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Report No. ARF-C6001-2
(Progress Report)

PREPARATION AND EVALUATION
OF NEW HYDRAULIC FLUIDS

Bureau of Ships
Washington 25, D.C.
The purpose of this project is to develop new fire-resistant hydraulic fluids based on fluorinated sulfur-containing compounds. The compounds will be synthesized specifically to meet the critical property requirements. Various derivatives of sulfur hexafluoride and other fluorinated materials will be investigated.

The electrolytic fluorination of di-n-propyl sulfide, \((C_3H_7)_2S\), is now being studied in an attempt to prepare the perfluoro derivative:

\[
\begin{align*}
(C_3H_7)_2S + HF & \xrightarrow{\text{electrolysis}} (C_3F_7)_2SF_4 \\
\end{align*}
\]

Hoffman and his coworkers (ref. 1) have prepared this compound. The reaction shown in Equation 1 has been carried out and the products are now being analyzed. The Simon's cell shown in Figures 1 and 2 was used. The di-n-propyl sulfide was placed in the cell and the cell was closed. The hydrogen fluoride was condensed into the metering reservoir, measured, and transferred into the cell. Although the cell itself was not refrigerated, the reflux condenser was cooled with dry ice. After the reaction was complete, the products were removed.
1/8-in. Nickel Lead and Electrode Support

To Reflux Condenser and Traps

Kel-F Insulator

1/8 x 1/4-in. Monel Swagelok Connector

1/4-in. Monel Top Plate

1/16-in. Teflon Gasket

47.2-mm I. D.

Nickel Cylinder

0.51-mm Nickel Electrodes

4 Anodes, 250 sq cm

3 Cathodes, 250 sq cm

3.1-mm Spacing

Kel-F Spacers

1/4-in. Monel Bottom

Sealing Yoke

Figure 2

SIMON'S CELL
The preparation of pentafluorosulfur pentafluoride, \( C_6F_5SF_5 \), is being carried out as shown in Equations 2 through 4.

\[
\begin{align*}
F^- & \quad \text{Br}_2 \quad \rightarrow \quad F^- \quad \text{S-S} \quad \text{F}^- \\
F^- & \quad \text{S-S} \quad \rightarrow \quad 2 \quad F^- \quad \text{SF}_3 \\
F^- & \quad \text{SF}_3 \quad \rightarrow \quad F^- \quad \text{SF}_5
\end{align*}
\]

About 100 g of product was obtained by means of the reaction shown in Equation 2. The fluorination of the disulfide, Equation 3, resulted in a colorless liquid which is now being characterized.

The viscosities of a number of fluorocarbons have been checked to determine the structural characteristics necessary for the desired viscosity index (Table 1). Generally, the viscosity and the viscosity index are of the same order of magnitude for hydrocarbons of the same skeleton. However, the absolute viscosities of the fluorocarbons for which data are available are higher than those of saturated hydrocarbons having the same structure. For example, \( n-C_7H_{16} \) has a viscosity of 3.397 millipoises at 38.34°C, while \( n-C_7F_{16} \) has a viscosity of 7.33 millipoises at 38.2°C. If the viscosities are expressed as kinematic viscosity, the ratio of absolute viscosity to density, the fluorocarbons will probably have lower values.
### Table 1

**VISCOSITIES OF SOME FLUOROCARBONS**

<table>
<thead>
<tr>
<th>Fluorocarbon</th>
<th>Viscosity at Temp., millipoises</th>
<th>Temp., °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Heptforane</td>
<td>13.67</td>
<td>0.42</td>
</tr>
<tr>
<td></td>
<td>8.61</td>
<td>27.5</td>
</tr>
<tr>
<td></td>
<td>8.05</td>
<td>32.1</td>
</tr>
<tr>
<td></td>
<td>7.33</td>
<td>38.2</td>
</tr>
<tr>
<td></td>
<td>6.64</td>
<td>45.0</td>
</tr>
<tr>
<td>C$<em>9$F$</em>{16}$ (saturated)</td>
<td>2.19 $^b$</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>1.39 $^b$</td>
<td>37.8</td>
</tr>
<tr>
<td>1, 3, 5-Trimethylcyclohexforane</td>
<td>37.49</td>
<td>0.28</td>
</tr>
<tr>
<td></td>
<td>17.27</td>
<td>35.7</td>
</tr>
<tr>
<td></td>
<td>11.25</td>
<td>62.2</td>
</tr>
<tr>
<td></td>
<td>7.32</td>
<td>94.6</td>
</tr>
<tr>
<td>Naphthalphorane</td>
<td>53.39</td>
<td>24.6</td>
</tr>
<tr>
<td></td>
<td>11.61</td>
<td>99.3</td>
</tr>
<tr>
<td>Anthracforane</td>
<td>22.4</td>
<td>99.5</td>
</tr>
<tr>
<td>Tetraisobutforane</td>
<td>32</td>
<td>99.5</td>
</tr>
<tr>
<td>Chrysforane (C$<em>{18}$F$</em>{30}$)</td>
<td>60</td>
<td>99.5</td>
</tr>
<tr>
<td>Retforane (C$<em>{18}$F$</em>{32}$)</td>
<td>60</td>
<td>99.5</td>
</tr>
</tbody>
</table>


$^b$Viscosity is given in centistokes.
than the corresponding hydrocarbons. This is a consequence of the greater density of the fluorocarbons.

The temperature coefficients of viscosity of n-heptforane and 1, 3, 5-trimethforylcy clohexforane are greater than those of the corresponding hydrocarbons (ref. 2). This is probably true of most fluorocarbons.

Fluorocarbon oils have been used as lubricants, and the results of tests on properties related to this use have been reported (ref. 3-7). Tests made on various fluorocarbon oils showed that they were good lubricants, comparable in this respect to good hydrocarbon lubricants (ref. 3). This is also true of stabilized polymers of $\text{CF}_2=\text{CFCI}$ (ref. 8).

Early qualitative data indicated that the carbon skeleton structure has less effect on the viscosity of a fluorocarbon oil than the corresponding structure does in the case of a hydrocarbon oil. Fluorocarbon oils made by the catalytic fluorination process, even when prepared from hydrocarbon oils of markedly different composition, showed about the same viscosity (ref. 3). It is expected that fluorocarbons in the lubricating oil range should have a boiling point range of 150 to 200°C at a pressure of 10 mm Hg.

Data on the vapor pressure of low-molecular-weight fluorocarbons (Table 2) indicate that the Trouton constant, $\Delta S_v$, is normal for these materials.
Table 2
VAPOR PRESSURE DATA
FOR SOME LOW-MOLECULAR-WEIGHT FLUOROCARBONS

<table>
<thead>
<tr>
<th>Fluorocarbon</th>
<th>$\Delta H_v$ at B. P., cal/mole</th>
<th>$\Delta S_v$, e. u./mole</th>
<th>B. P., °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF$_4$</td>
<td>2947</td>
<td>20.3</td>
<td>-128</td>
</tr>
<tr>
<td>C$_2$F$_6$</td>
<td>3860</td>
<td>19.8</td>
<td>-76.3</td>
</tr>
<tr>
<td>n-C$<em>5$F$</em>{12}$</td>
<td>6510</td>
<td>21.5</td>
<td>29.32</td>
</tr>
<tr>
<td>iso-C$<em>5$F$</em>{12}$</td>
<td>6490</td>
<td>21.4</td>
<td>30.12</td>
</tr>
<tr>
<td>cyclo-C$<em>5$F$</em>{10}$</td>
<td>6300</td>
<td>21.3</td>
<td>22.48</td>
</tr>
</tbody>
</table>


The list of fluorocarbons in Table 3 shows how some of the physical properties vary with structure.

During February all the data in Tables 1, 2, and 3 will be analyzed to determine the effect of structure on viscosity index. Also, the products obtained from reaction 1 through 4 will be characterized.

Respectfully submitted,

ARMOUR RESEARCH FOUNDATION
of Illinois Institute of Technology

Approved by:

Charles K. Hersh
Manager
Propellant Research

Irvine J. Solomon
Senior Chemist
Propellant Research

IJS:sc
1/31/63
Table 3

PHYSICAL PROPERTIES OF SOME FLUOROCARBONS

<table>
<thead>
<tr>
<th>Fluorocarbon</th>
<th>Carbon Structure</th>
<th>B.P., °C</th>
<th>Density, g/cc</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆F₆</td>
<td><img src="image" alt="Structure" /></td>
<td>81.0-82.0</td>
<td>1.612 (25°C)</td>
</tr>
<tr>
<td>C₇F₈</td>
<td><img src="image" alt="Structure" /></td>
<td>103.5</td>
<td>1.660 (25°C)</td>
</tr>
<tr>
<td>C₆F₁₂</td>
<td><img src="image" alt="Structure" /></td>
<td>76.32</td>
<td>1.7994 (20°C)</td>
</tr>
<tr>
<td>C₇F₁₄</td>
<td><img src="image" alt="Structure" /></td>
<td>76.32</td>
<td>1.7994 (20°C)</td>
</tr>
<tr>
<td>C₈F₁₆</td>
<td><img src="image" alt="Structure" /></td>
<td>102.12</td>
<td>1.8560 (20°C)</td>
</tr>
<tr>
<td>C₈F₁₆</td>
<td><img src="image" alt="Structure" /></td>
<td>100.97</td>
<td>1.8503 (20°C)</td>
</tr>
<tr>
<td>C₈F₁₆</td>
<td><img src="image" alt="Structure" /></td>
<td>97.98</td>
<td>1.295 (20°C)</td>
</tr>
<tr>
<td>C₉F₁₈</td>
<td><img src="image" alt="Structure" /></td>
<td>125.18</td>
<td>1.9025 (20°C)</td>
</tr>
<tr>
<td>C₉F₁₈</td>
<td><img src="image" alt="Structure" /></td>
<td>117-117.5</td>
<td>1.291 (20°C)</td>
</tr>
<tr>
<td>C₆F₁₄</td>
<td><img src="image" alt="Structure" /></td>
<td>55.9-56.7</td>
<td>1.253 (26°C)</td>
</tr>
</tbody>
</table>


Sublimes at 760 mm, 51°C.

Solid.

ARMOUR RESEARCH FOUNDATION OF ILLINOIS INSTITUTE OF TECHNOLOGY
REFERENCES


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