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# THE M. W. KELLOGG COMPANY

Petroleum and Chemical Research Department

# PROGRESS REPORT

# ARCTIC RUBBER

U.S. Army Contract DA-44-109-qm-1580
For the Period August-December, 1953

July 29, 1954

Copy No. 15 Report RL-54-329

Petroleum and Chemical Research Department
Laboratory Division, Jersey City, New Jersey

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

Report No. RL-54-329



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Subject: Artic Rubber - U.S. Army Contract DA-44-109-qm-1580
For the Period August-December 1953

Staff: J.W. Copenhaver, F.J. Honn, A.N. Bolstad, J.M. Hoyt, E.S. Lo, A.G. Davis

Authors: F.J. Honn and E.S. Lo

Period Covered: August 1, 1953 to December 31, 1953

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 |

Approved:

E.F. Schwarzenbek

E.F. SCHWARZENBEK

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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°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 fluoroolefins and fluoro-chloro-olefins among themselves and with olefinic and diolefinic hydrocarbons.

Monomer synthesis at Kellogg has been restricted to products arising from the thermal dimerization of $CF_2=CFCl$, namely, $CF_2=CF-CF=CF_2$, $CF_2-CF=CF-CF_2$, and $CF_3-CF=CF_2$. Where feasible, the preparation of other monomers, e.g., $CF_2=CF_2$ and $CF_2=CHF$, has also been undertaken in these laboratories. For the most part, however, 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 and Manufacturing Company and Polaroid Corporation.

Polymer preparation has proceeded through four phases: (a) exploratory copolymerization of new monomer pairs; (b) determination of the relative reactivities of monomers successfully copolymerized into elastomers; (c) synthesis of pound batches of these elastomers in several comonomer ratios for evaluation; and (d) pilot plant production of one elastomer (Kellogg "X-300 Rubber") which is of interest to the Quartermaster not so much as an Arctic Rubber but more precisely as an acid-and oxidant-resistant elastomer for protective suits, gloves, and boots. A new phase, initiated during the past quarter, involves the testing of small samples of unvulcanized, rubbery polymers, obtained from exploratory work, for oil-resistance and low temperature flexibility. This testing program is being carried on at the Quartermaster Depot at Philadelphia.

All the rubbery products obtained in the exploratory work have been tested for oil-and fuel-resistance and low temperature flexibility.

Small samples (1-2 g.) of the raw polymer are subjected to the Gehman torsional stiffness test and the solvent swell test in ASTM Reference Fuel No. 2.

Polymer compounding, testing, and evaluation has been carried forward most capably by Mr. C.B. Griffis and his staff at the Philadelphia Quartermaster Depot. The development of military uses for X-300 has been the joint responsibility of Mr. Griffis and the Kellogg Applications Laboratory.

C. Past Progress

1. Quarters completed as of August 1, 1953: 12
2. Monomers available for copolymerization: 56
   a. Purchased 28
   b. Minnesota Mining & Mfg. Co. 3
   c. Dr. Tarrant 12
   d. Dr. Syverson 7
   e. M.W. Kellogg Co. 6
3. Copolymer systems investigated: 357
   (where the numbers refer to the monomers listed in section III-A, below):

1-2, 1-2-4, 1-2-8, 1-2-9, 1-2-11, 1-2-14, 1-2-21, 1-2-22, 1-2-23, 1-2-24, 1-2-29, 1-2-30, 1-2-31, 1-2-32, 1-2-35, 1-2-40, 1-2-45, 1-2-45a, 1-2-45b, 1-2-52, 1-2-53, 1-3, 1-4, 1-5, 1-6, 1-7, 1-8, 1-9, 1-12, 1-13, 1-14, 1-16, 1-17, 1-18, 1-19, 1-20, 1-21, 1-22, 1-23, 1-27, 1-28, 1-30, 1-35, 1-36, 1-37, 1-39, 1-40, 1-41, 1-42, 1-43, 1-44, 1-45a, 1-47, 1-48, 1-49, 1-54, 2-3, 2-4, 2-6, 2-8, 2-9, 2-12, 2-13, 2-15, 2-16, 2-17, 2-18, 2-19, 2-21, 2-22, 2-23, 2-24, 2-28, 2-29, 2-30, 2-32, 2-34, 2-35, 2-37, 2-38, 2-39, 2-40, 2-42, 2-43, 2-44, 3-4, 3-7, 3-9, 3-14, 3-18, 3-19, 3-20, 3-21, 3-22, 3-23, 3-24, 3-25, 3-30, 3-32, 3-44, 4, 4-5, 4-6, 4-8, 4-9, 4-10, 4-11, 4-12, 4-14, 4-15, 4-17, 4-19, 4-20, 4-21, 4-22, 4-24, 4-25, 4-27, 4-28, 4-29, 4-32, 4-35, 4-37, 4-39, 4-40, 4-41, 4-42, 4-43, 4-44, 4-45a, 4-47, 4-48, 4-49, 5-9, 5-44, 6-8, 6-9, 6-30, 6-37, 6-41, 7-35, 7-37, 7-41, 7-42, 7-43, 7-44, 8-13, 8-24, 8-35, 8-37, 8-40, 8-41, 8-42, 8-44, 9, 9-12, 9-13, 9-14, 9-16, 9-17, 9-18, 9-22, 9-23, 9-27, 9-28, 9-35, 9-36, 9-37, 9-39, 9-40, 9-41, 9-42, 9-43, 9-44, 9-45a, 9-47, 9-48, 9-49, 10-14, 10-28, 11-41, 11-42, 11-44, 12-24, 12-35, 12-37, 12-40, 12-41, 12-42, 12-44, 13-17, 13-18, 14-22, 14-28, 14-35, 14-37, 14-40, 14-41, 14-42, 14-43, 14-44, 16-18, 16-24, 16-35, 16-37, 16-41, 16-44, 17-18, 17-24, 17-35, 17-37, 17-41, 17-44, 18-21, 19-22, 19-28, 19-35, 20-22, 20-28, 20-35, 20-37, 20-40, 20-41, 20-42, 21, 21-22, 21-28, 21-30, 21-35, 21-37, 21-40, 21-41, 21-42, 21-43, 21-44, 21-45a, 21-47, 21-48, 22, 22-24, 22-28, 22-30, 22-32, 22-35, 22-36, 22-37, 22-38, 22-40, 22-41, 22-42, 22-43, 22-44, 23-28, 23-35, 23-37, 23-40, 23-41, 23-42, 23-44, 24-28, 24-31, 24-35, 24-36, 24-37, 24-39, 24-40, 24-41, 24-42, 24-43, 24-44, 24-45a, 24-47, 24-48, 24-49, 25-28, 25-35, 25-37, 25-40, 25-41, 25-42, 25-44, 27, 27-37, 27-38, 27-41, 27-35, 27-40, 27-42, 27-44, 28, 28-30, 28-32, 29-35, 29-37, 29-40, 29-42, 29-43, 30, 30-35, 30-37, 30-40, 30-41, 30-42, 30-44, 31-35, 31-42, 32-35, 32-37, 32-40, 32-41, 32-42, 32-43, 32-44, 33-35, 33-37, 33-40, 33-41, 33-42, 33-44, 33-37, 34-41, 34-42, 34-44, 35, 35-36, 35-37, 35-40, 35-41, 35-42, 35-43, 35-44, 37, 37-38, 37-39, 37-40, 37-43, 38, 38-40, 38-41, 38-42, 38-44, 39, 39-40, 39-41, 39-42, 39-43, 39-44, 40, 40-42, 41, 41-42, 41-43, 41-44, 42, 42-44, 43 and 43-44.

4. Rubberlike systems: 145

1-2, 1-2-14, 1-2-21, 1-2-22, 1-2-23, 1-2-24, 1-2-29, 1-2-32, 1-2-34, 1-2-40, 1-2-45a, 1-2-45b, 1-3, 1-5, 1-13, 1-17, 1-22, 1-28, 1-37, 1-41, 1-43, 1-44, 1-45a, 1-47, 1-48, 1-49, 2-4, 2-6, 2-13, 2-17, 2-22, 2-24, 2-28, 2-30, 2-32, 2-34, 2-44, 3-4, 3-9, 3-14, 3-18, 3-19, 3-21, 3-22, 3-23, 3-24, 3-44, 4-5, 4-28, 4-37, 4-41, 4-43, 4-44, 4-47, 4-48, 4-49, 5-9, 5-44, 6-41, 7-41, 7-43, 7-44, 8-37, 8-41, 8-44, 9-12, 9-13, 9-17, 9-28, 9-37, 9-41, 9-43, 9-44, 12-28, 12-37, 12-41, 13-18, 14-22, 14-28, 14-43, 14-44, 16-41, 16-44, 17-18, 17-24, 17-35, 17-41, 17-44, 20-22, 21, 21-22, 21-28, 21-41, 21-43, 21-44, 21-45a, 22, 22-24, 22-28, 22-32, 22-41, 22-42, 22-43, 22-44, 23-44, 24-28, 24-37, 24-41, 24-43, 24-44, 24-45a, 24-47, 24-48, 24-49, 27-28, 27-37, 27-41, 27-44, 28, 28-30, 28-32, 28-35, 30-37, 30-44, 31-35, 32-43, 32-44, 33-44, 35-37, 35-40, 35-43, 35-44, 37, 37-38, 37-41, 37-43, 38-44, 39-41, 39-44, 41, 41-43, 41-44, 42-44, 43, and 43-44.

5. Monomer reactivity ratios determined: 9

| System | $M_1$ | $M_2$ | $r_1$ | $r_2$ |
|---|---|---|---|---|
| 1-2 | $CF_2$=CFCl | $CF_2$=$CH_2$ | 0.52 | 0.17 |
| 1-3 | $CF_2$=CFCl | Butadiene | 0.0 | 1.35 |
| 1-5 | $CF_2$=CFCl | Isoprene | 0.1 | 1.41 |
| 3-4 | $CF_2$=CF-CF=$CF_2$ | Butadiene | 0.0 | 1.35 |
| 3-9 | $CF_2$=$CCl_2$ | Butadiene | 0.0 | 0.80 |
| 3-24 | $CF_2$=$CF_2$ | Butadiene | 0.0 | 1.75 |
| 4-5 | $CF_2$=CF-CF=$CF_2$ | Isoprene | 0.0 | 0.75 |
| 5-9 | $CF_2$=$CCl_2$ | Isoprene | 0.0 | 0.45 |
| 22-24 | $CH_2$=CFCl | $CF_2$=$CF_2$ | 2.8 | 0.1 |

6 Status of rubberlike systems:

a. Most promising, in pilot plant and undergoing extensive tests: 1-2.

b. Evaluated and rejected as unpromising: 1-3, 1-5, 1-17, 3-4, 3-9, 3-24, 4-5, 5-9, 21, 22, 28, 37, and 41.

c. Promising, to be tested. 1-2-14, 1-2-21, 1-2-22, 1-2-24, 1-2-29, 1-2-32, 1-2-40, 1-13, 1-22, 1-28, 1-37, 1-41, 2-22, 2-24, 2-30, 2-32, 2-34, 2-44, 4-28, 4-37, 4-41, 6-41, 7-41, 8-37, 8-41, 9-13, 9-28, 9-37, 9-41, 12-28, 12-37, 12-41, 16-41, 16-44, 17-24, 17-35, 21-22, 21-41, 22-24, 22-41, 24-28, 24-41, 27-37, 27-41, 28-32, 28-35, 30-37, 35-37, 37-38, 37-41, 39-41, 41-43, 41-44, 43, and 43-44.

d. Interesting, but better recipes needed to increase yields or to increase proportion of fluorocarbon combined: 2-4, 2-28, 3-14, 3-18, 3-19, 3-21, 3-23, 4-43, 4-44, 4-47, 4-48, 7-43, 7-44, 14-22, 14-28, 14-43, 14-44, 21-28, 21-43, 21-44, 22-28, 22-32, 22-42, 22-43, 22-44, 24-48, 27-28, 28-30, 31-35, 32-43, 32-44, 35-40, 35-44, 38-44, and 42-44.

e. Relatively uninteresting (low F content or negligible amount of third monomer in 1-2-X systems): 1-2-23, 1-2-34, 1-2-45a, 1-2-45b, 1-43, 1-44, 1-45a, 1-47, 1-48, 1-49, 2-6, 2-13, 2-17, 3-22, 3-44, 4-49, 5-44, 8-44, 9-12, 9-17, 9-43, 9-44, 13-18, 17-18, 17-41, 17-44, 20-22, 21-45a, 23-44, 24-37, 24-43, 24-44, 24-45a, 24-47, 24-49, 27-44, 30-44, 33-44, 35-43, 37-43, and 39-44.

## II. Summary of Current Progress

During this period all work performed is covered by Quartermaster Contract DA-44-109-qm-1580, which supersedes the previous contract DA-44-109-qm-222.

The number of monomers available for copolymerization has been 56, the number of copolymer systems investigated 376, and the number of rubberlike systems 157.

A group of raw, unvulcanized polymers have been screened for oil-resistance (ASTM Reference Fuel II) and low temperature flexibility (Gehman stiffness). None of the systems screened is any better balanced than 30/70 molar $CF_2=CFCl/CH_2=CF_2$, which is still not good enough to qualify as an oil-resistant, Arctic Rubber. The copolymers of

$$CF_2=C(CH_3)-CH=CH_2$$

and $CF_3CH=CHCH=CH_2$ with other halogenated monomers offer no obvious advantage.

The screening of monomer $CF_2=CHC(CH_3)=CH_2$ is generally complete with the monomers currently available. Among its many rubbery copolymers the

$$CF_2=CHC(CH_3)=CH_2/CF_2=CFC_6H_5$$

system appears most interesting and will be investigated further.

Monomer $CF_2=C(CH_3)-CF=CH_2$ has been screened for copolymerization behavior with many available monomers. Most of the copolymers obtained were rubbery. However, only the homopolymer was sent for screening; the other rubberlike materials were not available in sufficient quantity.

Thirty-six other rubbery samples of homopolymers, copolymers and terpolymers have been submitted to the Quartermaster Depot as raw polymers to be screened for oil resistance and low temperature flexibility. Tests on these products are incomplete.

## III. Experimental Section

### A. Monomer Synthesis

Fifty-six 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. $\underline{CF_2-CF=CF-CF_2}$
8. $CH_2=CHCl$
9. $CF_2=CCl_2$
10. $CH_3-CH=CH_2$
11. $C_6H_5-CH=CH_2$
12. $CH_2=CCl_2$
13. $CH_2=CCl-CH=CH_2$
14. $CF_2-CF=CF_2$
15. $CF_2=CF-CN$
16. $CH_2=CH-CN$
17. $CH_2=CH-CO_2-C_4H_9(n)$

17a. $CH_2=CH-CO_2-CH_3$

18. $CF_2=CHCl$
19. $CF_3-CCl=CCl-CF_3$
20. $CF_3-C\equiv C-CF_3$
21. $CF_2=CFH$
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. $CH_2=C\diagup^{CF_3}$
28. $CH_2=CF-\overset{CH_3}{C}H=CH_2$
29. $CF_2=C\begin{matrix}\diagup CF_3\\ \diagdown CF_3\end{matrix}$
30. $CF_2=CFBr$
31. $CH_2=CH_2$
32. $CF_2=CCl-CF_3$
33. $CF_3-C(CH_3)=CH-COOH$
34. $CH_2=CH-\overset{O}{\overset{\|}{C}}-NH_2$
35. $CF_3-CH=CH_2$
36. $CH_2=CHBr$
37. $CF_2=CH-CH=CH_2$
38. $CF_3-CCl=CCl_2$
39. $CF_3-CCl=CH_2$
40. $CH_2=CHF$
41. $CF_2=CH-C(CH_3)=CH_2$
42. $CF_3-CH=CF_2$
43. $CF_3-CH=CH-CH=CH_2$

| | | | |
|---|---|---|---|
| 44. | $CF_2=C(CH_3)-CH=CH_2$ | 49. | $CH_2=CH-O-CH_2CH(CH_3)_2$ |
| 45. | $CH_2=CH-O-CO-CH_3$ | 50. | $CF_2=C(CH_3)-CF=CH_2$ |
| 45a. | $CH_2=CH-O-CO-CH_2-CH_2-CH_3$ | 51. | $CF_2=CH-CF=CH_2$ |
| 45b. | $CH_2=CH-O-CO-CH_2Cl$ | 52. | <u>trans</u> - $C_2H_5O_2C-CH=CH-CO_2C_2H_5$ |
| 46. | $C_6H_5-CH=CH-CO_2CH_3$ | 53. | <u>cis</u> - $C_2H_5O_2C-CH=CH-CO_2C_2H_5$ |
| 47. | $CH_2=CH-O-CH_2-CH_3$ | 54. | $CH_2=CH-Si(OC_2H_5)_3$ |
| 48. | $CH_2=CH-O-CH_2-CH_2-Cl$ | 55. | $C_6H_5CF=CF_2$ |

One hundred grams of $\alpha,\beta,\beta$-trifluorostyrene were obtained from Polaroid Corporation on an exchange basis (see monomers shipped, below).

Additional supplies of four monomers already on the list were obtained. Two were received from Dr. Syverson of the Ohio State University and two were prepared in this laboratory from precursors synthesized by Dr. Tarrant.

| No. | Monomer | Amount | Source |
|---|---|---|---|
| # 21 | $CF_2=CHF$ | 4 lbs. | Ohio State University |
| # 22 | $CH_2=CFCl$ | 5 lbs. | " " " |
| # 41 | $CF_2=CHC(CH_3)=CH_2$ | 12 g. | The M.W. Kellogg Co. |
| # 50 | $CF_2=C(CH_3)-CF=CH_2$ | 25 g. | " " " " " |

<u>Monomers Shipped</u>

The following monomers were sent to Dr. Elkin Blout, Polaroid Corporation, Cambridge, Massachusetts at the request of Dr. Montermoso:

| | |
|---|---|
| 100 g. | $CF_2=CFCF=CF_2$ |
| 100 g. | $(CF_3)_2C=CF_2$ |
| 100 g. | $CF_3CF=CF_2$ |

One pound of $CF_2=CFCl$ was shipped to L.M. Peterson, Wright Air Development Center, Wright Patterson Air Force Base, Ohio.

Fifty grams of $CF_2=CF_e$ were delivered in person to Lt. Rogers of Wright Air Development Center, who visited the laboratory on December 22.

B. Monomer Analysis

The following monomers have been analyzed during this period with the mass spectrometer:

1. $CH_2{=}CFCl$ (Ohio State University) Cylinder #3

   Approximate amounts of impurities:

| | |
|---|---|
| $CH_2{=}CCl_2$ | 0.1 mole % |
| $CF_2{=}CH_2$ | 0.2 |
| $C_3H_6$ | 0.1 |

2. $CH_2{=}CFCH{=}CH_2$ (Ohio State University)

   No impurities of higher molecular weight. Presence or absence of $CH{\equiv}CCH{=}CH_2$ cannot be established.

3. $CF_2{=}CH\overset{CH_3}{C}{=}CH_2$

   Approximate amounts of impurities:

| | |
|---|---|
| $C_5H_7F_3$ | 0.4 mole % |
| $C_4H_5F$ | 0.4 |
| $C_4H_8$ | 0.4 |

4. $CF_2{=}\overset{CH_3}{C}{-}CF{=}CH_2$

   Approximate amounts of impurities

| | | |
|---|---|---|
| $C_5H_6F_4$ | 4.1 mole % | One or both of these compounds contains-$C_2H_5$ group. |
| $C_5H_7F_3$ | 0.5 | |
| HCl | 0.4 | |

Vibrational Spectrum Measurements of Fluorinated Monomers

N.B.S. Report No. 2856 on the vibrational spectrum of bromotrifluoroethylene was received as per agreement with Dr. D.E. Mann to whom we supplied this chemical. This report also contains an abridged table of ideal-gas thermodynamic functions and infra-red spectra of $CF_2{=}CFBr$. An earlier paper, (J. Chem. Phys. 21 1949 (1953)) contains the spectra and thermodynamic functions for chlorotrifluoroethylene. More complete tables for $CF_2{=}CF_2$, $CF_2{=}CFCl$, $CF_2{=}CFBr$, and $CCl_2{=}CCl_2$ were also sent.

C. Polymer Preparation

Copolymerizations have now been attempted with 376 systems (where the numbers refer to the monomers listed in section III-A, above):

1-2, 1-2-4, 1-2-8, 1-2-9, 1-2-11, 1-2-14, 1-2-21, 1-2-22, 1-2-23, 1-2-24, 1-2-29, 1-2-30, 1-2-31, 1-2-32, 1-2-35, 1-2-40, 1-2-45, 1-2-45a, 1-2-45b, 1-2-52, 1-2-53, 1-3, 1-4, 1-5, 1-6, 1-7, 1-8, 1-9, 1-12, 1-13, 1-14, 1-16, 1-17, 1-18, 1-19, 1-20, 1-21, 1-22, 1-23, 1-27, 1-28, 1-30, 1-35, 1-36, 1-37, 1-39, 1-40, 1-41, 1-42, 1-43, 1-44, 1-45a, 1-47, 1-48, 1-49, 1-50, 1-54, 2-3, 2-4, 2-6, 2-8, 2-9, 2-12, 2-13, 2-15, 2-16, 2-17, 2-18, 2-19, 2-21, 2-22, 2-23, 2-24, 2-28, 2-29, 2-30, 2-32, 2-34, 2-35, 2-37, 2-38, 2-39, 2-40, 2-42, 2-43, 2-44, 3-4, 3-7, 3-9, 3-14, 3-18, 3-19, 3-20, 3-21, 3-22, 3-23, 3-24, 3-25, 3-30, 3-32, 3-41, 3-44, 3-50, 4, 4-5, 4-6, 4-8, 4-9, 4-10, 4-11, 4-12, 4-14, 4-15, 4-17, 4-19, 4-20, 4-21, 4-22, 4-24, 4-25, 4-27, 4-28, 4-29, 4-32, 4-35, 4-37, 4-39, 4-40, 4-41, 4-42, 4-43, 4-44, 4-45a, 4-47, 4-48, 4-49, 4-50, 5-9, 5-44, 6-8, 6-9, 6-30, 6-37, 6-41, 7-35, 7-37, 7-41, 7-42, 7-43, 7-44, 8-13, 8-24, 8-35, 8-37, 8-40, 8-41, 8-42, 8-44, 8-50, 9, 9-12, 9-13, 9-14, 9-16, 9-17, 9-18, 9-22, 9-23, 9-27, 9-28, 9-35, 9-36, 9-37, 9-39, 9-40, 9-41, 9-42, 9-43, 9-44, 9-45a, 9-47, 9-48, 9-49, 9-50, 10-14, 10-28, 11-41, 11-42, 11-44, 12-24, 12-35, 12-37, 12-40, 12-41, 12-42, 12-44, 12-50, 13-17, 13-18, 14-22, 14-28, 14-35, 14-37, 14-40, 14-41, 14-42, 14-43, 14-44, 14-50, 16-18, 16-24, 16-35, 16-37, 16-41, 16-44, 17-18, 17-24, 17-35, 17-37, 17-41, 17-44, 17-50, 18-21, 19-22, 19-28, 19-35, 20-22, 20-28, 20-35, 20-37, 20-40, 20-41, 20-42, 21, 21-22, 21-28, 21-30, 21-35, 21-37, 21-40, 21-41, 21-42, 21-43, 21-44, 21-45a, 21-47, 21-48, 22, 22-24, 22-28, 22-30, 22-32, 22-35, 22-36, 22-37, 22-38, 22-40, 22-41, 22-42, 22-43, 22-44, 22-50, 23-28, 23-35, 23-37, 23-40, 23-41, 23-42, 23-44, 24-28, 24-31, 24-35, 24-36, 24-37, 24-39, 24-40, 24-41, 24-42, 24-43, 24-44, 24-45a, 24-47, 24-48, 24-49, 25-28, 25-35, 25-37, 25-40, 25-41, 25-42, 25-44, 27, 27-37, 27-38, 27-41, 27-35 27-37, 27-40, 27-42, 27-44, 28, 28-30, 28-32, 28-41, 29-35, 29-37, 29-40, 29-42, 29-43, 30, 30-35, 30-37, 30-40, 30-41, 30-42, 30-44, 31-35, 31-42, 32-35, 32-37, 32-40, 32-41, 32-42, 32-43, 32-44, 32-50, 33-35, 33-37, 33-40, 33-41, 33-42, 33-44, 34-41, 34-42, 34-44, 34-50, 35, 35-36, 35-37, 35-40 35-41, 35-42, 35-43, 35-44, 37, 37-38, 37-39, 37-40, 37-43, 38, 38-40, 38-41, 38-42, 38-44, 39, 39-40, 39-41, 39-42, 39-43, 39-44, 40, 40-42, 41, 41-42, 41-43, 41-44, 41-45a, 41-47, 41-49, 41-55, 42, 42-44, 43, 43-44, and 50

Of these systems, 157 can be considered rubberlike:

1-2, 1-2-14, 1-2-21, 1-2-22, 1-2-23, 1-2-24, 1-2-29, 1-2-32, 1-2-34, 1-2-40, 1-2-45a, 1-2-45b, 1-3, 1-5, 1-13, 1-17, 1-22, 1-28, 1-37, 1-41, 1-43, 1-44, 1-45a, 1-47, 1-48, 1-49, 1-50, 2-4, 2-6, 2-13, 2-17 2-22, 2-24, 2-28, 2-30, 2-32, 2-34, 2-44, 3-4, 3-9, 3-14, 3-18, 3-19, 3-21, 3-22, 3-23, 3-24, 3-41, 3-44, 4-5, 4-28, 4-37, 4-41, 4-43, 4-44, 4-47, 4-48, 4-49, 4-50, 5-9, 5-44, 6-41, 7-41, 7-43, 7-44, 8-37, 8-41, 8-44, 8-50, 9-12, 9-13, 9-17 9-28, 9-37, 9-41, 9-43, 9-44, 9-50, 12-28, 12-37, 12-41, 12-50, 13-18, 14-22, 14-28, 14-43, 14-44, 14-50, 16-41, 16-44, 17-18, 17-24, 17-35, 17-41, 17-44, 20-22, 21, 21-22, 21-28, 21-41, 21-43, 21-44, 21-45a, 22, 22-24, 22-28, 22-32, 22-41, 22-42, 22-43, 22-44, 22-50, 23-44, 24-28, 24-37, 24-41, 24-43, 24-44, 24-45a, 24-47, 24-48, 24-49, 27-28, 27-37, 27-41, 27-44, 28, 28-30, 28-32, 28-35, 28-41, 30-37, 30-44, 31-35, 32-43, 32-44, 32-50, 33-44, 35-37, 35-40, 35-43, 35-44, 37, 37-38, 37-41, 37-43, 38-44, 39-41 39-44, 41, 41-43, 41-44, 41-55, 42-44, 43, 43-44, and 50.

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

1. Copolymers of $CF_2{=}CH{-}\overset{CH_3}{C}{=}CH_2$

A series of copolymerizations were run with $CF_2{=}CH\overset{CH_3}{C}{=}CH_2$ to complete the screening of this monomer with all monomers currently available. This diene forms a rubbery homopolymer and many of its copolymers are rubbery. The

$$CF_2{=}CH\overset{CH_3}{C}{=}CH_2/C_6H_5CF{=}CF_2$$

copolymer (see run 1421, Table 1) appears particularly interesting and will be investigated further.

2. Copolymers of $CF_2{=}\overset{CH_3}{C}{-}CF{=}CH_2$

The homopolymer of this diene is rubbery, and so are many of its copolymers. These rubbers, however, are generally rather short.

Both homopolymers and copolymers of $CF_2{=}CH\overset{CH_3}{C}{=}CH_2$ and $CF_2{=}\overset{CH_3}{C}{-}CF{=}CH_2$ are described in Table 1.

3. Copolymers of $CF_2{=}CFCl/CH_2{=}CFCl$

Three levels of the $CF_2{=}CFCl/CH_2{=}CFCl$ system were prepared for screening. (See runs 1432, 1433, and 1434 in Table 1).

4. Perfluorobutadiene Polymerization

This monomer copolymerizes competitively with various monomers listed in Section III-A. It does not give a high molecular weight homopolymer with the regular emulsion recipes. However, a high molecular polyperfluorobutadiene was obtained by Miller & Bridgman of Cornell University by polymerizing the monomer in presence of oxygen or peroxide under very high pressure. The product was described as exhibiting a number of the general characteristics of a rubber. It is with this aspect that the $CF_2{=}CFCF{=}CF_2$ system has been and will be investigated further.

A few polymerizations of $CF_2{=}CFCF{=}CF_2$ are described in Table 2. It appears that in the oxygen catalyzed polymerization the presence of a small amount of $SO_2$ tends to increase the rate of polymerization, while a large amount of $SO_2$ inhibits polymerization. (See runs 1410 and 1411 in Table 2 ). The small amount of sulfur incorporated in the polymer probably accounts for its partial solubility in acetone.

D. Polymer Evaluation

1. Screening of Raw Polymers

In an attempt to evaluate rapidly the large number of copolymers prepared in our exploratory work, it was decided after consultation with Mr. Griffis of the QM Depot, that small unvulcanized samples of each copolymer should be subjected to the Gehman stiffness and volume swell test (see progress report, RL-53-274, p. 16). It is hoped that this procedure will enable us to arrive at a useful comparison of the low temperature and oil-resistance properties of all rubbery materials prepared to date in a minimum of time.

It is difficult to predict how reliable a comparison of this type will be, based as it is on raw polymers and not on the final, cured and compounded rubber. However, it appears to be a realistic approach and should serve as a guide to future work.

The results of the screening tests of a group of rubbery polymers have been received. These results are reported in Table 3. The Gehman stiffness data are expressed in terms of $T_2$, $T_5$, $T_{10}$ and $T_{100}$ temperatures, i.e., the temperatures at which the specimen is 2, 5, 10 and 100 times stiffer than at 25°C. The per cent volume increase was determined in ASTM Reference Fuel No. 2, which consists of isooctane (60% by vol.), benzene (5%), toluene (20%) and xylene (15%). These swelling values are subject to some error because of the small samples used. The Gehman test samples were molded from raw polymer. The molding temperature and the appearance of the raw polymers after molding are also described in Table 3.

Some preliminary conclusions from the screening tests

None of the systems screened is better balanced than 30/70 molar $CF_2$=CFCl/$CF_2$=$CH_2$ with regard to low temperature properties and resistance to ASTM type II fuel. The 65/35 molar $CF_2$=$CF_2$/$CH_2$=CFCl copolymer (1347) is rather stiff at room temperature, but it does not stiffen further at lower temperatures as markedly as X-300, its $T_{100}$ being -55° as compared with -26.5 for X-300 (see RL-53-251, p. 7). This system will be investigated further in an attempt to find a more rubbery comonomer ratio with as good or better Gehman and volume swell properties. So far, copolymerization of the fluorinated dienes with halogenated monomers offers no obvious advantage (see Figures 1, 2, and 3), but some of the copolymer systems (notably those with a volume swell $<$100% will be screened further at other comonomer ratios.

2. Raw Polymers Shipped for Screening

A list of rubbery copolymers shown in Table 4 were shipped to the QM Depot for evaluation during the current period.

A 50 g. sample of $CF_2{=}CH\overset{CH_3}{\overset{|}{C}}{=}CH_2$ homopolymer (D-122-1396) was also sent to QM Depot for compounding and curing and further evaluation as an Arctic Rubber. This polymer was one of the more promising rubbers turned up in the screening test. However, in an Altax-sulfur recipe, the polymer charred to a brittle mass after 60 minutes at 300°F.

## IV. Final Report - Plans for Future Work under New Contract

A final report covering all work done under DA-44-109-qm-222 from July 1, 1950 through July 31, 1953 has been completed.

A new contract with the same objectives as the old, has been negotiated with QM . Under this new contract, the plans for future work include:

1. Improving X-300 polymer (better low temperature properties).
2. Screening the more promising rubbers noted in the "past progress" section by means of Gehman stiffness and volume swell measurements on pressed sheets of the raw polymers.
3. Exploratory polymerization of new monomer pairs and development of better recipes where needed to improve yields.
4. High pressure polymerization of unreactive fluoro-olefins.

Elizabeth S Lo
E. S. LO

F. J. Honn
F. J. HONN

References to original Records:

Notebook #234 (A.N. Bolstad) pp. 54-78, incl.
Notebook #226 (J.M. Hoyt), pp. 113-119
Notebook #269 (E.S. Lo), pp. 1-19, incl.

TABLE 1

EXPLORATORY COPOLYMERIZATION

| No. | Comonomer (X) | Moles $CF_2=C(CH_3)C=CH_2$ / X: Charged | Moles $CF_2=C(CH_3)C=CH_2$ / X: Combined | Hrs. of Polymerization | Recipe | % Conversion | Appearance |
|---|---|---|---|---|---|---|---|
| | | | Principal Monomer = $CF_2=C(CH_3)C=CH_2$ | | | | |
| 1416 | $CH_2=CFCH=CH_2$ | 50/50 | 25.23 % F found (Too low for either homopolymer) | 21 | (1) | 42 | Short rubber (turned black) |
| 1417 | $CH_2=CHCH=CH_2$ | 50/50 | .... | 21 | (1) | trace | Short rubber (turned black) |
| 1418 | $CH_2=CHOC_2H_5$ | 50/50 | 98/2 | 4 | (1) | 24 | Tacky paste |
| 1419 | none | 100 | ---- | 4 | (1) | 100 | Rubber |
| 1420 | $CH_2=CHOC_4H_9$ (iso) | 50/50 | 98/2 | 21 | (1) | 18 | Tacky paste |
| 1421 | $C_6H_5CF=CF_2$ | 50/50 | 34.68% F found (Too low for either homopolymer) | 4 | (1) | 93 | Snappy rubber |
| | | | Principal Monomer $CF_2=C(CH_3)CF=CH_2$ | | | | |
| 1437 | $CF_2=CFCl$ | 50/50 | 87/13 | [illegible] | [illegible] | [illegible] | Slow rubber |
| 1438 | $CF_2=CFCF=CF_2$ | 50/50 | 44.[illegible]% F found (Too low for either homopolymer) | [illegible] | [illegible] | [illegible] | Short rubber |
| 1439 | $CH_2=CHCl$ | 50/50 | [illegible] | [illegible] | [illegible] | [illegible] | Slow rubber |
| 1440 | $CF_2=CCl_2$ | 50/50 | 82/18 | [illegible] | [illegible] | [illegible] | Short rubber |
| 1441 | $CH_2=CCl_2$ | 50/50 | [illegible] | [illegible] | [illegible] | [illegible] | Short rubber |
| 1442 | $CF_3CF=CF_2$ | 50/50 | 43.[illegible]% F found (Too low for either homopolymer) | [illegible] | [illegible] | [illegible] | Slow rubber |
| 1443 | $CH_2=CHCOOC_4H_9$ [X] | 50/50 | [illegible] | [illegible] | [illegible] | [illegible] | Sticky gum |
| 1444 | $CH_2=CFCl$ | 50/50 | 88/12 | [illegible] | [illegible] | [illegible] | Tough slow rubber |
| 1446 | $CH_2=CHC(=O)NH_2$ | 50/50 | [illegible] | [illegible] | [illegible] | [illegible] | Tough plastic |
| 1447 | $CH_2=CHCH=CH_2$ | 50/50 | [illegible] | [illegible] | [illegible] | [illegible] | Soft gum |
| 1448 | $CF_3CCl=CF_2$ | 50/50 | 97/3 | [illegible] | [illegible] | [illegible] | Short rubber |
| 1449 | none | 100 | ---- | [illegible] | [illegible] | [illegible] | Rubber |
| 1422 | none | 100 | ---- | [illegible] | [illegible] | 18 | Short rubber |
| | | | Monomers $CF_2=CFCl$, $CH_2=CFCl$ | | | | |
| | Pressure, psig | | | | | Yield | |
| 1432 | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] g. | Low molecular weight rubber |
| 1433 | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] g. | Low molecular weight rubber |
| 1434 | 50 | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] g. | Stiff rubber |

(1) Recipe (pts by wt.) = Water 200; [illegible]COONH$_4$ [illegible]; $K_2S_2O_8$ [illegible]; [illegible]; Borax [illegible]; Tertiary Dodecyl Mercaptan 0.1; Monomers 100; temp. 50°C.
(2) Recipe (pts by wt.) = Same as (1) except Water 180 and Conc. Buffer solution 20.
(3) Recipe (pts by wt.) = Same as (1) except no Tertiary dodecyl Mercaptan used and emulsifier = 3 pts. KORR and 3 pts $C_7F_{15}COONH_4$.
(4) Recipe (pts by wt.) = Water 200; Monomers at constant vapor pressure; $K_2S_2O_8$ 1.0; $Na_2S_2O_5$ 0.4; Temperature 50°C.

FILE NO: D-3995
ESL:MMB 8/2/54

TABLE 2

PERFLUOROBUTADIENE POLYMERIZATION

| No. | Polymerization Conditions | Analysis | % Conversion | Appearance |
|---|---|---|---|---|
| 1410 | $O_2$ initiator /1/ | 68% F., 0.53% S (96/4 molar $CF_2=CFCF=CF_2/SO_2$) | 56 | tacky paste (partially acetone soluble) |
| 1411 | $O_2$ initiator /2/ | ---- | 3 | tacky paste (partially acetone soluble) |
| 1412 | $H_2O_2$ initiator /3/ | ---- | trace | tacky paste |

/1/ Oxygen bubbled thru liquid at reflux temperature for 18 hours ( 1.2 parts $SO_2$ to 100 parts by weight $CF_2=CFCF=CF_2$). A 50% conversion was obtained in 30 hours previously with no $SO_2$.

/2/ Oxygen bubbled thru refluxing solution (75 parts $SO_2$ to 100 parts by weight $CF_2=CFCF=CF_2$) for 18 hours.

/3/ Recipe (parts by weight): Monomer 100; 30% $H_2O_2$-50; Fluoro-chloro monoacid Tumbled 115 hours at 20°C.

TABLE 3

SCREENING TESTS ON EXPLORATORY POLYMERS

| Sample No. | Mold Temp. °F. | Mole % Ratio | Composition | Gehman Stiffness °C. $T_2$ | $T_5$ | $T_{10}$ | $T_{100}$ | % Volume Increase in Fluid II | Sample Cond. after Molding |
|---|---|---|---|---|---|---|---|---|---|
| 1221 | 300 | 75/25 | $CF_2$=C($CH_3$)-CH=$CH_2$/$CF_2$=CFCl (DFI) | -2 | -8.5 | -11.5 | -16 | 99 | soft rubber. |
| 1222 | 300 | 48/52 | DFI/$CH_2$=CH-CH=$CH_2$ | -22.5 | -32 | -38.5 | -45.5 | 338 | soft rubber. |
| 1226 | 300 | 82/18 | DFI/$CH_2$=CHCl | +5 | -2.5 | -6 | -11 | 92 | soft rubber. |
| 1227 | 300 | 50/50 | DFI/$CH_2$=C($CH_3$)-CH=$CH_2$ | -16 | -21 | -25 | -38 | Gel | soft tacky |
| 1229 | 300 | 88/12 | DFI/$CH_2$=CHCN | +24 | +22 | +20.5 | +15.5 | 4 | hard stiff |
| 1232 | 150 | 81/19 | DFI/$CF_3$-CCl=$CH_2$ | +19.5 | + 9 | + 5.5 | - 2 | Gel | soft flex. |
| 1233 | 300 | ? | DFI/$CF_2$=CH-C($CH_3$)=$CH_2$ | + 3.5 | - 9.5 | -13.5 | -22.5 | 84 | soft flex. |
| 1234 | 300 | 82/18 | DFI/$CF_3$-CH=$CH_2$ | 0 | - 2 | - 4.5 | -19 | 81 | soft flex. |
| 1273 | 300 | 78/22 | DFI/$CF_2$=$CCl_2$ | + 2 | - 2.5 | - 4.5 | - 6.5 | 146 | soft flex. |
| 1211 | 300 | 90/10 | DFI/$CH_2$=$CF_2$ | - 7.5 | -17.5 | -20 | -28 | 88 | soft flex. |
| 1212 | 300 | 90/10 | DFI/$CF_2$=$CF_2$ | +10 | - 2 | - 9 | -17.5 | 86 | soft flex. |
| 1213 | 300 | 90/10 | DFI/$CF_2$=CFH | - 1 | -14 | -15 | -22 | 90 | soft flex. |
| 1243 | 300 | 82/18 | $CF_3$-CH=CH-CH=$CH_2$/$CF_2$=CF-CF=$CF_2$ | ** | | | | Gel | firm flex. |
| 1246 | 300 | 81/19 | $CF_3$-CH=CH-CH=$CH_2$/$CH_2$=CFCl | +19.5 | +18 | +17.5 | +14 | Gel | stiff plas. |
| 1249 | 300 | 90/10 | $CF_3$-CH=CH-CH=$CH_2$/$CF_2$=CH C($CH_3$)=$CH_2$ | + 4.5 | + 2 | 0 | - 3.5 | 107 | soft flex. |
| 1251 | 300 | 90/10 | $CF_3$-CH=CH CH=$CH_2$/$CF_2$=CH-CH=$CH_2$ | 0 | - 4 | - 5 | -10 | 62 | soft flex. |
| 1252 | 300 | 86/14 | $CF_3$-CH=CH-CH=$CH_2$/$CF_3$-CH=$CH_2$ | +19 | +17.5 | +17 | +14 | Gel | stiff plas. |
| 1253 | 300 | 100/0 | $CF_3$-CH=CH-CH=$CH_2$ only | +19 | +17 | +16 | +13 | 55 | stiff plas. |
| 1254 | 300 | 97/3 | $CF_3$-CH=CH-CH=$CH_2$/$CF_2$=($CH_3$)-CH=$CH_2$ | +18 | +14 | +11.5 | + 5 | Gel | soft flex. |
| 1216 | 300 | 86/14 | $CF_3$-CH=CH-CH=$CH_2$/$CF_2$=$CF_2$ | +22 | +19.5 | +18.5 | +14 | Gel | soft plas. |
| 1277 | 300 | 18/82 | $CF_2$=$CF_2$/n-butyl acrylate | +10 | - 9 | -24 | -37 | Gel | soft flex. |
| 1138 | 300 | [illegible] | $CF_2$=CFCl/$CF_2$=$CH_2$/$CH_2$=CFCl | + 8.5 | - 1.5 | - 6.5 | -21 | 20 | firm flex. |
| 1225 | 300 | 91/9 | $CF_2$=C($CH_3$)-CH=$CH_2$/$CF_3$-C($CH_3$)=$CH_2$ | + 5 | - 5.5 | - 8.5 | -17.5 | 111 | soft rubber. |
| 1348 | 300 | 48/52 | $CF_2$=$CF_2$/vinyl ethyl ether | - 0.5 | - 4.5 | - 6.5 | -11 | Gel | firm flex. |
| 1317 | 450 | 35/65 | $CF_2$=$CF_2$/vinyl butyrate | +12 | + 6 | + 3 | -24 | 16 | firm flex. |
| 1340 | 300 | 49/51 | $CF_2$=$CF_2$/vinyl 2-chloroethyl ether | +14.5 | +11.5 | + 9.5 | + 5 | 78 | firm flex. |
| 1396 | 350*** | 100 | $CF_2$=CHC($CH_3$)=$CH_2$ | - 5 | -16 | -21 | -30.5 | 93 | soft flex. |
| 1313 | 450 | 50/50A | $CF_2$=$CF_2$/$CH_2$=CFCl | +13.5 | + 5 | + 0.5 | - 8 | 38 | firm flex. |
| 1347 | 300 | 63/35A | $CF_2$=$CF_2$/$CH_2$=CFCl | +17 | + 7.5 | + 3 | -55 | 19 | stiff flex. |
| 1339 | 425 | 60/40 | $CF_2$=CFCl/vinyl 2-chloroethyl ether | +23.5 | +23 | +21.5 | +13.5 | 101 | stiff boardy |
| 1331 | 300 | 51/49 | $CF_2$=CFCl/vinyl ethyl ether | +23.5 | +22.5 | +22 | + 1 | Gel | stiff boardy |
| 770 | 325 | 37/42/21 | $CF_2$=CFCl/$CF_2$=$CH_2$/$CF_3$-CCl=$CF_2$ | +14 | +11 | +10 | + 6.5 | 25 | soft flex. |
| 1278 | 300 | 45/48/7 | $CF_2$=CFCl/$CF_2$=$CH_2$/vinyl acetate | +21 | +17 | +15.5 | + 6 | 17 | stiff boardy |
| 1315 | 350 | 50/46/4 | $CF_2$=CFCl/$CF_2$=$CH_2$/vinyl butyrate | +16 | +13 | +11 | + 7 | fell apart | soft flex. |
| 1316 | 375 | 41/39/20 | $CF_2$=CFCl/$CF_2$=$CH_2$/vinyl butyrate | +23 | +21 | +19 | +13 | fell apart | stiff boardy |
| 1328 | --- | 22/68 | $CF_2$=$CF_2$/$CH_2$=CFCl | insufficient | sample | | | | |
| 1341 | --- | 15/85 | $CF_2$=CF CF=$CF_2$/vinyl 2-chloroethyl ether | " | " | | | | |
| 1203 | --- | 47.2% F. | Residue from $CF_2$-CF-CF=$CF_2$ tank | " | " | | | | |

*Charge ratio
**Sample bubbled in mold - insufficient material for remolding but sample was completely stiff at 20°F. in cold box and gave [illegible]° twist with black wire.
***Very rapid decomposition of this sample occurred when molding was attempted at 300°F.
A-Constant feed runs.

FILE NO.: LAS-113
ANB:LAS 1-9-54

TABLE 4

**POLYMERS TO BE SCREENED FOR GEHMAN STIFFNESS AND VOLUME SWELL IN ASTM TYPE II FUEL**

| Run No. | Comonomer | % Molar Composition | Grams Shipped | Remarks |
|---|---|---|---|---|
| 880 | $CF_2=CFCl/CH_2=CF_2/CF_2=CF_2$ | 42/41/17 | 0.5 | all of sample |
| 958 | $CF_2=CFCl/CH_2=CF_2/CF_2=CF_2$ | ~40/40/20 | 2.0 | --- |
| 951 | $CF_2=CFCl/CH_2=CF_2/(CF_3)_2C=CF_2$ | 53/44/3 | 1.0 | --- |
| 954 | $CF_2=CFCl/CH_2=CF_2/CH_2=CHCONH_2$ | 47/51/2 | 1.0 | --- |
| 1297 | $CF_2=CFCl/CH_2=CF_2/ClCH_2C(=O)\text{-}OCH=CH_2$ | 40/32/28 | 1.0 | --- |
| 96 | $CF_2=CFCl/CH_2=C(Cl)\text{-}CH=CH_2$ | 88/12 | 2.0 | --- |
| 763 | $CF_2=CFCl/CH_2=CHCOOCH_3$ | 35/65 | 2.0 | --- |
| 1301 | $CF_2=CFCl/CH_2=CHOCH_2CH(CH_3)_2$ | 52/48 | 1.0 | --- |
| 613 | $CF_2=CH_2/CH_2=C(Cl)\text{-}CH=CH_2$ | 8/92 | 2.0 | --- |
| 471 | $CH_2=CHCH=CH_2/CH_2=CFCl$ | 6/94 | 2.0 | composition does not check with conversion |
| 489 | $CH_2=CHCH=CH_2/CF_3CH=CHCF_3$ | 97/3 | 1.0 | check if low fluorine content is effective |
| 670 | $CH_2=CHCH=CH_2/CF_3CCl=CF_2$ | 80/20 | 1.0 | --- |
| 1036 | $CF_2=CHCH=CH_2/(CH_3)_2C=CH_2$ | 99/1 | 1.0 | test because the 1% comonomer makes polymer rubbery |
| 1140 | $CF_2=CHC(CH_3)=CH_2/(CH_3)_2C=CH_2$ | 85/15 | 1.0 | --- |
| 177 | $CF_2=CCl_2/CH_2=CCl_2$ | 39/61 | 2.0 | not very rubbery but test to get effect of Cl atms. |
| 161 | $CF_2=CCl_2/CH_2=CClCH=CH_2$ | 20/80 | 2.0 | loses HCl; sent two levels to get trend |
| 163 | $CF_2=CCl_2/CH_2=CClCH=CH_2$ | 12/88 | 2.0 | (see 161) |
| 223 | $CF_2=CCl_2/CH_2=CHCOOC_4H_9$ | 8/92 | 3.0 | --- |
| 614 | $CF_2=CHCl/CH_2=CClCH=CH_2$ | 7/93 | 2.0 | low $CF_2=CHCl$, but may indicate merit of system |
| 808 | $CF_3CF=CF_2/CH_2=CFCl$ | 8/92 | 1.0 | |
| 1038 | $CF_3CF=CF_2/CF_2=CHCH=CH_2$ | 8/92 | 1.0 | |
| 1143 | $CF_3CF=CF_2/CF_2=CHC(CH_3)=CH_2$ | 2/98 | 1.2 | analysis shows 2% $CF_3CF=CF_2$, but conversion would indicate much more incorporated |
| 1291 | $CF_3CF=CF_2/CF_2=C(CH_3)\text{-}CH=CH_2$ | 2/98 | 0.8 | low $CF_3CF=CF_2$ but to be compared with 1143 |
| 837 | $CH_2=CHCOOC_4H_9/CF_3CH=CH_2$ | 88/12 | 1.0 | --- |
| 1089 | $CH_2=CHCOOC_4H_9/CF_2=CHCH=CH_2$ | 3/97 | 1.3 | low in acrylate but copolymer much more rubbery than homopolymer of $CF_2=CHCH=CH_2$ |
| 422 | $CF_3C\equiv CCF_3/CH_2=CFCl$ | 7/93 | 1.1 | --- |
| 1103 | $CH_2=CFCl/CH_2=CHF$ | 56/44 | 1.0 | --- |
| 1172 | $CH_2=CFCl/CF_3CH=CF_2$ | 97/3 | 1.0 | low in $CF_3CH=CF_2$ but polymer sufficiently different in appearance from $CH_2=CFCl$ homopolymer |
| 1289 | (cis) $CF_3CH=CHCF_3/CF_2=C(CH_3)\text{-}CH=CH_2$ | 1/99 | 0.8 | very low in $CF_3CH=CHCF_3$, but we have no homopolymer of $CF_2=C(CH_3)\text{-}CH=CH_2$ yet to evaluate |
| 1248 | $CF_3CCl=CF_2/CF_3CH=CHCH=CH_2$ | 5/95 | 1.0 | --- |
| 1230 | $CF_3CCl=CF_2/CF_2=C(CH_3)\text{-}CH=CH_2$ | 4/96 | 0.8 | --- |
| 1432 | $CF_2=CFCl/CH_2=CFCl$ | charged 15/85 | 5.0 | --- |
| 1433 | $CF_2=CFCl/CH_2=CFCl$ | charged 25/75 | 5.0 | --- |
| 1434 | $CF_2=CFCl/CH_2=CFCl$ | charged 50/50 | 3.0 | --- |
| 1421 | $CF_2=CHC(CH_3)=CH_2/CF_2=CFC_6H_5$ | charged 50/50 | 1.0 | --- |
| 1449 | $CF_2=C(CH_3)\text{-}CF=CH_2$ only | --- | 1.0 | --- |

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FIGURE 1

$CF_2=C(CH_3)-CH=CH_2$ COPOLYMERS

Raw Polymer Screening Test

| Run No. | Comonomer (X) | Mole Ratio Combined $CF_2=C(CH_3)CH=CH_2/X$ |
|---|---|---|
| 1221 | $CF_2=CFCl$ | 75/25 |
| 1222 | $CH_2=CHCH=CH_2$ | 48/52 |
| 1226 | $CH_2=CHCl$ | 82/18 |
| 1227 | $CH_2=C(CH_3)CH=CH_2$ | 50/50 |
| 1229 | $CH_2=CHCN$ | 88/12 |
| 1232 | $CH_3CCl=CH_2$ | 81/19 |
| 1233 | $CF_2=CHC(CH_3)=CH_2$ | -- |
| 1234 | $CF_3CH=CH_2$ | 82/18 |
| 1273 | $CF_2=CCl_2$ | 78/22 |
| 1211 | $CH_2=CF_2$ | 90/10 |
| 1212 | $CF_2=CF_2$ | 90/10 |
| 1213 | $CF_2=CFH$ | 90/10 |
| 1225 | $CF_3C(CH_3)=CH_2$ | 91/9 |
| X-300 | $CF_2=CFCl/CF_2=CH_2$ | 30/70 |

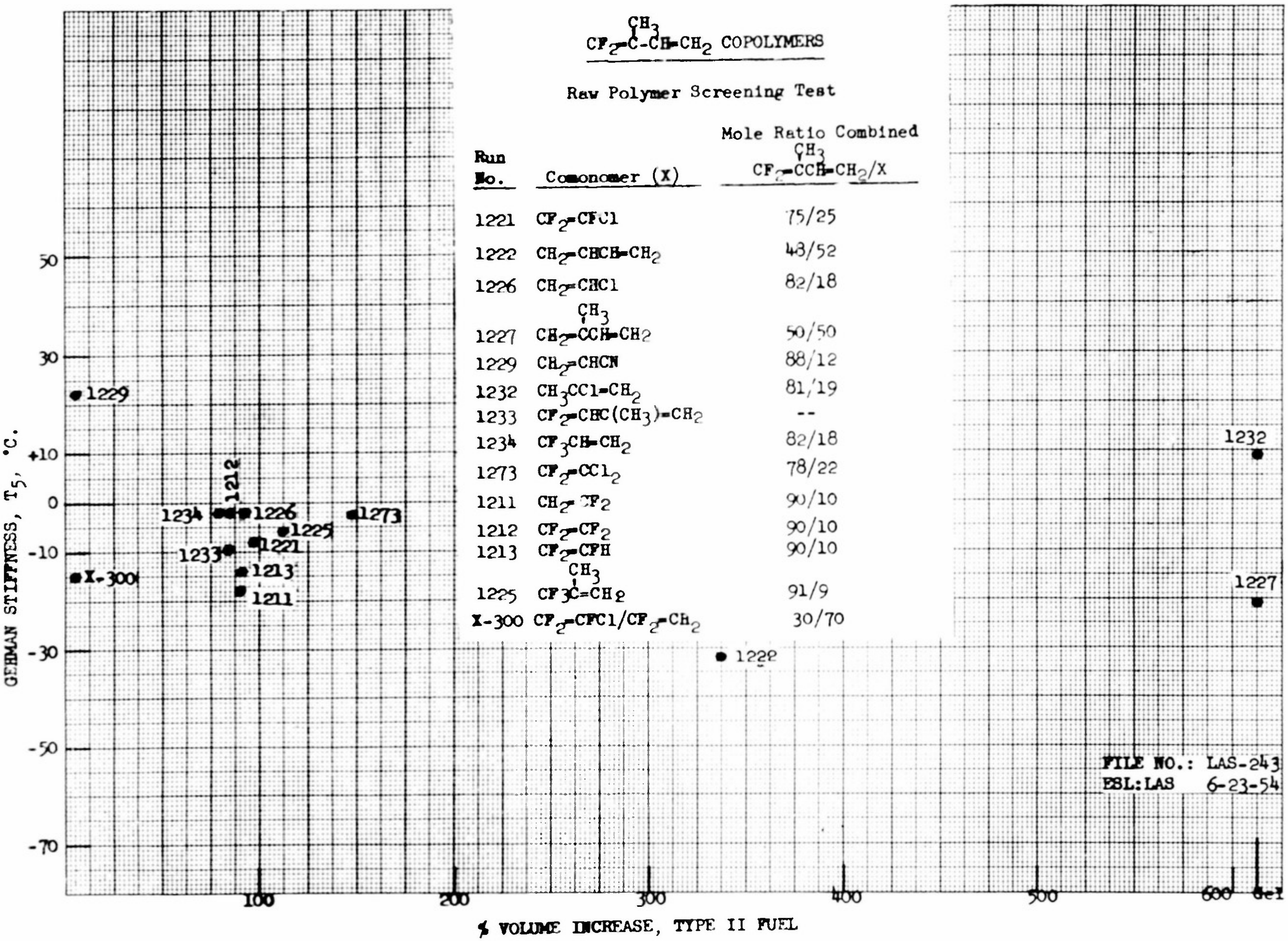

FIGURE 2

**$CF_3CH{=}CHCH{=}CH_2$ COPOLYMERS**

Raw Polymer Screening Test

| Run No. | Comonomer (X) | Mole Ratio Combined $CF_3CH{=}CHCH{=}CH_2/X$ |
|---|---|---|
| 1246 | $CH_2{=}CFCl$ | 81/19 |
| 1249 | $CF_2{=}CHC(CH_3){=}CH_2$ | 90/10 |
| 1251 | $CF_2{=}CHCH{=}CH_2$ | 90/10 |
| 1252 | $CF_3CH{=}CH_2$ | 86/14 |
| 1253 | none | 100/0 |
| 1254 | $CF_2{=}C(CH_3)CH{=}CH_2$ | 97/3 |
| 1216 | $CF_2{=}CF_2$ | 86/14 |
| X-300 | $CF_2{=}CFCl/CF_2{=}CH_2$ | 30/70 |

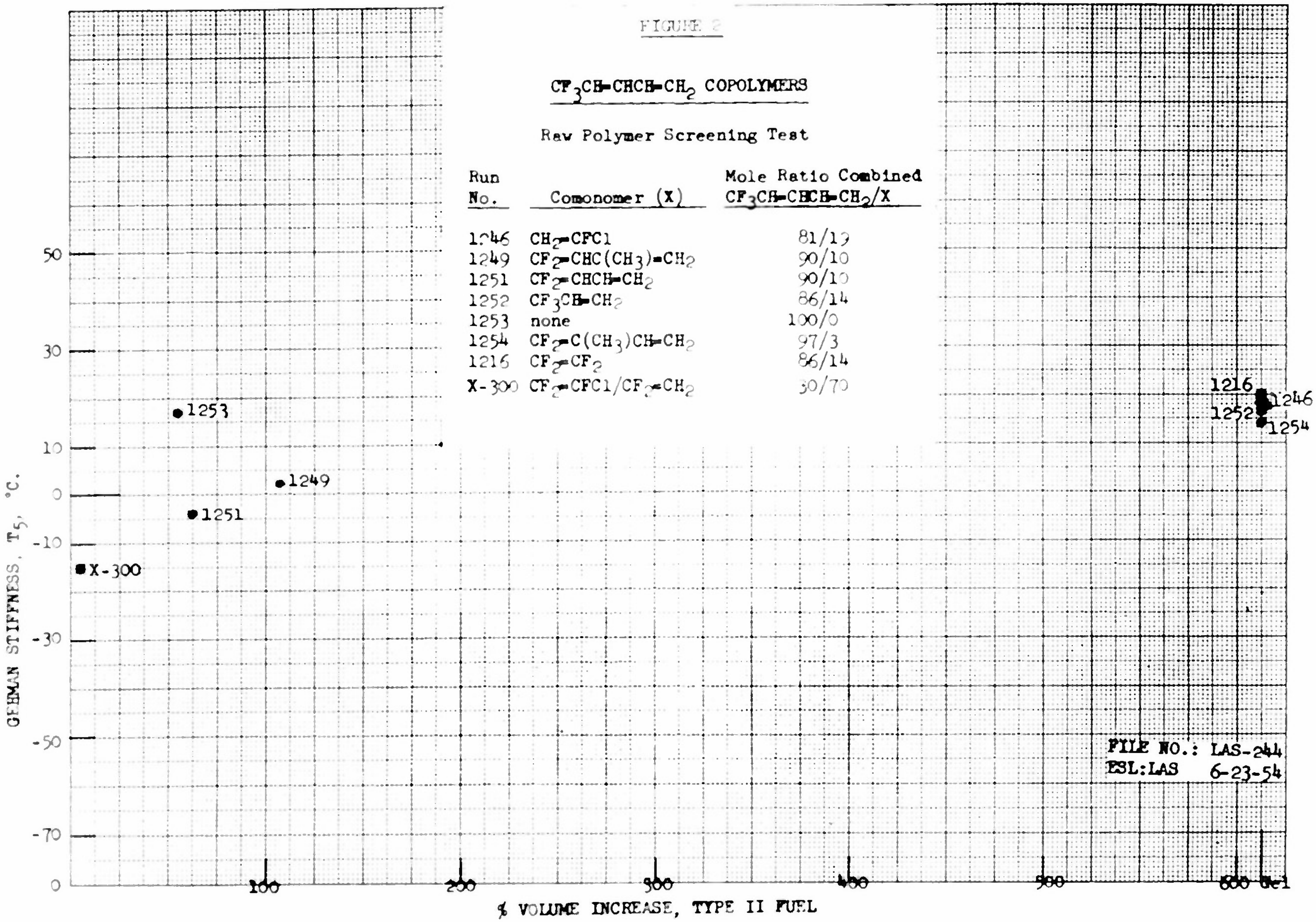


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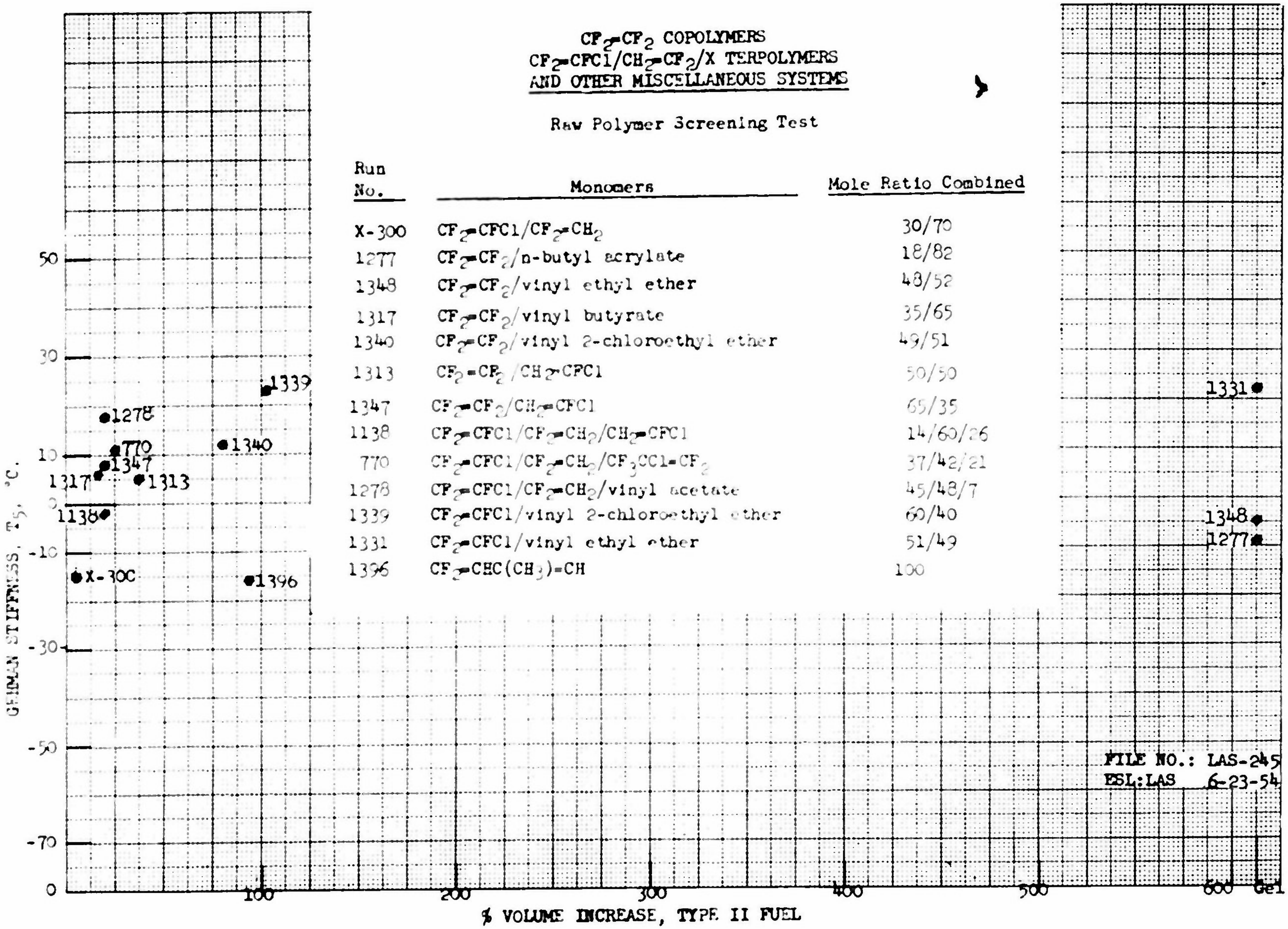
FIGURE 1

**CF₂=CF₂ COPOLYMERS**
**CF₂=CFCl/CH₂=CF₂/X TERPOLYMERS**
**AND OTHER MISCELLANEOUS SYSTEMS**

Raw Polymer Screening Test

| Run No. | Monomers | Mole Ratio Combined |
|---|---|---|
| X-300 | $CF_2=CFCl/CF_2=CH_2$ | 30/70 |
| 1277 | $CF_2=CF_2$/n-butyl acrylate | 18/82 |
| 1348 | $CF_2=CF_2$/vinyl ethyl ether | 48/52 |
| 1317 | $CF_2=CF_2$/vinyl butyrate | 35/65 |
| 1340 | $CF_2=CF_2$/vinyl 2-chloroethyl ether | 49/51 |
| 1313 | $CF_2=CF_2/CH_2=CFCl$ | 50/50 |
| 1347 | $CF_2=CF_2/CH_2=CFCl$ | 65/35 |
| 1138 | $CF_2=CFCl/CF_2=CH_2/CH_2=CFCl$ | 14/60/26 |
| 770 | $CF_2=CFCl/CF_2=CH_2/CF_3CCl=CF_2$ | 37/42/21 |
| 1278 | $CF_2=CFCl/CF_2=CH_2$/vinyl acetate | 45/48/7 |
| 1339 | $CF_2=CFCl$/vinyl 2-chloroethyl ether | 60/40 |
| 1331 | $CF_2=CFCl$/vinyl ethyl ether | 51/49 |
| 1396 | $CF_2=CHC(CH_3)=CH$ | 100 |

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