Petroleum and Chemical Research Department

PROGRESS REPORT

ARCTIC RUBBER

For the Period August - September 1955

December 1, 1955

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PROGRESS REPORT

Arctic Rubber - U.S. Army Contract DA-44-109-qm-1580

Subject: for the period August - September, 1955

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Period Covered: August - September, 1955

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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-54-353 " 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. SCHWARZENBERG
CONTENTS

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 CP₂=CHCH=CH₂ 8
      3. " CF₂=CF₂Cl 8
      4. " CH=CH₂ 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: CF$_2$=CHCH=CH$_2$, CF$_2$=CFCF$_2$Cl and vinyl pyridines.

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>b.p., °C.</th>
<th>Amount, g.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂=CHOCF₂CHClF</td>
<td>73-74/atm.</td>
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<tr>
<td>CHCl₂CHClOCF₂CHClF</td>
<td>86.5-87.5/30 mm.</td>
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<tr>
<td>CH₂ClCHClOCF₂CHClF</td>
<td>71-73/30 mm.</td>
<td>25</td>
</tr>
<tr>
<td>CH₂ClCH₂OCF₂CHClF</td>
<td>80-82/100 mm.</td>
<td></td>
</tr>
<tr>
<td>CF₃CCl₂OCF₂CF₂Cl</td>
<td>90.5-90.7/741 mm.</td>
<td></td>
</tr>
<tr>
<td>CH₃CF=CH₂</td>
<td>-22 to -21.5</td>
<td>1870</td>
</tr>
</tbody>
</table>

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 CF₂=CFCF₂Cl (monomer 82) obtained by the decarboxylation of the sodium salt of C₄ telomer acid was fractionated. The major fraction (ca. 630 g.) boiled between 78.5°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 N₂ 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)

\[
\begin{array}{ll}
\text{Mole} \% & (\text{app.}) \\
\text{CF}_2=\text{CHCH}=\text{CH}_2 & \sim 70 \\
\text{C}_4\text{H}_5\text{F}_3 & \sim 22 \\
\text{C}_5\text{H}_{10} & \sim 8 \\
\text{C}_4\text{H}_4\text{F}_4 & \text{trace}
\end{array}
\]

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)

\[
\begin{array}{ll}
\text{Mole} \% & (\text{app.}) \\
\text{CF}_2=\text{CHCF}=\text{CH}_2 & \sim 85 \\
\text{C}_4\text{H}_4\text{F}_4 & \sim 15
\end{array}
\]

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, 16-56-74, 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 CF₃CF=CF₂, CF₃CCl=CF₂ and CF₂=CFCF₂Cl (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 CF₂=CHCH=CH₂ (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 CF₂=CFCF₂Cl (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 CH=CH₂ (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 T₅ value of the copolymer system CF₂=CHCF=CH₂/CF₂=CFCF₂Cl=CH₂ was lowered six degrees by terpolymerizing the fluorinated dienes with a third monomer CH₂=CHCOF₂CF₂H (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 CF₂=CH₂/CF₂=CF₂ copolymers (see Table VIII, RL-55-434) have stimulated the copolymerization of other fluorinated propenes and butenes with vinylidene fluoride or other fluorinated ethylenes.

CF₂=CFCF₂Cl (monomer 62) copolymerizes with CF₂=CH₂ 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 CF₂=CHCF=CH₂ and CF₂=CFCH=CH₂ will be determined.

4. One pound batches of the appropriate molar ratios of the following systems: CF₂=CHCF=CH₂/CF₂=CF₂=CH₂, CF₂=CH₂/CF₂=CF₂ and CF₂=CH₂/CF₂=CF₂ will be prepared for evaluation of cured samples.

5. Preparation of ether-linked fluorocarbon polymers will be attempted.

[Signature]

References to Original Records

" " 308, pp. 176-180 "
<table>
<thead>
<tr>
<th>No.</th>
<th>Polymer</th>
<th>Molar Ratio Charged (%)</th>
<th>% movies</th>
<th>Den.</th>
<th>% Mov</th>
<th>Density</th>
<th>Appearance of Sample</th>
<th>Tackiness</th>
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<td>1257</td>
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<td>99.6</td>
<td>0.5</td>
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<tr>
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<td>-</td>
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<td>-</td>
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<td>-</td>
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<td>Powder</td>
<td>-</td>
<td>-</td>
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<td>Powder</td>
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<td>-</td>
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<td>-</td>
<td>-</td>
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<td>1244</td>
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<td>-</td>
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<td>Cr/Fe2</td>
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<td>-</td>
</tr>
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<td>1242</td>
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<td>-</td>
</tr>
<tr>
<td>1241</td>
<td>Cr/Fe2</td>
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<td>99.6</td>
<td>0.5</td>
<td>1</td>
<td>Powder</td>
<td>-</td>
<td>-</td>
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<td>1240</td>
<td>*</td>
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<td>99.6</td>
<td>0.5</td>
<td>1</td>
<td>Powder</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

**Note:**
- Data are given as single values. Exceptions are noted in the table.
- Normal X-ray powder diffraction and X-ray diffraction studies were performed on the samples.
- All samples were examined by X-ray diffraction and X-ray diffraction studies were performed on the samples.
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### TABLE II

**ARCTIC RIDGE SCREEENING TEST**

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Hoosier Structure</th>
<th>Muller Ratio</th>
<th>% Cont.</th>
<th>Average of Sample</th>
<th>Column Diffusion (C1)</th>
<th>Vol. of Increase</th>
<th>Terminal Grind</th>
<th>Measuring Temp. (°C)</th>
<th>Sample Condition</th>
<th>After Melting</th>
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<td>C4 + C21 + CI + C15 + C41 + C42</td>
<td>95/50</td>
<td>59</td>
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<td>-10.4 -24.0 -24.6 -27.6</td>
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<td>Firm &amp; rubber</td>
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<td>61</td>
<td>372</td>
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<td>Soft &amp; rubber</td>
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Note:
- All the samples heated on mill at 25°C.
- Hold time unless otherwise noted are 10 minutes. Longer periods are totals of individual 10 minute periods.
- Reason for unexpected analytical results not determined.
- *//
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<td>White Rubber</td>
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/1/ Recipe: Water 150; C₈ Talamor 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. HM-1403
ESL4M 9-30-55