

UNCLASSIFIED

AD 93212

Armed Services Technical Information Agency

Reproduced by

DOCUMENT SERVICE CENTER

KNOTT BUILDING, DAYTON, 2, OHIO

This document is the property of the United States Government. It is furnished for the duration of the contract and shall be returned when no longer required, or upon recall by ASTIA to the following address: Armed Services Technical Information Agency, Document Service Center, Knott Building, Dayton 2, Ohio.

NOTICE: WHEN GOVERNMENT OR OTHER DRAWINGS, SPECIFICATIONS OR OTHER DATA ARE USED FOR ANY PURPOSE OTHER THAN IN CONNECTION WITH A DEFINITELY RELATED GOVERNMENT PROCUREMENT OPERATION, THE U. S. GOVERNMENT THEREBY INCURS NO RESPONSIBILITY, NOR ANY OBLIGATION WHATSOEVER; AND THE FACT THAT THE GOVERNMENT MAY HAVE FORMULATED, FURNISHED, OR IN ANY WAY SUPPLIED THE SAID DRAWINGS, SPECIFICATIONS, OR OTHER DATA IS NOT TO BE REGARDED BY IMPLICATION OR OTHERWISE AS IN ANY MANNER LICENSING THE HOLDER OR ANY OTHER PERSON OR CORPORATION, OR CONVEYING ANY RIGHTS OR PERMISSION TO MANUFACTURE USE OR SELL ANY PATENTED INVENTION THAT MAY IN ANY WAY BE RELATED THERETO.

UNCLASSIFIED

Kellogg/AL 55-442

AD NO. 73212

ASTIA FILE COPY



FC

THE M.W.KELLOGG COMPANY

PROPERTY OF
OASD (R&D)

LIBRARY

Gallant

12-22

THE M. W. KELLOGG COMPANY
Petroleum & Chemical
Research Dept.
Jersey City, N. J.



Report No. RL-55-442

1

Petroleum and Chemical Research Department

PROGRESS REPORT

ARCTIC RUBBER

U.S. Army Contract DA-44-109-qm-1580
For the Period August - September 1955

December 1, 1955

Copy No.

15

Report RL-55-442

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



PROGRESS REPORT

Subject: Arctic Rubber - U.S. Army Contract DA-44-109-qm-1580
for the period August - September, 1955

Staff: J.W. Copenhaver, B.F. Landrum, E.S. Lo, A.N. Bolstad,
A.G. Davis, K.S. Tenney

Author: E.S. Lo

Period Covered: August - September, 1955

L.O. No. D-221; Job No. 5675

Previous Reports on this Subject:

RL-50-139	dated	November 1, 1950
RL-51-146	"	February 1, 1951
RL-51-156	"	April 1, 1951
RL-51-163	"	July 1, 1951
RL-51-174	"	October 1, 1951
RL-52-183	"	February 1, 1952
RL-52-195	"	May 1, 1952
RL-52-209	"	August 1, 1952
RL-52-248	"	October 1, 1952
RL-53-259	"	January 1, 1953
RL-53-274	"	April 1, 1953
RL-53-289	"	August 1, 1953
RL-54-329	"	July 29, 1954
RL-54-333	"	August 4, 1954 (Final Sum. Report- DA-44-109-qm-222)
RL-54-353	"	September 30, 1954
RL-54-367	"	December 1, 1954
RL-55-401	"	April 1, 1955
RL-55-422	"	July 1, 1955
RL-55-434	"	September 1, 1955


E. F. SCHWARZENBEK



CONTENTS

	<u>Page</u>
I. Introduction	4
A. Purpose of the Project	4
B. Research Program	4
C. Past Progress	5
II. Summary of Current Progress	5
III. Experimental Section	5
A. Total Monomers	5
B. Chemicals Received	6
C. Monomer Purification	6
D. Monomer Analysis	7
E. Polymer Preparation	7
1. Homopolymerization of Halogenated Propenes	8
2. Copolymers of $\text{CF}_2=\text{CHCH}=\text{CH}_2$	8
3. " " $\text{CF}_2=\text{CFCF}_2\text{Cl}$	8
4. " " $\text{CH}=\text{CH}_2$	8
	
5. Exploratory Terpolymers	8
F. Polymer Evaluation	8
IV. High Temperature Rubber Program	9
V. Plans for Future Work	9



I. Introduction

A. Purpose of the Project

The preparation of an oil and fuel-resistant rubber which retains its elastic properties over the range -70°F. to 160°F. ; the development of a rubber suitable for use at 500°F. ; the investigation and solution of the accompanying problems of monomer preparation, polymerization techniques, and polymer evaluation.

B. Research Program

To achieve this purpose, the Quartermaster Corps. has authorized the M. W. Kellogg Company to conduct a broad investigation of fluorine-containing polymers, which involves monomer synthesis, polymer preparation, and polymer testing.

Many of the monomers desired for investigation are unavailable commercially. In a few cases, these have been synthesized at M. W. Kellogg. Otherwise, the monomers or their precursors are prepared by Dr. Paul Tarrant of the University of Florida, and Dr. Aldrich Syverson of Ohio State University, or obtained on an exchange basis from the Minnesota Mining and Manufacturing Co. and the Polaroid Corporation.

Polymer preparation has received chief emphasis at M. W. Kellogg. The initial phase of this work is the exploratory copolymerization of each new monomer with selected monomers on hand. The results of screening tests on polymers so obtained are used in the selection of new monomer structures, more suitable monomer combinations and mole ratios, and better recipes and polymerization conditions.

Polymer systems exhibiting solvent swell resistance and low temperature characteristics comparable or superior to the chlorotrifluoroethylene-vinylidene fluoride copolymer originally developed on this project are investigated in greater detail. The more outstanding of these will be prepared in pound batches for a more thorough evaluation.

Polymer compounding, testing, and evaluation are conducted by Mr. C. B. Griffis, Angus Wilson, and staff at the Quartermaster Research and Development center at Natick, Mass. ASTM procedures D-471-52T (solvent swell), and D-1053-52T (Gehman Stiffness) are employed in screening the specimens obtained in the exploratory copolymerizations.



C. Past Progress

The copolymer systems investigated were 660, and the rubber-like systems, 332. (Refer to RL-55-434)

II. Summary of Current Progress

The number of monomers available for copolymerization is 84; the number of different polymer systems investigated, 686, and the number of rubberlike systems, 348.

The following monomers have been copolymerized with selected monomers now available: $\text{CF}_2=\text{CHCH}=\text{CH}_2$, $\text{CF}_2=\text{CFCH}_2\text{Cl}$ and vinyl pyridines.

The development of a new high temperature rubber $\text{CF}_2=\text{CF}_2/\text{CF}_2=\text{CFCH}_2\text{Cl}$ is in progress. The most promising copolymer systems remain to be $\text{CF}_2=\text{CH}_2/\text{CF}_3\text{CF}=\text{CF}_2$ and $\text{CF}_2=\text{CH}_2/\text{CF}_2=\text{CF}_2$.

III. Experimental Section

A. Total Monomers

Eighty-four monomers are now available for copolymerization study. (Refer to RL-55-434).



B. Chemicals Received

The following samples were received during the current period from the Ohio State University:

<u>Compound</u>	<u>b.p., °C.</u>	<u>Amount, g.</u>
$\text{CH}_2=\text{CHO CF}_2\text{CHClF}$	73-74/atm.	
$\text{CHCl}_2\text{CHCl OCF}_2\text{CHClF}$	86.5-87.5/30 mm.	
$\text{CH}_2\text{ClCHCl OCF}_2\text{CHClF}$	71-73/30 mm.	25
$\text{CH}_2\text{ClCH}_2\text{OCF}_2\text{CHClF}$	80-82/100 mm.	
$\text{CF}_3\text{CCl}_2\text{OCF}_2\text{CF}_2\text{Cl}$	90.5-90.7/741 mm.	
$\text{CH}_3\text{CF}=\text{CH}_2$	-22 to -21.5	1870

The following pyridines were purchased from Reilly Tar & Chemical Corp.:

2-vinyl pyridine (monomer 83)	79-82°/24 mm.	1 lb.
4- " " (" 84)	70-74°/15 mm.	1 lb.

C. Monomer Purification

The crude $\text{CF}_2=\text{CF CF}_2\text{Cl}$ (monomer 82) obtained by the decarboxylation of the sodium salt of C_4 telomer acid was fractionated. The major fraction (ca. 630 g.) boiled between 7-8.5°C., was collected. The mass spectrometric analysis indicates the monomer to be pure.

2 and 4 vinyl pyridine (monomers 83 and 84) were each fractionated under vacuum in order to remove inhibitor and impurities. The water-white purified monomers were stored under N_2 at -70°C.



D. Monomer Analysis

Mass spectrometric analyses of the three fluorinated butadienes received from Dr. Tarrant are as follows:

1. $\text{CF}_2=\text{CHCH}=\text{CH}_2$ (monomer 37)

	<u>Mole % (app.)</u>
$\text{CF}_2=\text{CHCH}=\text{CH}_2$	~ 70
$\text{C}_4\text{H}_5\text{F}_3$	~ 22
C_5H_{10}	~ 8
$\text{C}_4\text{H}_4\text{F}_4$	trace

2. $\text{CF}_2=\text{CFCH}=\text{CH}_2$ (monomer 56)

This sample appears to be pure. (Water vapor is the only impurity noted).

3. $\text{CF}_2=\text{CHCF}=\text{CH}_2$ (monomer 51)

	<u>Mole % (app.)</u>
$\text{CF}_2=\text{CHCF}=\text{CH}_2$	~ 85
$\text{C}_4\text{H}_4\text{F}_4$	~ 15

E. Polymer Preparation

Polymerization using 686 monomer systems has been attempted. The 26 new systems are: 1-82, 1-84, 2-10, 2-14-72, 2-84, 16-51-56, 16-51-74, 16-56-74, 21-32, 24-84, 37-42, 37-56, 37-72, 37-73, 37-74, 37-84, 51-82, 51-84, 56-82, 56-84, 74-82, 74-83, 74-84, 82, 82-84, and 84.

Of the systems investigated 348 can be considered rubberlike. The 16 new systems are listed below: 2-14-72, 16-51-56, 16-51-74, 16-56-74, 21-32, 24-84, 37-42, 37-56, 37-72, 37-73, 37-74, 51-82, 56-82, 74-82, 74-84, and 82-84.

Experimental data relative to the exploratory work carried out during the current period are set forth below:



1. Homopolymerization of Halogenated Propenes

A few attempts to homopolymerize $\text{CF}_3\text{CF}=\text{CF}_2$, $\text{CF}_3\text{CCl}=\text{CF}_2$ and $\text{CF}_2=\text{CFCF}_2\text{Cl}$ (monomers 14, 32 and 82 respectively) in both solution and emulsion recipes failed to give high molecular weight polymers (see runs 3007-8, 3021-22, 3053 and 3060, Table I). In some cases small amounts of yellow oil or powder were obtained.

2. Copolymers of $\text{CF}_2=\text{CHCH}=\text{CH}_2$ (Monomer 37)

This monomer gives a powdery homopolymer. It copolymerizes with fluorinated dienes and propenes to give short rubbery products in good yields (see runs 3009-11, 3023-30, 3036-43, Table I).

3. Copolymers of $\text{CF}_2=\text{CFCF}_2\text{Cl}$ (Monomer 82)

This monomer does not homopolymerize in the regular emulsion recipe (see run 3053, Table I). However, it copolymerized with various fluorinated dienes and ethylenes giving rubbery polymers in good yields (see runs 3054-58, Table I and Table III).

4. Copolymers of (Monomer 84)

This monomer gives a plastic homopolymer. It copolymerizes with fluorinated dienes, propenes and ethylenes giving colored resinous or stiff rubbery polymers (see runs 3012-23 and 3058, Table I) in good yields.

5. Exploratory Terpolymers

The Gehman T_5 value of the copolymer system $\text{CF}_2=\text{CHCF}=\text{CH}_2/\text{CF}_2=\text{CFCH}=\text{CH}_2$ was lowered six degrees by terpolymerizing the fluorinated dienes with a third monomer $\text{CH}_2=\text{CHOCHF}_2\text{CF}_2\text{H}$ (see run 1979, Table II). A series of terpolymers (see runs 3035, 3044-47, Table I) have been made during this current period. They will be sent to QM for evaluation as soon as the analytical data are complete.

F. Polymer Evaluation

During the past two months the data of the low temperature flexibility and fuel resistant properties of 25 rubbery polymers were received from the Quartermaster Corps (see Table II).



Among the 25 copolymers, the following five samples: 1-51, 14-51, 18-51, 51-56 and 51-73 (see runs 1959, 1971, 1977, 1984 and 1999, Table II) have volume swells and torsional moduli comparable with X-300 Elastomer, but have better Gehman T₅ values. Different molar ratios of these copolymer systems will be prepared.

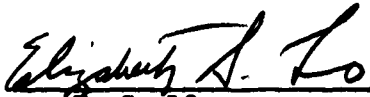
IV. High Temperature Rubber Program

The excellent thermal stability, fuel and acid resistance of the $\text{CF}_2=\text{CH}_2/\text{CF}_3\text{CF}=\text{CF}_2$ copolymers (see Table VIII, RL-55-434) have stimulated the copolymerization of other fluorinated propenes and butenes with vinylidene fluoride or other fluorinated ethylenes.

$\text{CF}_2=\text{CFCF}_2\text{Cl}$ (monomer 82) copolymerizes with $\text{CF}_2=\text{CH}_2$ to give rubbery products in good yield. The results of a few physical and chemical tests are summarized in Table III. Its resistance to "Esso Turbo Oil 15", the diester type hydraulic fluid, is poor. The tests for thermal stability and fuel resistance are now in progress, and will be reported when the data are available.

V. Plans for Future Work

1. Exploratory polymerizations of new monomers will continue with selected monomers, based upon past experiences.
2. Some theoretical work on the development of new monomer structures and methods of monomer synthesis is planned.
3. The reactivity ratios of $\text{CF}_2=\text{CHCF}=\text{CH}_2$ and $\text{CF}_2=\text{CFCH}=\text{CH}_2$ will be determined.
4. One pound batches of the appropriate molar ratios of the following systems: $\text{CF}_2=\text{CHCF}=\text{CH}_2/\text{CF}_2=\text{CFCH}=\text{CH}_2$, $\text{CF}_2=\text{CH}_2/\text{CF}_3\text{CF}=\text{CF}_2$ and $\text{CF}_2=\text{CH}_2/\text{CF}_2=\text{CF}_2$ will be prepared for evaluation of cured samples.
5. Preparation of ether-linked fluorocarbon polymers will be attempted.


E. S. LO

References to Original Records

Notebook No. 339, pp. 167-189 incl.
" " 308, pp. 176-180 "

TABLE I
EXPLORATORY POLYMERIZATION

No.	Comonomers	Mole Ratio Charged /10/	Polymerization Conditions			% Conv.	Appearance of Sample /11/	
			Time hrs.	Temp. °C.	Recipe		Before Milling	After Milling
2097	CF ₂ -CFC1	100	22	↑	/1/	41	Powder	-
2098	"	100	22	↑	/2/	23	Powder	-
2099	"	100	22	↑	/3/	80	Powder	-
3000	CH ₂ =CFCH=CH ₂	100	22	↑	/1/	96	Short Rubber	Short Rubber
3001	CH ₂ =CFCH=CH ₂ /CF ₂ =CFCH=CH ₂	50/50	22	↑	/1/	84	"	"
3002	CF ₃ CCl=CH ₂ /CH ₂ =CFCH=CH ₂	50/50	72	↑	/3/	45	"	"
3003	" /CH ₂ =C(CH ₃)=CH ₂	50/50	72	↑	/3/	28	Soft Resin	-
3004	" /CH ₂ =CFC1	50/50	72	↑	/3/	1	Low Mol.Wt. Polymer	-
3007	CF ₃ CF=CF ₂	100	68	50	/4/	0.3	Powder	-
3021	"	100	48	↑	/5/	1	Powder	-
3008	CF ₃ CCl=CF ₂	100	68	↑	/4/	0.5	Powder	-
3022	"	100	48	↑	/5/	zero	-	-
3009	CF ₂ =CHCH=CH ₂ /CH ₂ =CHOCF ₂ CF ₂ H	80/20	68	↑	/3/	54	Short rubber	Short rubber
3010	" /CF ₃ CF=CF ₂	70/30	68	↑	/3/	44	Powder	-
3011	" /CF ₃ CCl=CF ₂	70/30	68	↑	/3/	40	Rubbery powder	Short rubber
3023	" /CF ₃ CH=CH ₂	70/30	25	↑	/6/	58	Short rubber	Smooth short rubber
3024	" /CF ₃ CH=CF ₂	70/30	25	↑	/6/	48	Rubbery powder	Smooth short rubber
3025	CF ₂ =CHCH=CH ₂ /C1(CF ₃ CF ₂) ₂ CF ₂ CO ₂ - CH ₂ CH=CH ₂	90/10	25	↑	/6/	60	"	"
3026	" /CF ₂ =CHCF=CH ₂	90/10	70	25	/6/	68	"	Very short rubber
3027	" /	80/20	70	25	/6/	62	Short rubber	Tough short rubber
3028	" /	50/50	70	25	/6/	92	"	"
3029	" /	25/75	70	25	/6/	90	Tough short rubber	Rubbery sheet
3030	CF ₂ =CHCH=CH ₂	100	70	25	/3/	40	Powder	-
3012	 / CF ₂ =CHCH=CH ₂	50/50	20	40	/3/	50	Yellow flakes	-
3013	" /CF ₂ CHCF=CH ₂	50/50	20	40	/3/	26	Brown flakes	-
3014	" /CF ₂ =CFCH=CH ₂	50/50	20	40	/3/	83	Brown flakes	-
3015	" /CH ₂ =CHC(CF ₃)=CH ₂	50/50	20	40	/3/	23	Soft yellow rubber	-
3016	 homopolymer	100/0	24	25	/3/	64	Yellow plastic	-
3017	" /CH ₂ =CF ₂	40/60	24	25	/3/	40	Lt. yellow plastic	-
3018	" /CF ₂ =CFC1	50/50	24	25	/3/	80	Black flakes	-
3019	" /CF ₂ =CF ₂	45/65	24	25	/3/	43	Yellow chips	-
3020	" /CH ₂ =CHC(CF ₃)=CH ₂	5/95	60	25	/3/	92	Soft rubber	Weak crepe sheet
3021	" /	15/85	60	25	/3/	92	Short stiff rubber	Stiff crepe sheet
3023	" /	5/95	60	25	/3/	92	Soft rubber	Crepe sheet
3022	 CH ₂ =CH ₂ /CH ₂ =CHC=CH ₂	5/95	60	25	/3/	96	Soft sticky rubber	Weak sticky sheet
3036	CF ₂ =CHCH=CH ₂ /CF ₂ =C(CH ₃)CH=CH ₂	75/25	40	25-40	/3/	8	Soft rubber	Short snappy rubber
3037	" /CF ₂ =CFCH=CH ₂	90/10	40	25-40	/3/	51	Short stiff rubber	Tough stiff sheet
3038	" /	80/20	40	25-40	/3/	64	Short stiff rubber	Tough stiff sheet
3039	" /	50/50	40	25-40	/3/	70	"	Tough flexible sheet
3040	" /	40/60	40	25-40	/3/	80	Short tough rubber	Tough stiff sheet
3041	" /CH ₂ =C(CF ₃)CH=CH ₂	75-25	40	25-40	/3/	51	Soft rubber	Soft, translucent rubber
3042	" /	50/50	40	25-40	/3/	65	Soft rubber	Soft, snappy rubber
3043	" /	25/75	40	25-40	/3/	75	Soft, weak rubber	Soft, translucent rubber
3034	CF ₂ =CH ₂ /CF ₃ CF=CF ₂	95/5	18-1/2	50	/6/	80	Rubbery powder	Plastic
3048	CF ₂ =CFH/CF ₃ -C=CF ₂	70/30	24	50	/6/	47	Sl. rubbery particles	Flexible plastic sheet
3049	" /	60/40	24	50	/6/	60	Sl. rubbery crumbs	"
3052	CF ₂ =CH ₂ /CH ₃ CH=CH ₂	70/30	22	50	/6/	zero	-	-
3053	CF ₂ =CFCF ₂ Cl	100/0	24	50	/6/	zero	-	-
3054	CF ₂ =CFCF ₂ Cl/CF ₂ =CHCF=CH ₂	30/70	24	50	/6/	28	Rubber	Snappy rubber
3055	" /CF ₂ =CFCH=CH ₂	30/70	24	50	/6/	58	Hard short rubber	Very short rubber
3056	" /CH ₂ =C(CH ₃)=CH ₂	30/70	24	50	/6/	51	Snappy rubber	Soft rubber
3057	" /CF ₂ =CFC1	30/70	24	50	/6/	34	White powder	-
3058	" /CH=CH ₂	30/70	24	50	/7/	50	Brown short rubber	-
3060	CF ₃ CCl=CF ₂	100/0	66	25	/8/	low	Yellow oil	-
Terpolymers								
3035	CF ₂ =CH ₂ /CF ₃ CF=CF ₂ /CH ₂ =CHOCF ₂ CF ₂ H	80/10/10	18-1/2	50	/6/	76	Very short rubber	Tough leathery sheet
3044	" / " /	60/36/4	17-1/2	50	/6/	73	Soft rubber	Soft rubber
3045	CF ₂ =CHCF=CH ₂ /CH ₂ =C(CH ₃)CH=CH ₂ /CH ₂ =CHCH=CH ₂	50/40/10	24	50	/9/	82	Soft rubber	Crepe rubber
3046	" /CF ₂ =CFCH=CH ₂ /CH ₂ =CHCH=CH ₂	40/50/10	24	50	/6/	90	Sl. short rubber	Crepe short rubber
3047	CF ₂ =CFCH=CH ₂ /CH ₂ =C(CH ₃)CH=CH ₂ /	50/40/10	24	50	/6/	92	Tough rubber	Crepe short rubber

- /1/ Recipe: Water 200; Perfluorooctanoic acid 0.75; K₂S₂O₈ 1; H₂O₂ 0.4; monomer 100; n-hexane 1.32; pH of polymerization medium 7.
- /2/ Recipe: Same as recipe /1/, except n-hexane 2.64.
- /3/ Recipe: Same as recipe /1/, except no n-hexane.
- /4/ Recipe: Acetone 200; benzoyl peroxide 1; monomer 100.
- /5/ Recipe: Tetrahydrofuran 200; benzoyl peroxide 1; monomer 100.
- /6/ Recipe: Water 200; perfluorooctanoic acid 1; K₂S₂O₈ 1; H₂O₂-7H₂O 4; monomer 100.
- /7/ Recipe: Water 200; H₂O₂ 5; K₂S₂O₈ 1; H₂O₂ 0.4; pH of polymerization medium 7.
- /8/ Recipe: CF₃CCl=CF₂ 8.5 g.; Freon 11A 5 cc.; H₂O 0.12 g. (as 45 cc.); Sealed in stainless steel bomb and stood for 66 hrs.
- /9/ Recipe: Water 200; Perfluorooctanoic acid 1; K₂S₂O₈ 1; H₂O₂ 0.4; pH of polymerization medium 7.
- /10/ Recipe: The combined molar ratios of these polymers will be reported when the analytical data are available.
- /11/ Recipe: All the samples banded on mill at 25°C., except runs 3024, 3025 and 3026 which banded at 80°C.

THE M. W. KELLOGG COMPANY
Petroleum & Chemical
Research Dept.
Jersey City, N. J.

Report No. RT-55-1442



TABLE II
ARCTIC RUBBER SCREENING TEST

Run No.	Monomer Structure Concylmer	Molar Ratio		% Conv.	Appearance of Sample		Gelatin Stiffness (°C.)					Vol. of Increase Type II Film	Torsional Modulus (psi)	Molding Temp. (°F.) / 2	Sample Condition After Molding
		Charged	Combined		Before Milling	After Milling //	T ₂	T ₅	T ₁₀	T ₁₀₀					
1999	CF ₂ =CFCl/CF ₂ =CHCF=CH ₂	50/50	13/87	49	Rubber	-	-16.4	-24.0	-27.6	-37.6	15	372	30/250; 250, 200	Firm & rubbery	
1971	CF ₃ CF=CF ₂ /CF ₂ =CHCF=CH ₂	25/75	Loss of F	43	"	Short rubber	-12.9	-18.8	-23.3	-37.8	9	372	30/250; 30/110	Stiff & rubbery	
1972	" / CH ₂ =CCH=CH ₂ CF ₃	25/75	Loss of F	64	"	Soft rubber	+19.8	-1.0	-11.7	-24.7	0e1	5	Cold mold	Soft & gummy	
1973	CH ₂ =CHCN/ "	25/75	20/80	95	"	Slightly tough rubber	+9.0	-7.8	-15.3	-28.9	27	136	250	Firm & plastic	
1959	CF ₂ =CHCl/CF ₂ =CHCF=CH ₂	10/90	1.5/98.5	62	"	Slightly short rubber	-11.3	-20.6	-23.8	-33.0	12	222	250	Stiff & rubbery	
1960	CF ₂ =CHCl/ "	25/75	2/98	50	"	"	-15.4	-21.1	-24.7	-36.1	10	589	250	Stiff & plastic	
1961	CF ₃ CCl=CH ₂ / "	10/90	11/89	66	Snappy rubber	Crape rubbery sheet	+4.2	-10.3	-14.3	-24.9	15	24	30/250	Soft & rubbery	
2001	CF ₂ =CHCF=CH ₂ /CF ₂ =CFCH=CH ₂	95/5	-	87	Short rubber	Soft rubber	-14.1	-24.1	-27.1	-42.9	7	988	250	Stiff & plastic	
2000	" / "	90/10	-	84	"	"	-15.1	-24.3	-27.3	-39.6	11	637	250	Stiff & plastic	
1984	" / "	80/20	-	70	Rubber	Crape rubbery sheet	-15.2	-23.5	-25.5	-33.8	20	191	250	Firm & rubbery	
1983	" / "	75/25	-	84	Rubber	"	-20.4	-24.4	-27.1	-37.0	24	120	250	"	
1982	" / "	60/40	-	78	"	"	-6.7	-23.9	-24.5	-34.3	37	71	250	"	
1986	" / "	50/50	-	76	"	Tough crape rubbery sheet	-17.4	-26.9	-29.1	-39.8	40	133	250	Stiff & rubbery	
1985	" / "	40/60	-	80	"	"	-15.3	-27.3	-29.5	-39.7	37	504	250	"	
1976	" / Cl(CF ₂ CFCl) ₂ CF ₂ CO ₂ CH ₂ CH=CH ₂	79/21	95.5/4.5	35	"	Rubbery crape sheet	-8.0	-14.3	-17.0	-26.3	67	135	250	"	
1977	" / "	90/10	97.5/2.5	49	"	"	-11.5	-20.0	-23.1	-33.8	4	464	250	"	
2002	CF ₂ =CFCH=CH ₂ /CH ₂ =CCH=CH ₂ CF ₃	80/20	69/31 / 3/	99	"	Soft rubber	-26.8	-30.7	-32.8	-41.7	80	126	250	Firm & rubbery	
2003	" / "	75/25	65/35 / 3/	91	"	"	-23.8	-29.3	-32.0	-40.7	85	130	250	"	
2004	" / "	60/40	15/85 / 3/	99	"	"	-2.8	-19.3	-24.5	-33.4	96	34	250	Soft & rubbery	
Terpolymers															
1978	CF ₂ =CHCF=CH ₂ /CF ₂ =CFCH=CH ₂ /CF ₃ CCl=CH ₂	50/40/10	-	72	Rubber	Rubbery crape sheet	-15.3	-22.5	-23.9	-31.8	43	62	250	Soft & rubbery	
1979	" / " / CH ₂ =CHOCF ₂ CF ₂ H	50/40/10	-	56	Soft rubber	Short rubber	-26.7	-32.5	-34.2	-39.6	46	289	250	Stiff & rubbery	
1980	" / " / Cl(CF ₂ CFCl) ₂ CF ₂ CO ₂ - CH ₂ CH=CH ₂	"	-	60	Rubber	Slightly tough rubber	-15.6	-22.3	-25.6	-34.3	40	72	250	"	
1981	" / " / CH ₂ =CCH=CH ₂ CF ₃	50/40/10	-	78	Rubber	Rubbery crape sheet	-20.9	-25.4	-27.3	-37.0	48	40	250	Firm & rubbery	
1964	" / CH ₂ =CCH=CH ₂ /CF ₂ =CHCl CF ₃	40/40/20	-	74	Soft rubber	Soft rubber	-20.5	-27.2	-29.2	-35.0	83	263	30/200, 250	Soft & rubbery	
1963	" / " / CF ₃ CCl=CH ₂	40/50/10	-	62	hubber	hubbery crape sheet	-17.0	-23.4	-25.9	-33.9	92	196	20/110	Soft & gummy	

1/ All the samples banded on mill at 25°C.
2/ Mold times unless otherwise noted are 10 minutes. Longer periods are totals of individual 10 minute periods.
3/ Reason for unexpected analytical results not determined.

TABLE III
COPOLYMERS OF $CF_2=CH_2/CF_2=CFCF_2Cl$

Run No.	3050	3051	3052	3061
Molar Ratio of $CF_2=CH_2/CF_2=CFCF_2Cl$:				
Charged	70/30	60/40	50/50	25/75
Combined	75.5/24.5	68.4/31.6	64.8/35.2	55.2/44.8
Polymerisation Conditions				
Time, hrs.	22-1/2	22	69	23
Recipe	/1/	/1/	/1/	/1/
% Conversion	88	77.5	66.7	34
Appearance of Sample:				
Before milling	White Rubber	White Rubber	White Rubber	Sl. hard Rubber
After milling /2/	Crepe rubbery sheet	Crepe rubbery sheet	Crepe rubbery sheet	Crepe rubbery sheet
Torsional Modulus, psi	180	169	168	178
Gehman values, °C. /3/				
T ₂	+3	+9	+11	+13
T ₅	-3	+3	+5	+10
T ₁₀	-6	0	+3	+9
T ₁₀₀	-16	-9	-6	+4
Resilience (Bayshore)	7	10	5	-
"Esso Turbo Oil 15"				
18 hrs. at 77°F. wt. % increase	35	19	47.8	-
1 hr. at 600°F.		Partially soluble		-

/1/ Recipe: Water 150; C₈ Telomer Acid 0.75; Na₂HPO₄·7H₂O 3;
K₂S₂O₈ 0.75; Monomer 50-60

/2/ All samples banded on mill at 25°C.

/3/ All samples were molded at 300°F.

FILE NO. MM-1403
ESL:MM 9-30-55