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Petroleum & Chemical Research Department

PROGRESS REPORT

Arctic Rubber

U.S. Army Contract DA-44-109-qm-222
For the Period January-March, 1952

May 1, 1952

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Elastomers

Materials - Low temperature
application

Fluoro-organic compounds

Polymers

Materials, Non-Metallic (8)
Rubber (3)

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



PROGRESS REPORT

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

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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 $+160^{\circ}\text{F}$.

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 fluorochloro-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 $\text{CF}_2=\text{CFCl}$, namely, $\text{Cl}_2\text{CF}-\text{CF}=\text{CF}_2$, $\text{CF}_2-\text{CF}=\text{CF}-\text{CF}_2$, and $\text{CF}_3-\text{CF}=\text{CF}_2$. 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 December 31, 1951: 6
2. Monomers available for copolymerization: 22
 - a. Purchased: 12
 - b. Minnesota Mining & Mfg. Co.: 2
 - c. Dr. Tarrant: 3
 - d. Dr. Syverson: 1
 - e. M. W. Kellogg Co.: 4
3. Copolymer systems investigated: 47

4. Rubberlike copolymers selected for evaluation: 18

5. Monomer reactivity ratios determined: 4

M_1	M_2	r_1	r_2
$CF_2=CFC1$	butadiene	0.00	1.35
$CF_2=CFC1$	isoprene	0.11	1.41
$CF_2=CFC1$	$CF_2=CH_2$	0.52	0.17
$CF_2=CCl_2$	isoprene	0.00	0.45

6. Rubbers evaluated: /1/

System	Combined Molar Ratio	Tensile	Elonga- tion	% Swell		TR-10	TR-70
				SR-6	SR-10		
$CF_2=CFC1$ /butadiene	10/90	1360 psi	180%	218	168	-61°C.	-47°C.
$CF_2=CFC1$ /isoprene	13/87	1750	250	226	196	-43	-33
$CF_2=CFC1$ / $CF_2=CH_2$	50/50	-	-	10	2	-	-

Tentative conclusions: (1) Better low temperature properties if polymerization is carried out at 50°C. rather than 20°C; (2) No difference in solvent resistance between equivalent 50° and 20° rubbers; (3) Butadiene copolymers are better at low temperatures than isoprene copolymers.

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

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

II. Summary of Current Progress

The number of monomers available for copolymerization studies has increased to 25, the number of copolymer systems investigated to 53, and the number of rubberlike systems to 21. Monomer reactivity ratios have been determined for one additional pair, $CF_2=CCl_2$ /butadiene. The effect of conversion on instantaneous copolymer composition has been calculated for this system.

In the $CF_2=CCl_2$ /isoprene series, adequately homogeneous copolymers have been tested at the 25/75 and 40/60 molar levels. The 10/90 copolymer is ready for test. Of the three $CF_2=CCl_2$ /butadiene rubbers scheduled for test, two (at the 10/90 and 25/75 molar levels) have been tested and the third (at the 40/60 level) is in process. Test results on several $CF_2=CCl_2$ /butadiene

/1/ Well-cured black stocks except for $CF_2=CFC1$ / $CF_2=CH_2$ rubber, for which raw gum values are presented.

and $\text{CF}_2=\text{CHCl}$ /butadiene rubbers, received from the Office of the Rubber Reserve through the Quartermaster Corps, have been compared with data obtained for our presumably more homogeneous products.

In the $\text{CF}_2=\text{CFCl}$ /butadiene and $\text{CF}_2=\text{CFCl}$ /isoprene series, adequately homogeneous products containing 25 mole % or more of the fluorocarbon must be prepared by increment feeding techniques. Pound batches of 25/75 and 40/60 molar $\text{CF}_2=\text{CFCl}$ /butadiene rubber are now being prepared for test, and pilot quantities of the corresponding $\text{CF}_2=\text{CFCl}$ /isoprene copolymers have been prepared. In both series, the 10/90 molar products have been evaluated previously. A deliberately heterogeneous 40/60 molar $\text{CF}_2=\text{CFCl}$ /butadiene copolymer has also been prepared for test.

Progress has been made in the vulcanization of "saturated" rubbers, exemplified by the $\text{CF}_2=\text{CFCl}/\text{CF}_2=\text{CH}_2$ copolymers in the neighborhood of 50/50 molar. These rubbers process readily on a warm mill, but incorporation of fillers is facilitated by the addition of 5-15 parts KEL-F oil. Polysulfide and peroxide-amine cures seem most effective at the moment.

The homopolymer of $\text{CH}_2=\text{CFCl}$, one of the 18 rubberlike products selected for evaluation, has been rejected because of poor processibility.

Copolymers of $\text{CF}_2=\text{CFCl}/n$ -butyl acrylate, which are rubberlike over a wide range of fluorocarbon content, have given evidence of being "grafted" polymers composed of an acrylate backbone and fluorocarbon side chains.

The production of $\text{CF}_2=\text{CF}-\text{CF}=\text{CF}_2$ from $\text{CF}_2=\text{CFCl}$ has been interrupted temporarily because of the apparent toxicity of some of the by-products. As soon as improved ventilating facilities are available, production will be resumed.

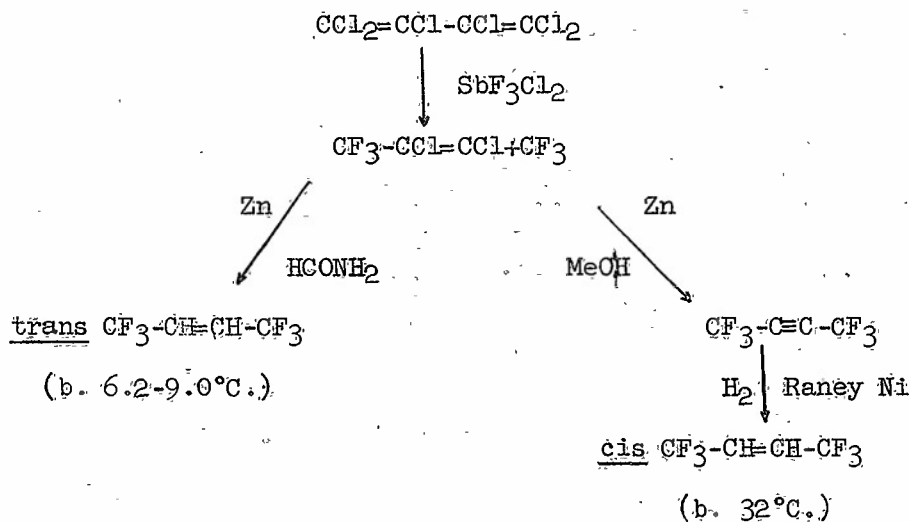
III. Experimental Section

A. Monomer Synthesis

Twenty-five monomers are now available for copolymerization studies:

- | | |
|--|---|
| 1. $\text{CF}_2=\text{CFCl}$ | 13. $\text{CH}_2=\text{CCl}-\text{CH}=\text{CH}_2$ |
| 2. $\text{CF}_2=\text{CH}_2$ | 14. $\text{CF}_3-\text{CF}=\text{CF}_2$ |
| 3. $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ | 15. $\text{CF}_2=\text{CF}-\text{CN}$ |
| 4. $\text{CF}_2=\text{CF}-\text{CF}=\text{CF}_2$ | 16. $\text{CH}_2=\text{CH}-\text{CN}$ |
| 5. $\text{CH}_2=\text{C}(\text{CH}_3)-\text{CH}=\text{CH}_2$ | 17. $\text{CH}_2=\text{CH}-\text{COO}.\text{C}_4\text{H}_9$ (n) |
| 6. $(\text{CH}_3)_2\text{C}=\text{CH}_2$ | 18. $\text{CF}_2=\text{CHCl}$ |
| 7. $\text{CF}_2-\text{CF}=\text{CF}-\text{CF}_2$ | 19. $\text{CF}_3-\text{CCl}=\text{CCl}-\text{CF}_3$ |
| 8. $\text{CH}_2=\text{CHCl}$ | 20. $\text{CF}_3-\text{C}\equiv\text{C}-\text{CF}_3$ |
| 9. $\text{CF}_2=\text{CCl}_2$ | 21. $\text{CF}_2=\text{CHF}$ |
| 10. $\text{CH}_3-\text{CH}=\text{CH}_2$ | 22. $\text{CH}_2=\text{CFCl}$ |
| 11. $\text{C}_6\text{H}_5-\text{CH}=\text{CH}_2$ | 23. <u>cis</u> $\text{CF}_3-\text{CH}=\text{CH}-\text{CF}_3$ |
| 12. $\text{CH}_2=\text{CCl}_2$ | 24. $\text{CF}_2=\text{CF}_2$ |
| | 25. <u>trans</u> $\text{CF}_3-\text{CH}=\text{CH}-\text{CF}_3$ |

During the current quarter, Dr. Syverson has submitted one pound lots of cis and trans $\text{CF}_3-\text{CH}=\text{CH}-\text{CF}_3$ prepared as follows:



Dr. Tarrant has submitted 8.7 pounds of $\text{CH}_2=\text{CFCl}$ to supplement the one pound batch previously sent to us, as well as one pound of $\text{CF}_3-\text{CF}=\text{CF}_2$ (b. -31° to -29°C.) prepared by decomposition of sodium perfluorobutyrate.

Several pounds of $\text{CF}_2=\text{CF}_2$ have been prepared in our laboratories by zinc-methanol dehalogenation of $\text{CF}_2\text{Br}-\text{CF}_2\text{Br}$ received from Kinetic Chemicals Division.

The synthesis of $\text{CF}_2=\text{CF}-\text{CF}=\text{CF}_2$ (FBD) from $\text{CF}_2=\text{CFCl}$ has been interrupted temporarily because of the apparent toxicity of certain by-products, notably $\text{CF}_2-\text{CF}=\text{CF}-\text{CF}_2$. However, approximately two and one-half pounds of the highly purified diene (b. $6.4-6.5^\circ\text{C}$.) were isolated prior to the shutdown. This quantity will suffice for the determination of FBD/butadiene and FBD/isoprene reactivity ratios and for the preparation of some larger batches of these copolymers for tests. The synthetic program will be resumed as soon as improved ventilating facilities are available.

B. Polymer Preparation

The twenty-one 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, 3-4, 3-9, 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 detailed in the following sections.

1. Copolymers of $\text{CF}_2=\text{CFCl}$ (KF) and $\text{CF}_2=\text{CH}_2$ (VF_2)

During the current quarter, no further attempts have been made to prepare a homogeneous 50/50 molar KF/ VF_2 copolymer by increment feeding techniques. Instead, several batches of admittedly heterogeneous product with an average composition of about 50/50 molar have been synthesized in persulfate-bisulfite suspension at 20°C ., blended, and sent to the Depot for vulcanization studies (see Section III-C for results). Until a satisfactory curing recipe has been developed for this type of "saturated" rubber, there will be no need for homogeneous products for final evaluation.

2. Copolymers of $\text{CF}_2=\text{CFCl}$ (KF) and Butadiene (BD)

In the last quarterly report (RL-52-183), it was shown that adequately homogeneous ($\pm 2\%$) KF/BD copolymers can be prepared at the 10/90 molar level by a single initial charge of monomer (composition = 15/85 molar) if the conversion is limited to about 60%. Such a polymer has been made and tested (Polymer 323-G, in section III-C, report RL-52-183). Copolymers of KF/BD at the 25/75 and 40/60 molar levels, on the other hand, can be prepared homogeneously on a practical scale only by increment feeding techniques, since the limiting conversions for homogeneity are excessively low.

To date, there have been four attempts to prepare a homogeneous 25/75 molar copolymer by increment feeding. In each case 500 grams of monomer (composition: 40/60 molar, as determined from reactivity ratios) have been charged into a one gallon autoclave initially, and seven 60-gram increments

(composition: 25/75 molar) added periodically at a rate supposedly equal to the rate of polymerization. In theory, the yield should have been 480 grams and the average composition 25/75 molar at the end of eight intervals. Data are tabulated below for the four runs in the Mutual recipe at 50°C.

<u>Code</u>	<u>Charging Interval</u>	<u>Actual Yield</u>	<u>Polymer Composition (KF/BD)</u>	<u>Remarks</u>
454-G	1 hour	172 gm.	16/84 molar	Conversion too low
465-G	2	356	21/79	" " "
512-G	3	691	22/78	" " high
527-G	2.5	456	-	Being dried

The yield from run 527-G seems to be close to the desired 480 grams. If this is the case when the sample is thoroughly dried, and if the composition is close to 25/75 molar KF/BD, it will be sent to the Depot for test.

There have been two similar attempts to prepare a homogeneous 40/60 molar KF/BD copolymer. In each case, 500 grams of monomer (composition: 72/28 molar) have been charged initially and 30 gram increments (composition: 40/60 molar) added periodically at a rate supposedly equal to the rate of polymerization. Data are tabulated below for two trial runs, in which the theoretical yield should have been 90 grams. A third trial run is under way.

<u>Code</u>	<u>Charging Interval</u>	<u>Actual Yield</u>	<u>Remarks</u>
519-G	3 hours	216 gm.	Conversion too high
528-G	2 "	138 gm.	Conversion too high

There is no assurance that homogeneous copolymers are necessarily the best Arctic Rubbers. Homogeneity is being stressed primarily so that the effect of copolymer composition upon properties might be evaluated with some precision. For comparative purposes, a deliberately heterogeneous 40/60 molar KF/BD copolymer (529-G) has been prepared in the Mutual recipe at 50°C. by charging the entire quantity of monomer initially (composition: 40/60 molar) and carrying the conversion to as high a level as possible. The actual conversion was 75%, but the sample must still be analyzed before it is released for test.

3. Copolymers of $\text{CF}_2=\text{CFCl}$ (KF) and Isoprene (I).

Here, too, adequately homogeneous copolymers can be prepared at the 10/90 molar level by a single initial charge of monomer (composition: 15/85 molar). For test results, confer the last quarterly report, RL-52-183, section III-C, run 316-G. At the 25/75 and 40/60 molar levels, however, the monomers must be charged incrementally to maintain copolymer homogeneity.

Two trial runs have been made at the 40/60 molar level. In each case, 500 grams of monomer (composition: 64/36 molar KF/I) were charged initially, and two 50-gram increments (composition: 40/60 molar) added at two-hour intervals. In the first run (535-G), in which 0.1 part $\text{K}_2\text{S}_2\text{O}_8$ was used in the Mutual recipe at 50°C., virtually no polymer was obtained after six hours. In the second run (538-G), in which the $\text{K}_2\text{S}_2\text{O}_8$ was increased from 0.1 to 0.3 part, the yield was 207 grams, somewhat greater than the 150 grams predicted by theory. After further adjustment is made in charging procedure, a full scale run will be attempted.

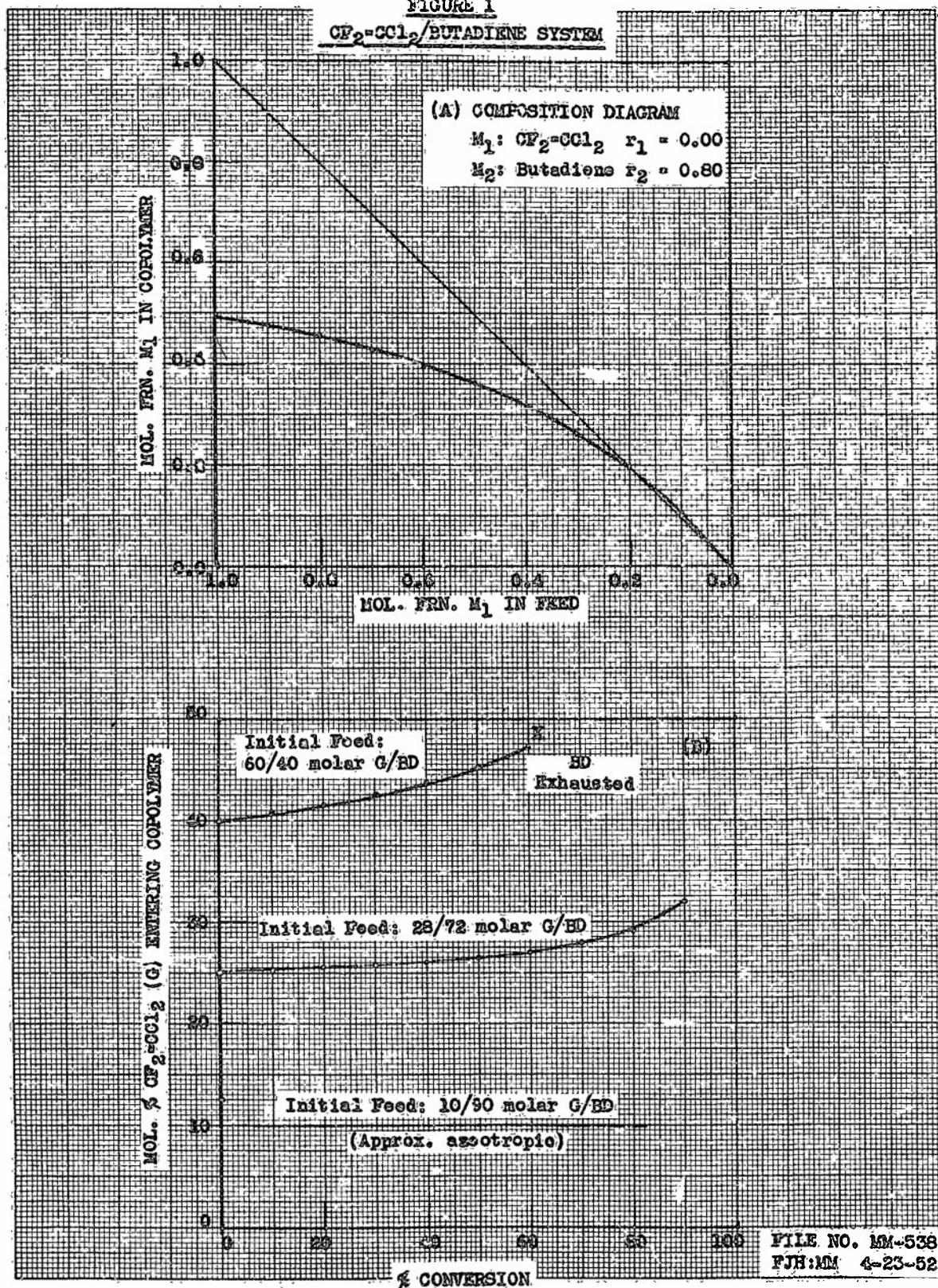
Trial runs have also been made at the 25/75 molar KF/I level, but conversion-composition data are not yet available.

4. Copolymers of $\text{CF}_2=\text{CCl}_2$ (G) and Butadiene (BD)

Monomer reactivity ratios have now been computed for $\text{CF}_2=\text{CCl}_2$ (M_1) and butadiene (M_2) on the basis of previously reported kinetic data. These parameters ($r_1 = 0.00 \pm 0.06$ and $r_2 = 0.80 \pm 0.05$) are similar to those already reported for the $\text{CF}_2=\text{CCl}_2$ /isoprene system. In both cases, the fact that r_1 equals zero indicates that the $-\text{CF}_2-\text{CCl}_2\cdot$ radical cannot add to $\text{CF}_2=\text{CCl}_2$ but must add to the diene, whereas the diene radical may add to either $\text{CF}_2=\text{CCl}_2$ or its own monomer but prefers to add to $\text{CF}_2=\text{CCl}_2$ by a ratio of 2.2/1 in the case of isoprene and 1.2/1 in the case of butadiene. An instantaneous copolymer-feed composition diagram based on the G/BD constants appears in Figure 1 (A). Up to about 20 mole % G, the curve follows closely the azeotropic line, so that in this region a given feed will produce a polymer of essentially the same composition from 0-100% conversion. Above 20 mole % G the deviation becomes more marked, but it seems likely that copolymers containing as much as 40 mole % G can be made adequately homogeneous if conversions are somewhat below 50% (cf. Figure 1 (B)).

Of the three G/BD rubbers slated for test, two (at the 10/90 and 25/75 molar levels) have been prepared homogeneously on a pound scale and tested. The third, at the 40/60 molar level, is now being synthesized. Polymerization data are tabulated below, and test results in Section III-C. All polymerizations were run in the Mutual recipe at 50°C. in a one-gallon autoclave.

FIGURE 1
CF₂-CCl₂/BUTADIENE SYSTEM



Code	Moles G/BD		% Conversion	Remarks
	Charged	Combined		
492-G	10/90	11/89	22	Too little rubber for test.
498-G	10/90	10/90	70	Sent to Depot for test
493-G	25/75	23/77	90	Sent to Depot for test
500-G	60/40	-	53	Conversion too high; heterogeneous powdery product. Run being repeated with conversion $\ll 50\%$

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

Adequately homogeneous G/I copolymers can be prepared from a single, initial charge of monomer if the conversion is limited to values calculable from the reactivity ratios (cf. the last quarterly report, RL-52-183, Figs. 3,4). At the 10/90 molar G/I level, the limiting conversion is 40%; at the 25/75 level, 50%; and at the 40/60 level (which is azeotropic), 100%. Two of these copolymers have been prepared on a pound scale and tested; the third, at the 10/90 level, is ready for shipment to the Depot. Data for the various products, polymerized in the Mutual recipe at 50°C., are summarized below:

Code	Moles G/I		% Conversion	Remarks
	Charged	Combined		
477-G	7/93	9/91	28	(To be blended for test as soon
499-G	7/93	12/89	38	(as 533-G is analyzed
533-G	7/93	-	26	(
478-G	21/79	23/77	51	Tests complete. Cf. Section III-C.
452-G	40/60	39/61	85	" " " " "

6. Copolymers of $CF_2=CFC1$ (KF) and n-Butyl Acrylate (BA)

A number of KF/BA copolymerizations have been carried out at 20°C. in a persulfate-bisulfite suspension recipe, which is capable of forming both homopolymers (and therefore a mixture of polymers) as well as a true copolymer. When these reactions are carried to high conversion a large proportion of KF can be incorporated in the product.

Code	Moles KF/BA		Wt. charged KF/BA	% Conversion	Hours Polymerization	Appearance
	Charged	Found				
218	75/25	78/22	73/27	72	16	Powder
219	50/50	46/54	48/52	72	16	Rubber
220	25/75	10/90	23/77	93	16	Tacky rubber

If the reactions are shortstopped early in the polymerization process, the yield of polymer is almost identical with the weight of BA charged, and the KF content of the polymers is very low.



Code	Moles KF/BA		Wt. KF/BA Charged	% Conversion	Hours Polymerization	Appearance
	Charged	Found				
506	70/30	6/94	68/33	32	2	Tacky rubber
507	60/40		58/42	42	2	Rubber
508	50/50		47/53	53	2	"
509	40/60		38/62	61	2	"
510	30/70	2/98	28/72	70	2	"

At first glance these results seem to indicate that the products containing large proportions of KF are mixtures of polybutylacrylate and KEL-F. But acetone extraction of one of these polymers (#219) which originally contained 46 mole per cent KF has led to a weight loss of 39% and an insoluble residue containing only 43.5 mole per cent KF. Since acetone is a solvent for polybutylacrylate but not for KEL-F, it now appears that the products are true copolymers, but of the "grafted" type; that is, polymers composed of an initially formed polybutylacrylate backbone on which polychlorotrifluoroethylene side chains grow during the latter stages of polymerization by a process of chain transfer. If this picture is correct, the resultant copolymers should be highly branched structures with a hydrocarbon backbone and fluorocarbon appendages. From this point of view alone they are worth evaluating as Arctic Rubbers.

7. Copolymers of $\text{CF}_2=\text{CFCl}$ (KF) and Chloroprene (CP)

Because chloroprene is far more reactive than $\text{CF}_2=\text{CFCl}$, it is virtually impossible to prepare copolymers, and especially homogeneous copolymers, with appreciable amounts of combined $\text{CF}_2=\text{CFCl}$. To date, the highest KF level attained has been 12 mole per cent. The first attempt to prepare a product with more than 12 mole % KF by charging all the KF initially and adding chloroprene slowly has failed because of the unreliability of the Milton-Roy Mini-Pump. Another run is planned in which chloroprene will be fed to the autoclave continuously through manually controlled rotameters.

8. Copolymers of $\text{CF}_2=\text{CF}-\text{CF}=\text{CF}_2$ (FBD)

FBD copolymerizes with butadiene (BD) and isoprene (I) to form rubberlike polymers suitable for evaluation as Arctic Rubbers. There is enough FBD monomer on hand now to permit the determination of the reactivity ratios for these systems and to begin the preparation of larger samples for test. Kinetic data gathered recently for the calculation of reactivity ratios is tabulated below:



Code	Moles FBD/BD		Moles FBD/I		% Conversion	Appearance
	Charged	Combined	Charged	Combined		
513	30/70	22/78	-	-	35	Rubber
514	50/50	32/68	-	-	61	Rubber
515	70/30	28/72	-	-	22	Tacky rubber
518	-	-	30/70	12/88	39	" "
517	-	-	50/50	-	Very low	-
516	-	-	70/30	34/66	21	Tacky rubber

9. Polymers and Copolymers of $\text{CH}_2=\text{CFC}_1$

The homopolymer and many of the copolymers of $\text{CH}_2=\text{CFC}_1$ are rubberlike. The preparation of a number of these systems has been reported in RL-52-183. Data are presented below for additional pairs and for a pound batch of homopolymer sent to the Depot for test. (cf. section III-C for evaluation).

Code	Moles Charged	Moles Found	% Conversion	Hours Polymerization	Remarks
<u>$\text{CH}_2=\text{CFC}_1$ only /1/</u>					
468-G	-	-	90	30	Tacky rubber, For test results, cf. section III-C.
<u>$\text{CF}_2=\text{CCl}_2/\text{CH}_2=\text{CFC}_1$ /1/</u>					
461	70/30	- /2/	2	26	Flaky solid
462	60/40	- /2/	6	26	Hard solid
463	40/60	11/89	14	26	" "
464	30/70	- /2/	12	26	Sl. tacky solid
<u>$\text{CF}_2=\text{CFC}_1/\text{CH}_2=\text{CFC}_1$ /1/</u>					
457	70/30	70/30	96	8	Hard, flaky solid
458	60/40	61/39	97	8	" " "
459	40/60	42/58	100	8	Tough, short rubber
460	30/70	31/69	82	8	Tough rubber
<u>Butadiene/$\text{CH}_2=\text{CFC}_1$ /3/</u>					
469	70/30	98/2	44	24	Rubber
470	50/50	95/5	5	24	Tacky solid
471	30/70	99/1	57	24	Rubber

- /1/ Persulfate-bisulfite suspension recipe at 20°C.
/2/ Analyses inaccurate because of retained impurities or loss of F and Cl.
/3/ Mutual recipe at 50°C.

10. Other Butadiene (BD) Copolymers

Copolymerization of all available fluorocarbon monomers with butadiene is being attempted because these products are invariably rubberlike and vulcanizable by ordinary sulfur-based recipes. Comparison of the copolymers at the same molar levels of fluorocarbon comonomer content should give some indication of the more satisfactory fluorocarbon structures for oil resistance and low temperature flexibility. All runs were carried out in the Mutual recipe at 50°C.

See table on next page.

Code	Moles Charged	Moles Found	% Conversion	Hours Polymerization	Remarks
<u>CF₂CF=CF-CF₂/BD</u>					
472	30/70	-	5	24	Sticky, semi-solid
473	50/50	-	zero	24	-
474	70/30	-	zero	24	-
<u>CF₂=CHCl/BD</u>					
484	25/75	-	zero	4	-
496	25/75	4/96	39	24	Sl. tacky rubber
482	50/50	-	zero	4	-
483	"	"	zero	8	-
495	"	2/98	5	24	Tacky rubber
480	75/25	-	zero	4	-
481	"	-	zero	8	-
494	"	-	zero	24	-
<u>CF₂=CHF/BD /1/</u>					
525	50/50	-	very low	5	-
526	30/70	-	very low	7	-
<u>CF₂=CF₂/BD</u>					
522	50/50	19/81	28	6	-
523	30/70	13/87	31	7	-
<u>cis CF₃-CH=CH-CF₃/BD</u>					
490	25/75		33	20	Rubber
491	"	trace	39	24	"
<u>CF₃-CH=CH-CF₃</u>					
488	50/50	1/99	14	20	"
489	"	2/98	16	24	"
486	75/25	-	very low	20	-
487	"	-	very low	24	-

/1/ Better yields of rubbery material have been observed in later runs where polymerization times have been increased to 24 hours. These products are still being dried and analyzed. Of all the exploratory systems tabulated here, the CF₂=CF₂ and CF₂=CHF copolymers look best from the standpoint of yield and comonomer content.

11. Miscellaneous Exploratory Copolymerization

<u>Code</u>	<u>Moles Charged</u>	<u>Moles Found</u>	<u>% Conversion</u>	<u>Hours Polymerization</u>	<u>Remarks</u>
<u>CF₂=CHCl only /1/</u>					
497	-	-	zero	24	-
<u>CF₂=CH₂/CF₂-CF=CF-CF₂ /2/</u>					
475	50/50	/3/	1	24	Dry, flaky solid

12. Alfin Polymerization

Alfin polybutadiene has been reported to be exceptionally solvent resistant as well as flexible at low temperatures. Earlier attempts to polymerize fluorocarbons such as CF₂=CFCl and CF₂=CF-CF=CF₂ with PP catalyst (cf. RL-52-183, p 13) were unsuccessful because of rapid side reactions leading to a brown methanol-soluble precipitate and probably NaF. More recent experiments with Alfin PP catalyst and 50/50 molar mixtures of CF₂=CFCl/BD and CF₂=CF-CF=CF₂/BD have been equally unsuccessful.

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

1. Copolymers of CF₂=CFCl (KF) and Butadiene (BD)

An adequately homogeneous member of this series has been tested at the 10/90 molar KF/BD level (cf. RL-52-183, section III-C, sample 323-G). Copolymers at the 25/75 and 40/60 levels will be ready for test shortly.

2. Copolymers of CF₂=CFCl (KF) and Isoprene (I)

An adequately homogeneous member of this series has also been tested at the 10/90 molar level. (cf. RL-52-183, section III-C, sample 316-G). Here, too, copolymers at the 25/75 and 40/60 levels are in process.

3. Copolymers of CF₂=CCl₂ (G) and Butadiene (BD)

Of the three copolymers in this series slated for test, two (at the 10/90 and 40/60 molar levels) have been tested. Polymerization recipes for these two rubbers (498-G and 493-G) appear in Table 1; compounding and curing recipes and test results in Table 2. Also included in Table 2 are results reported recently by M. Feldon and R. W. Laundrie of the Government Laboratories, University of Akron, and relayed to us by Mr. Griffis.

- /1/ Mutual Recipe at 50°C.
- /2/ Persulfate-bisulfite suspension recipe at 20°C.
- /3/ Analysis inaccurate because of retained impurities or loss of F.



TABLE I
POLYMERIZATION RECIPES

Run Number	Water, parts by weight	498-G	493-G	378-G	452-G	328	431-G	Blend
CF ₂ =CHCl (EF)	-	-	-	-	-	59.6	77.1	24.6
CF ₂ =CH ₂ (VF ₂)	-	-	-	-	-	40.4	22.9	25.4
CF ₂ =CCl ₂ (G)	21.4	44.8	34.2	56.6	-	-	-	-
CF ₂ =CHCl (Y)	-	-	-	-	-	-	-	-
Butadiene (BD)	78.6	55.2	65.8	43.4	-	-	-	-
Isoprene (I)	-	-	-	-	-	-	-	-
KORR Soap	5.	5.	5.	5.	-	-	-	-
K ₂ S ₂ O ₈ (NH ₄) ₂ S ₂ O ₃	0.3	0.3	0.1	0.15	-	-	-	-
Na ₂ S ₂ O ₅	-	-	-	-	-	1.0	1.0	1.0
FeSO ₄ · 7 H ₂ O	-	-	-	-	-	0.4	0.4	0.4
DM	0.47	0.33	0.2	0.2	0.2	0.1	0.2	0.2
pH	10.2	10.2	10.2	10.2	10.2	-	-	-
Temp., °C.	50	50	50	50	50	20	20	20
Time, Hours	18	17	6	6	18	18	23	3-8
% Conversion	70	90	51	85	85-90	85-90	68	8-15
Composition, Molar	10/90 G/BD	23/77 G/BD	23/77 G/I	39/61 G/I	52/48 EF/VF ₂	70/30 EF/VF ₂	37-52/63-48 EF/VF ₂	

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TABLE 2
EVALUATION OF CF₂-CCl₂/BUTADIENE RUBBERS

Kellogg Code No. QM Code No. Mole % CF ₂ -CCl ₂ Combined Polymerization Temp., °C. % Conversion	498-G		493-G		Govt. Lab. Data	
	1F 32	10.0	1F 31	23.0	5.8	7.2
	50	50	50	50	50	50
	70	70	90	90	73	74
						73
COMPOUNDING & CURING RECIPES						
Polymer	100	100	100	100	Not available.	
Philblack "O"	30	30	30	30	Presumably black stocks cured to optimum levels.	
Zinc Oxide	5	5	5	5		
Stearic Acid	1	1	1	1		
Altax	1	1	1	1		
Sulfur	2	2	2	2		
Min./300°F.	20	40	60	20	40	60
TEST RESULTS						
Tensile, psi	1400	1500	1700	2900	2950	2160
Elongation, %	260	200	205	390	260	370
Stress at 300%, psi	-	-	-	1950	-	-
Hardness, Shore A	67	70	71	67	70	-
% Vol. Swell, SR-6	175	152	140	157	142	205
% Vol. Swell, SR-10	123	109	100	108	83	135
Retraction Test						
Initial Elongation, %	200	150	150	250	150	-
TR-10 (Mins. °C.)	58	56	55	29	26	-
TR-30 " "	53	52	50	24	23	-
TR-50 " "	47	47	47	21	20	-
TR-70 " "	38	40	40	14	15	-
Gelman Stiffness						
T 100 (Mins. °C.)	59	59	59	33	30	66
T 10 " "	55	54	53	23	22	59
T 5 " "	53	52	50	21	19	54
T 2 " "	46	45	45	15	9	34

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4. Copolymers of $\text{CF}_2=\text{CCl}_2$ (G) and Isoprene (I)

Polymerization recipes for two of the three members of this series scheduled for test are recorded in Table 1 (samples 478-G and 452-G). Curing recipes and test results are summarized in Table 3. The last of this series to be evaluated, viz., 10/90 molar G/I, is now ready for shipment to the Depot.

5. Copolymers of $\text{CF}_2=\text{CFCl}$ (KF) and $\text{CF}_2=\text{CH}_2$ (VF_2)

Vulcanization of "saturated" rubbers, such as the KF/ VF_2 copolymers, which are normally soluble in acetone in the range 30-70 mole % VF_2 , has been attempted in a variety of recipes. The solubility data tabulated below indicate that oxide, peroxide-amine, and polysulfide cures are most effective in cross-linking KF/ VF_2 copolymers. Further studies are being conducted on benzoyl peroxide cures at various levels of concentration, time, and temperature, and also on the hydrated sodium metasilicate-calcium hydroxide cure developed by Minnesota Mining & Mfg. Co. for vulcanizing polyheptafluoro-dihydro butyl acrylate.

Copolymers of KF/ VF_2 are especially interesting because of their oil resistance. Volume swell of the raw gum after one day at 73°F. in SR-6 has averaged 10%, and in SR-10, 2%. Mechanical and low temperature properties cannot be evaluated until a vulcanization recipe is worked out. For polymerization recipes, consult Table 1, samples 328, 431-G, blend.

QM Code	Polymer	Method of Cure	Appearance after 48 hours in acetone at 73°F.
1F15	328 /1/	Red lead, TETA	Swollen
1F17	"	Red lead	Dispersed, partially dissolved
1F20	431-G /2/	NaS_x	Swollen
1F24	Blend /3/	Benzoyl peroxide	Dissolved
1F26	431-G	Benzoyl peroxide, TETA	Swollen
1F29	Blend	Hydrophobic Silica	Dispersed, partially dissolved

Incorporation of carbon black and silica into KF/ VF_2 has been facilitated considerably by the addition of 5-15 parts of KEL-FLO plasticizer. Although the unsoftened polymers band readily on warm rolls, they do not become plastic enough to take up fillers easily. This is especially true of the copolymers which differ markedly in composition from the 50/50 molar level where the rubberlike properties of the system are most pronounced. KEL-FLO oils blend with KF/ VF_2 copolymers in an unusual manner. The addition of a few drops of oil to the banded sheet causes the rubber to disintegrate

- /1/ Heterogeneous 50/50 molar KF/ VF_2 copolymer
- /2/ Homogeneous 70/30 " " "
- /3/ Mixture of small batches of KF/ VF_2 copolymers with an average composition of about 50/50 molar

TABLE 3.

EVALUATION OF $\text{CF}_2=\text{CCl}_2$ /ISOPRENE RUBBERS

Kellogg Code No.	478-G	452-G			
QM Code No.	1F 30	1F 23			
Mole % CP2=CCl2 combined	23	39			
Polymerization Temp., °C.	50	50			
% Conversion	51	85			
<u>COMPOUNDING & CURING RECIPES</u>					
Polymer	100	100			
Philtblack "Q"	30	30			
Zinc Oxide	5	5			
Stearic Acid	1	1			
Altex	1	1			
Sulfur	2	1.5			
Min./300°F.	20	40	20	40	60
<u>TEST RESULTS</u>					
Tensile, psi	3300	2700	2800	3060	3310
Elongation, %	460	290	260	390	320
Stress at 300%, psi	1700	-	-	2280	2990
Hardness, Shore A	66	71	72	71	73
% Vol. Swell, SR-6	182	158	149	217	161
% Vol. Swell, SR-10	133	111	101	124	106
<u>Retraction Test</u>					
Initial Elongation	250	200	150	250	200
TR-10 (Mins °C.)	28	25	24	15	14
TR-30 "	24	22	21	13	13
TR-50 "	21	19	18	9	7
TR-70 "	16	14	13	1	1
<u>Gehran Stiffness</u>					
T-100 (Mins °C.)	33	26	26	0	0
T-10 "	26	16	16	2	2
T-5 "	23	14	14	4	4
T-2 "	19	10	10	11	11

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into a fine crumb, which on continued milling soon re-bands into a continuous sheet. Although this effect is encountered after each addition of plasticizer up to the 15% level, KEL-FLO oils seem quite compatible with the rubber. There is no evidence of bleeding or surface tack, as is the case where hydrocarbon or silicone oils are used as plasticizers.

6. Homopolymer of $\text{CH}_2=\text{CFCl}$

This rubber, designated 468-G, processes poorly. At room temperature it is fairly tough and rubbery but at milling temperature it softens so much that it must be scraped from the rolls. This softening is not permanent but it does interfere with normal compounding procedures. Moreover, the polymer is difficult to vulcanize (e.g., benzoyl peroxide is ineffective) and its solvent resistance and low temperature flexibility are obviously poor. It will not be further characterized.

7. Copolymer of $\text{CF}_2=\text{CHCl}$ (Y) and Butadiene (BD)

This series has been prepared in these laboratories on an exploratory scale but not in batches large enough for test. Data are available, however, from the recent work of M. Feldon and R. W. Landrie of the Government Laboratories, University of Akron. Consult Table 4.

IV. Plans for Future Work

A. Preparation of homogeneous samples of $\text{CF}_2=\text{CFCl}$ /butadiene and $\text{CF}_2=\text{CFCl}$ /isoprene rubbers at the 25/75 and 40/60 molar levels; of $\text{CF}_2=\text{CFCl}/\text{CF}_2=\text{CH}_2$ rubber at the 70/30, 50/50, and 30/70 molar levels as soon as compounding and curing recipes are worked out; and of $\text{CF}_2=\text{CF}-\text{CF}=\text{CF}_2$ /butadiene rubber at the 10/90, 25/75, and 40/60 molar levels. Preparation of homogeneous samples of the remaining rubberlike systems at three comonomer levels wherever feasible.

B. Evaluation of the products for oil resistance, low temperature flexibility, and mechanical properties.

C. Computation of reactivity ratios for other rubberlike systems.

D. Continued production of $\text{CF}_2=\text{CF}-\text{CF}=\text{CF}_2$ from $\text{CF}_2=\text{CFCl}$.

E. Synthesis of other fluorinated dienes by thermal dimerization of olefins.

F. Exploratory copolymerization of additional monomer pairs as new monomers are made available by Drs. Tarrant and Syverson.


F. J. HONN


J. W. COPENHAVER



TABLE 4

PROPERTIES OF $\text{CF}_2=\text{CHCl}$ /BUTADIENE RUBBERS

Mole % $\text{CF}_2=\text{CHCl}$ combined	2.8
Polymerization Temp., °C.	50
% Conversion	68
Tensile, psi	1160
Elongation, %	290
% Vol. Swell, SR-6	205
% Vol. Swell, SR-10	157
<u>Gehman Stiffness</u>	
T 100 (Minus °C.)	74
T 10 "	68
T 5 "	64
T 2 "	42

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References to Original Records:

Notebook #135 (Bolstad), pp. 45-
" #149 (Honn), pp. 22-37
" #159 (Martin), pp. 1-127 incl.