FOREIGN TECHNOLOGY DIVISION

ANTISEIZE AND ANTIWEAR ADDITIVES BASED ON DIETHERDITHIOPHOSPHORIC ACIDS DERIVED FROM ALKYL AND ARYL ESTERS OF GLYCERINE \(\alpha\)-MONOCHLOROHYDRIN

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EDITED TRANSLATION

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Dietherdithiophosphoric acids with the general formula \( [\text{ROCH}_2(\text{CHCl})\text{CHO}]_2\text{PSSH} \) are interacted with ethylene oxide and epichlorohydrin and the resultant compounds are tested as antiseize and antiwear additives in an attempt to develop organic compounds combining at least three active elements in a single molecule. Analysis of the products of interaction between dietherdithiophosphoric acids and ethylene oxide shows that they are very close in composition to trietherdithiophosphoric acids formed by the equation

\[
\text{ROCH}_2(\text{CHCl})\text{CHO} + \text{CH}_2\text{CH}_2\text{CH}_2\text{OH} \rightarrow \text{ROCH}_2(\text{CHCl})\text{CHO} + \text{CH}_2\text{CH}_2\text{CH}_2\text{OH}
\]

Physically, the \( \beta \)-hydroxyethyl esters obtained from the dietherdithiophosphoric acids studied are thick liquids with a weak yellowish tinge which dissolve well in organic solvents. The results for reaction with epichlorohydrin show compounds which are close in composition to trietherdithiophosphoric acids formed according to the equation

\[
\text{ROCH}_2(\text{CHCl})\text{CHO} + \text{CH}_2\text{CH}_2\text{CH}_2\text{Cl} \rightarrow \text{ROCH}_2(\text{CHCl})\text{CHO} + \text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}
\]
The γ-chloro-β-hydroxypropyl esters of the dietherdithiophosphoric acids studied are viscous liquids with a weak yellowish tinge which dissolve readily in most organic solvents. The resultant trietherdithiophosphoric acids were tested as antiseize and antiwear additives in AK-15 oil on a four-ball tetrahedral friction machine with ShKh-6 steel balls (GOST 9490-60). The results show that both additives have high antiseize and antiwear properties with about equal numerical values for the generalized wear index. Tests of the anticorrosion properties of the additives (GOST 8245-56) showed a reduction in the corrosiveness of AK-15 oil from 106 g/m² without the additives to 5-13 g/m² after introduction of the additives. Orig. art. has: 3 tables, 2 formulas.
ANTISIEZE AND ANTIWEAR ADDITIVES BASED ON DIETHERDITHIOPHOSPHORIC ACIDS DERIVED FROM ALKYL AND ARYL ESTERS OF GLYCERINE α-MONOCHLOROHYDRIN

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As we showed earlier [1], the reaction between alkyl and aryl esters of glycerin α-monochlorohydrin and phosphorus pentasulfide occurs with formation of dietherdithiophosphoric acids with the general formula \([\text{ROCH}_2(\text{CH}_2\text{Cl})\text{CHO}]_2\text{PSSH}\). Zinc salts of these dietherdithiophosphoric acids are highly effective antisieze and antiwear additive for lubricating oils.

Continuing our research in the direction of obtaining organic compounds containing three and more active elements in one molecule we established as our goal the study of the reaction of the interaction of the cited dietherdithiophosphoric acids with ethylene oxide and epichlorohydrin and testing of the obtained compounds as antisieze and antiwear additives.

Addition of ethylene oxide to dietherdithiophosphoric acids [2] was carried out in a round-bottomed flask equipped with a mixer, reflux condenser, gas-feed tube, and thermometer.
In the flask, we mixed 0.06 mole of the investigated diether-
dithiophosphoric acid with 50 ml of toluene. After this, about
0.09 mole of predried ethylene oxide, diluted with purified
nitrogen, was slowly added to the solution at room temperature and
with constant agitation. The reaction was accompanied by the
liberation of a small amount of heat. The end of the reaction was
established by the disappearance of the methyl orange acid reaction.
Upon completion of the reaction, the product was freed from the
solvent and analyzed. The results of the analysis (Table 1) showed
that the obtained compounds are very close in composition to
trietherdithiophosphoric acids formed according to the equation

\[
\begin{align*}
\text{ROCH}_2
\end{align*}
\]

\[
\text{CH}_2\text{Cl}\text{CHO} \quad \text{P}^8 \quad \text{SH} \quad \text{O} \quad \text{SCH}_2\text{CH}_2\text{OH}
\]

Table 1. Characteristics of trietherdithiophosphoric acids of
the type \([	ext{ROCH}_2\text{(CH}_2\text{Cl)}\text{CHO}]_2\text{PSSCH}_2\text{CH}_2\text{OH}\).

<table>
<thead>
<tr>
<th>R</th>
<th>Yield, %</th>
<th>(\text{P}^\text{20})</th>
<th>(\text{P}_\text{D}^\text{20})</th>
<th>(\text{Phosphorus})</th>
<th>(\text{Sulfur})</th>
<th>(\text{Chlorine})</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃</td>
<td>91.4</td>
<td>1.2267</td>
<td>1.5211</td>
<td>8.00</td>
<td>8.69</td>
<td>15.56</td>
</tr>
<tr>
<td>C₂H₅</td>
<td>91.7</td>
<td>1.2787</td>
<td>1.2150</td>
<td>7.46</td>
<td>8.12</td>
<td>15.44</td>
</tr>
<tr>
<td>n-C₃H₇</td>
<td>91.7</td>
<td>1.2298</td>
<td>1.3064</td>
<td>6.16</td>
<td>7.20</td>
<td>14.46</td>
</tr>
<tr>
<td>n-C₄H₉</td>
<td>92.3</td>
<td>1.2176</td>
<td>1.5043</td>
<td>6.57</td>
<td>6.93</td>
<td>15.09</td>
</tr>
<tr>
<td>n-C₅H₁₁</td>
<td>91.1</td>
<td>1.1975</td>
<td>1.5013</td>
<td>6.20</td>
<td>6.43</td>
<td>12.84</td>
</tr>
<tr>
<td>n-C₆H₁₃</td>
<td>92.1</td>
<td>1.1273</td>
<td>1.4829</td>
<td>5.87</td>
<td>5.69</td>
<td>12.15</td>
</tr>
<tr>
<td>C₇H₈</td>
<td>99.0</td>
<td>1.2688</td>
<td>1.5721</td>
<td>6.06</td>
<td>5.88</td>
<td>17.54</td>
</tr>
<tr>
<td>p-C₆H₅C₆H₄</td>
<td>95.7</td>
<td>1.2576</td>
<td>1.5665</td>
<td>5.74</td>
<td>5.58</td>
<td>11.89</td>
</tr>
</tbody>
</table>

The obtained \(\beta\)-hydroxyethyl esters of the investigated
dietherdithiophosphoric acids are thick liquids with a weak yellow
inge. They dissolve well in organic solvents.

The reaction between dietherdithiophosphates and epichloro-
hydrin was conducted in the same instrument, but in place of the
gas-feed tube a dropping funnel was installed. A sample of 0.06
mole of dietherdithiophosphoric acid and 50 ml toluene were placed
in the flask. A solution of 0.06 mole epichlorohydrin in 10 ml
toluene was added slowly to the mixture through the dropping
funnel. The reaction was accompanied by the liberation of heat, with the temperature of the reaction mixture increasing from room temperature to 33-34°. The mixture was heated on a water bath at a temperature of 60-70° for half an hour. The end of the reaction was determined by the absence of the methyl orange acid reaction.

Data from the analysis of the obtained products after distillation of the solvent (Table 2) show that they are very close in composition to the trietherdithiophosphoric acids formed according to the equation

$$\begin{align*}
\text{ROCH}_2\text{CHO} + \text{CH}_3\text{CH} - \text{CHCl} & \rightarrow \text{ROCH}_2\text{CHO} \\
\text{SCH}_2\text{CHOHCH}_2\text{Cl} & \rightarrow \\
\text{ROCH}_2\text{CHO} & \rightarrow \\
\text{SCH}_2\text{CHOHCH}_2\text{Cl}.
\end{align*}$$

Table 2. Characteristics of trietherdithiophosphoric acids of the type [ROCH\(_2\)(CH\(_2\)Cl)CHO\(_2\)]\(_2\)PSSCH\(_2\)-CHOH-CH\(_2\)Cl.

<table>
<thead>
<tr>
<th>R</th>
<th>Yield, %</th>
<th>d(_20)</th>
<th>p(_D)</th>
<th>Phosphorus (%)</th>
<th>Sulfur (%)</th>
<th>Chlorine (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_3)</td>
<td>93.0</td>
<td>1.3421</td>
<td>1.5210</td>
<td>7.11</td>
<td>7.25</td>
<td>14.71</td>
</tr>
<tr>
<td>C(_2)H(_5)</td>
<td>93.1</td>
<td>1.3029</td>
<td>1.5160</td>
<td>6.67</td>
<td>6.09</td>
<td>13.82</td>
</tr>
<tr>
<td>n-C(_3)H(_7)</td>
<td>93.6</td>
<td>1.0222</td>
<td>1.5109</td>
<td>6.30</td>
<td>6.54</td>
<td>13.03</td>
</tr>
<tr>
<td>n-C(_4)H(_9)</td>
<td>93.8</td>
<td>1.2485</td>
<td>1.5082</td>
<td>5.96</td>
<td>6.13</td>
<td>12.53</td>
</tr>
<tr>
<td>n-C(_5)H(_11)</td>
<td>91.2</td>
<td>1.3041</td>
<td>1.5058</td>
<td>5.65</td>
<td>6.05</td>
<td>11.70</td>
</tr>
<tr>
<td>C(_6)H(_5)</td>
<td>88.7</td>
<td>1.2016</td>
<td>1.5004</td>
<td>5.38</td>
<td>5.43</td>
<td>11.13</td>
</tr>
<tr>
<td>C(_6)H(_5)-C(_6)H(_5)</td>
<td>97.3</td>
<td>1.3230</td>
<td>1.5731</td>
<td>5.53</td>
<td>5.48</td>
<td>11.49</td>
</tr>
<tr>
<td>p-C(_6)H(_4)Cl</td>
<td>90.3</td>
<td>1.2816</td>
<td>1.5060</td>
<td>5.27</td>
<td>4.83</td>
<td>10.91</td>
</tr>
</tbody>
</table>

The γ-chlor-β-hydroxypropyl esters of the investigated dietherdithiophosphoric acids are viscous liquids with a weak yellow color. They dissolve readily in the majority of organic solvents.

The trietherdithiophosphoric acids shown in Tables 1 and 2 were tested in AK-15 oil as antisieze and antiwear additives. The generalized wear index (GWI) was determined on a four-ball friction machine with ShKh-6 balls (GOST 9490-60).
Comparison of the data in Tables 1 and 2 shows a clear distinction in the contents of sulfur, phosphorus, and chlorine. Thus, a molecule of additive of the type \([\text{ROCH}_2(\text{CH}_2\text{Cl})\text{CHO}]_2\text{PSSCH}_2\text{CH}_2\text{OH}\) [A] contains 1.33 times as much chlorine and approximately 12% less phosphorus and sulfur than an additive of the type \([\text{ROCH}_2(\text{CH}_2\text{Cl})\text{CHO}]_2\text{PSSCH}_2\text{CHOCH}_2\text{Cl}\) [B].

Table 3. Results of tests of AK-15 oil with trietherdithiophosphates.

<table>
<thead>
<tr>
<th>R</th>
<th>C₁₅</th>
<th>1.07</th>
<th>95.5</th>
<th>9.1</th>
<th>1.06</th>
<th>95.0</th>
<th>9.6</th>
<th>1.14</th>
<th>100.7</th>
<th>8.8</th>
<th>1.13</th>
<th>92.3</th>
<th>10.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-C₆H₆</td>
<td>1.22</td>
<td>96.2</td>
<td>7.0</td>
<td>1.19</td>
<td>90.8</td>
<td>7.7</td>
<td>1.25</td>
<td>95.7</td>
<td>12.2</td>
<td>1.32</td>
<td>92.3</td>
<td>13.7</td>
<td></td>
</tr>
<tr>
<td>n-C₇H₈</td>
<td>1.36</td>
<td>94.7</td>
<td>0.4</td>
<td>1.28</td>
<td>95.3</td>
<td>4.3</td>
<td>1.36</td>
<td>102.4</td>
<td>5.4</td>
<td>1.36</td>
<td>102.4</td>
<td>5.4</td>
<td></td>
</tr>
<tr>
<td>C₆H₆</td>
<td>1.32</td>
<td>96.3</td>
<td>0.0</td>
<td>1.28</td>
<td>95.3</td>
<td>4.3</td>
<td>1.36</td>
<td>102.4</td>
<td>5.4</td>
<td>1.36</td>
<td>102.4</td>
<td>5.4</td>
<td></td>
</tr>
<tr>
<td>p-C₆H₅Cl</td>
<td>1.36</td>
<td>100.3</td>
<td>12.7</td>
<td>1.36</td>
<td>102.4</td>
<td>5.4</td>
<td>1.36</td>
<td>102.4</td>
<td>5.4</td>
<td>1.36</td>
<td>102.4</td>
<td>5.4</td>
<td></td>
</tr>
<tr>
<td>without additive</td>
<td></td>
<td>23.0</td>
<td>106.0</td>
<td></td>
<td>23.0</td>
<td>106.0</td>
<td></td>
<td>23.0</td>
<td>106.0</td>
<td></td>
<td>23.0</td>
<td>106.0</td>
<td></td>
</tr>
</tbody>
</table>

Despite this distinction, both additives possess high-antisieze and antiwear properties and are practically equal in the effectiveness of their action (Table 3).

The anticorrosion properties of the compounds prepared were determined according to GOST 8245-56. The results of the investigations (Table 3) showed that all of these compounds have a strong anticorrosion effect; in their presence the corrosivity of AK-15 was reduced from 106 \(g/m^2\) to 5-13 \(g/m^2\).

Conclusions

1. It has been shown, that the condensation of dietherdithiophosphoric acids obtained from alkyl and aryl esters of glycerin \(\alpha\)-monochlorhydrin with ethylene oxide and epichlorohydrin will produce the corresponding trietherdithiophosphoric acids.
2. It was established that the investigated trietherdithiophosphoric acids possess high antisieze, antiwear, and anticorrosion properties.

References


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