recipe at 50°C.
/2/ Persulfate-bisulfite suspension at 20°C.
/3/ Persulfate-ferricyanide recipe at 20°C.

15. Miscellaneous Exploratory Copolymerizations

Because the properties of fluorocarbon polymers are not easily foreseen, a broad exploratory study is being made of all possible fluorine-containing copolymer pairs derived from the monomer list. For the time being simpler recipes such as the Mutual, cumene-redox, and persulfate-bisulfite suspension are being used, but in those cases where the products are interesting as rubbers but where the yields are poor, new recipes or techniques of polymerization will be tried. The most recent results are tabulated below:

Code	Moles Charged	Moles Found	% Conversion	Hours Polymerization	Appearance
			$CF_2{=}CFCl$/trans $CF_3{-}CH{=}CH{-}CF_3$ /1/		
539	50/50	-	trace	47	Powder
			$CF_2{=}CFCl$/cis $CF_3{-}CH{=}CH{-}CF_3$ /1/		
540	50/50	97/3	4	23	Powder
			$CF_2{=}CCl_2$/cis $CF_3{-}CH{=}CH{-}CF_3$ /1/		
592	50/50	-	trace	53	-
			$CF_2{=}CFCl/CF_3{-}CF{=}CF_2$ /1/		
541	25/75	-	0.4	47	Powder
			$CF_2{=}CCl_2/CF_3{-}CF{=}CF_2$ /1/		
595	50/50	-	trace	53	-
			$CF_2{=}CF_2/CF_2{=}CF{-}CF{=}CF_2$ /2/		
548	50/50	-	zero	24	-
			$CF_2{=}CCl_2/CF_2{=}CHCl$ /1/		
593	50/50	-	trace	53	-
			$CF_2{=}CCl_2/CH_2{=}C(CH_3)(CF_3)$ /1/		
596	50/50	-	zero	53	-
			$CF_2{=}CFCl/CH_2{=}C(CH_3)(CF_3)$ /2/		
619	50/50	-	0.5	22	Powder
			$CF_2{=}CCl_2/CH_2{=}CHCN$ /1/		
603	50/50	2/98	26	16	Powder
			$CF_2{=}CHCl/CH_2{=}CHCN$ /1/		
602	50/50	3/97	34	16	Powder

(cont'd next page)

Code	Moles Charged	Moles Found	% Conversion	Hours Polymerization	Appearance
			$CF_2=CHCl$/chloroprene /3/		
614	50/50	7/93	51	16	rubber
			$CH_2=C(CH_3)(CF_3)$ /2/		
618	-	-	trace	22	Powder
			$CF_2=CF_2$/n-butyl acrylate /1/		
621	50/50	25/75	71	89	rubber
			$CF_2=CHCl$/n-butyl acrylate /1/		
622	50/50	1/99	52	96	tacky rubber

/1/ Persulfate-bisulfite suspension at 20°C.
/2/ Mutual recipe at 50°C.
/3/ Cumene-redox at 20°C.

The yields in most cases have been very poor, and in the acrylonitrile and chloroprene series the quantities of fluorocarbon monomer incorporated in the polymer have been too low to merit further serious attention. But in 621, the properties, yield, and composition have been such as to encourage additional work. This $CF_2=CF_2$/n-butyl acrylate polymer may resemble the corresponding $CF_2=CFCl$ product, which is thought to be of the "grafted" type. Experiments are being set up to throw more light on both these structures.

16. Polysulfide Polymer

An attempt to condense $Cl-CF_2-CF=CF-CF_2-Cl$ (a by-product of the FBD synthesis) with Na_2S_x to form a polysulfide polymer resulted only in a small yield of brown powder.

17. Gel Content

The gel contents of a number of rubbers already evaluated have been determined by the ORR bottle method with benzene as the solvent.

Code	Composition (molar)	% Conversion	% Gel
527-G	22/78 $CF_2=CFCl$/butadiene	increment fed	89
529-G	21/79 " "	75	93
556-A-G	39/61 " "	increment fed	91
316-G	13/87 " /isoprene	50	39
498-G	10/90 $CF_2=CCl_2$/butadiene	70	79
493-G	23/77 " "	90	84
500-G	44/56 " "	53	91
555-G	46/54 " "	19	8
477-G	9/91 " /isoprene	28	6
499-G	12/88 " "	38	1
478-G	23/77 " "	51	40

C. Polymer Evaluation (with Mr. C. B. Griffis of the Philadelphia Quartermaster Depot)

1. Copolymers of $CF_2=CCl_2$ (G) and Isoprene (I)

The last of the G/I rubbers scheduled for test has now been evaluated. Data are presented in Table 1 for this copolymer, which has a composition of 10/90 molar G/I, and in the previous report (RL-52-195) for the other two members of the series, the 23/77 and 39/61 molar G/I copolymers. A review of the data supports these tentative conclusions:

As the $CF_2=CCl_2$ content of the rubber is increased,

(1) Tensile strength increases.

(2) The solvent resistance remains more or less constant.

(3) The low temperature properties (retraction and stiffness) deteriorate.

(4) There is no tendency toward low temperature crystallization.

The failure of increased amounts of $CF_2=CCl_2$ to improve the solvent resistance is somewhat surprising. However, it should be noted that all swelling measurements to date have been made on a general purpose black stock. Experiments are now under way at the Depot to recheck these values in a stock specifically for oil resistance. It has already been shown that the low temperature properties (e.g., TR-10 values) are unaffected by the type or extent of cure.

TABLE 1

EVALUATION OF A $CF_2=CCl_2$/ISOPRENE RUBBER

Kellogg Code No.		477-499-G blend
QM Code No.		1F33
Mole % $CF_2=CCl_2$ combined		10.2
Polymerization Temperature, °C.		50
% Conversion		32
Compounding recipe:	Polymer	100 parts by weight
	Philblack "O"	30
	Zinc Oxide	5
	Stearic Acid	1
	Altax	1
	Sulfur	2

Cure, min./300°F.	20	40	60
Tensile, psi	2000	1800	1900
Elongation, %	350	240	240
Stress at 300%, psi	1625	-	-
Hardness, Shore A	66	70	71
% Volume Swell, SR-6	175	163	159
% Volume Swell, SR-10	145	127	127
Retraction Test			
Initial Elongation, %	250	150	150
TR-10 (minus °C.)	44	42	42
TR-30 "	40	38	38
TR-50 "	36	34	34
TR-70 "	29	28	28
Gehman Stiffness			
T-100 (minus °C.)	35	33	32
T-10 "	28	27	27
T-5 "	26	24	24
T-2 "	20	19	19

FILE NO. MM-574
FJH:MM 6-4-52

IV. Plans for Future Work

A. Completion of tests on the KF/BD, KF/I, G/BD, and G/I series. These data are being compiled for presentation at the Fluorine Symposium, ACS, in September.

B. Vulcanization of "saturated" rubbers exemplified by the $CF_2=CFCl/CF_2=CH_2$ series.

C. Preparation and evaluation of other fluorocarbon-butadiene rubbers (e.g. $CF_2=CF-CF=CF_2$/BD, $CF_2=CF_2$/BD) to provide a means for determining the effect of fluorocarbon structures on properties.

D. Increased emphasis on saturated polymers containing methylene groups (e.g., those derived from VF_2) and on copolymers of fluoroprene.

E. Further study of the acrylate copolymers on which fluorocarbon side chains seem to be "grafted".

F. Calculation of monomer reactivity ratios for other rubberlike systems.

G. Exploratory copolymerization of additional monomer pairs.

H. Continued production of $CF_2=CF-CF=CF_2$.

F J Honn
F. J. HONN

JW Copenhaver
J. W. COPENHAVER per FJH

References to Original Records:

Notebook #135 (Bolstad) pp. 45-131 incl.
Notebook #168 (Hoyt) pp. 1-57 incl.
Notebook #173 (Martin) pp. 1-76 incl.

SUPPLEMENTARY

INFORMATION

AD-494 852 Kellogg (M W) Co., Jersey City, N. J. Progress rept. 1 Apr-30 Jun 52. Rept. no. RL-52-209 1 Aug 52 Contract DA-44-109- QM-222	DDC users only.	No limitation	OCRD, D/A ltr, 11 Mar 69